UNIVERSITY OF NOVI SAD
TECHNICAL FACULTY „MIHAILO PUPIN“
ZRENJANIN, REPUBLIC OF SERBIA

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Politehnica University, Timisoara, Romania
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INTRODUCTION

University of Novi Sad, Technical faculty “Mihajlo Pupin” from Zrenjanin, in partnership with Politechnica University from Timisoara in Romania, Obuda University from Hungary and Mogilev State University of Food Technologies from Belarus has organized the Fourth International Conference of Ecology of Urban Areas 2014 (URBANECO 2014). This partnership significaly improves the quality of conference organization and work, as well as contribution in area of regional cooperation with other universities and scientific institutions.

The objectives of the Conference URBANECO 2014 are: presentation of current knowledge and the exchange of experiences from the field of sustainable development of urban areas which is one of the major problems of modern civilization. The ecological aspect is the dominant factor in achieving sustainability. The importance of ecological aspect has developed a need for an International Conference "Ecology of Urban Areas 2014" which has the goal to integrate scientific, technological and experimental knowledge in this field. Another importance is gathering researchers from this field with aim of expanding regional and international cooperation, raising the level of professional and scientific work at University of Novi Sad and Technical faculty “Mihajlo Pupin”, expanding cooperation with institutions and encouraging young researchers within this field. Taking into account that this Conference is international, the importance of this event is obvious for the town of Zrenjanin, Banat region, Vojvodina and Serbia. Organization of URBANECO 2014 by University of Novi Sad, Technical faculty “Mihajlo Pupin” from Zrenjanin represents this scientific-educational institution as one of the major representatives of economic and social development in Banat.

Within this Collection of papers are presented all accepted papers received for IV International Conference Ecology of Urban Areas 2014. The papers are divided into following sessions: Air quality, Management of solid urban waste, Water quality in urban areas (ground water, drinking water, waste water and facilities), System of ecological management (ISO 14000), Economics of sustainable development of urban areas, Noise and vibrations in urban areas, Electro and electro-magnetic pollution in urban areas, Climate changes and urban pollution, Spatial planning and greening in urban areas, Development of urban ecology through educative and information activities, ICT in the ecology of urban areas, Accidents in urban areas, Environmental aspects of traffic in urban areas, Impact of agricultural activities to urban area, Public health and the ecology of urban areas, Soil and degradation of soil, Nanotechnology in environmental protection, and Transfer stations in the system of management of solid communal waste.

We would like to express our gratitude to the Ministry of Education, Science and Technological Development of Republic of Serbia; Ministry of Energy, Development and Environmemnatl Protection; Provincial Secretariat for Science and Technological Development; Provincial Secretariat for Protection of Environment and Sustainable Development.

Finally, we wish to thank all the authors of papers and participants in the Conference in hope that we will continue our cooperation successfully in the future and that each new year will bring better ideas and solutions to help raise awareness of the responsibility we hold today for the well-being of future generations.

President of the Organizing Committee
Ph.D Milan Pavlović

Zrenjanin, October 2014.

WORD OF THANKS

We wish to thank Provincial Secretariat for Science and Technological Development, Republic of Serbia for supporting the organization of IV International Conference „ECOLOGY OF URBAN AREAS 2014“

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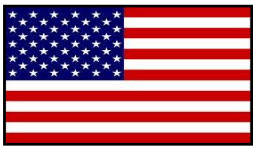
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AIR QUALITY

IV International Conference
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AEROSOL POLLUTION EPISODES ANALYSES OVER TIMISOARA

Delia–Gabriela Calinoiu[1*], Gavrila Trif-Tordai[2], Francisc Popescu[2], Adrian Eugen Cioabla[2]
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ABSTRACT

The present paper presents the analyses of two different aerosol pollution episodes over Timisoara, Romania. For this work, ground based sun photometer data were used during 2011 and 2012. By analyzing aerosol optical depth (AOD), Ångström parameter, single scattering albedo and size distribution the types of aerosol are determined. The analysis reveals a relatively high average aerosol optical depth at 440 nm (AOD_{440}) associated with a low/high Ångström parameter (α). A high AOD and a low value of Angstrom parameter ($\alpha > 0.6$) represents an atmosphere with dust, and if $\alpha > 1.5$ the atmosphere is loaded with biomass burning aerosol. Dust and biomass dispersion was investigated by using NOOA HYSPLIT model (Hybrid Single – Particle Lagrangian Integrated Trajectory). Global Fire Maps from MODIS (Moderate Resolution Imaging Spectroradiometer) were used to identify biomass burning sites.

Key words: *aerosol, aerosol optical depth, Ångström parameter, single scattering albedo*.

INTRODUCTION

Desert dust aerosols are tiny soil particles suspended in the atmosphere which are carried by air masses. Desert dust aerosol have a significant impact on local and global climate, regional air quality, visibility, cloud processes, human health (Mahowalda et al., 2013). Also, desert or mineral dusts have a key role in the atmospheric radiation budget thought scattering of the solar radiation (Alizadeh et al., 2014; Calinoiu et al., 2013).

Biomass burning aerosol (BB) of two major chemical components: black carbon, leading to absorption of solar radiation, and organic carbon, resulting in scattering solar radiation. (www.ipcc.ch). BB aerosols are product of natural fires (burning of forest and vegetation) and human – induced burning, such as agricultural waste, coal, wood, dung, etc. Biomass burning aerosol have a significant impact on local and global climate, regional air quality, visibility, cloud processes, human health (Gustafsson et al., 2009; Adler et al., 2011).

Consequently it is absolutely necessary to monitor aerosols, by diverse possibilities and techniques, and at different levels, not only at soil. The mentioned global effects strongly depend on the physical and optical properties of aerosol particles. Several studies about accuracy of aerosol optical properties from sun and sky radiance measurements were conducted by Dubovik (Dubovik et al., 2000a; Dubovik et al., 2000b; Dubovik et al., 2002; Dubovik et al., 2006.

Therefore, aerosol measurements on global scale are essential. This is achieved for example at ground - based by automatic sun and sky scanning spectral radiometer, by means of so – called sun photometer. These instruments have the advantage that they are able to monitored continuous aerosol optical depth (AOD), with high accuracy, fact that is essential for the measuring procedure.

The aim of this paper is to investigate the optical and physical properties of the dust and biomass burning aerosol based on the AERONET sun photometer data/observations in the Timisoara city from

Romania. The city is located in the Western part of Romania and it is situated on the southeastern edge of the Pannonia plain, Timisoara (45°46' N, 21°26' E) lies at an altitude of 85 m.

A sun photometer is an optical instrument for the measurement of the spectral solar radiation. The range of wavelength for instrument is between 0.34 – 1.65 µm. The sun photometer accomplishes two basic measurements, either direct sun (nine spectral bands: 340, 380, 440, 500, 670, 870, 940, 1020 and 1640 nm) or sky (440, 670, 870 and 1020 nm) both within several programmed sequences.

The aerosol optical depth is generated applying the Beer - Lambert - Bouger law to irradiance data and by removing the contribution due to Rayleigh scattering and absorption of atmospheric gases. Ångström parameter was calculated in the spectral interval 440 - 870 nm.

RESULTS AND DISCUSSIONS

Figure 1 illustrates the frequency distribution of AOD at 440 nm and α between 440 and 870 nm during the observation period. AOD frequency shows an obvious peak, with values between 0.2 and 0.4, accounting 45 % of total distribution. For Ångström parameter, the frequency histogram shows two peaks, with values between 1.2 - 1.4 and 1.4 - 1.6 representing around 30 %.

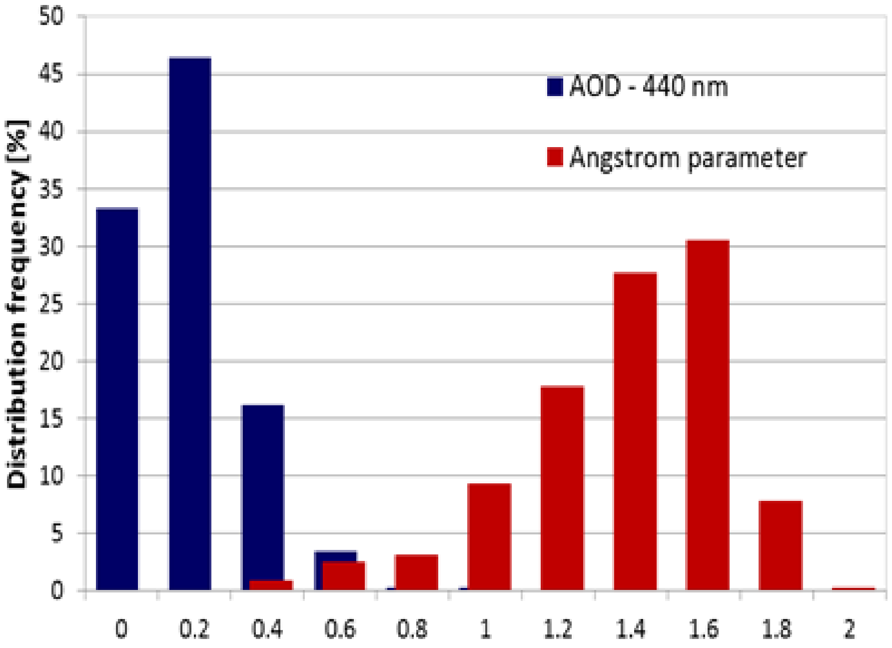

Figure 1. Frequency distribution of daily AOD$_{440}$ and Ångström parameter for 2011 and 2012 in Timisoara

The type of aerosol particles was determined by means of aerosol optical depth, Ångström parameter, single scattering albedo, volume size distribution and real part of refractive index. We specified the biomass burning event by considerable daily increase in AOD and Ångström parameter (see also Figure 2).

Based on the sun photometer data, the increase of the aerosol optical depth (larger than 0.6) while the water column content was low, the high values of the Ångström parameter ($1.5 \leq \alpha \geq 2$) and a single scattering albedo decreasing with wavelength are usually characterized the aerosol resulted from biomass burning. Also, in case of dust event, the AOD value is high and Ångström parameter is low.

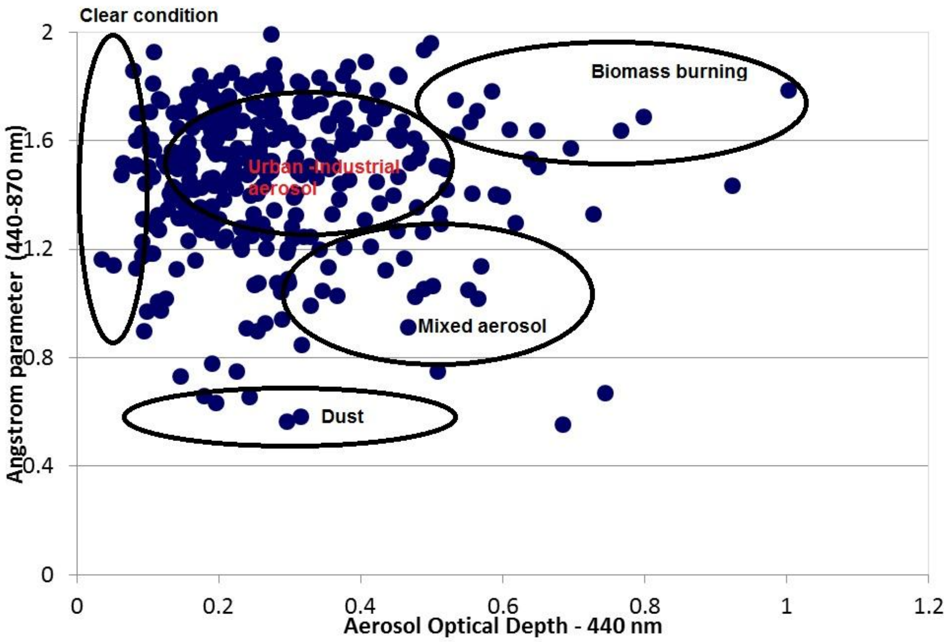

Figure 2. Correlation between AOD$_{440}$ and Ångström parameter at 440–870 nm for different aerosol types over Timisoara during 2011 and 2012

In Table 1 are presented several pollution episodes with desert dust and biomass burning aerosol. In the table N is the number of recording respectively average values for AOD and Ångström parameter during 2011 - 2012 from the measurements achieved at the Timisoara station.

Table 1: The most relevant pollution episodes with desert dust and biomass burning aerosol

Nr. crt.	Date	Aerosol Type	N	AOD$_{440}$	Angstrom parameter
1	26 April 2011	Desert dust	15	0.58	0.43
2	27 May 2011	Biomass burning	31	0.32	1.52
3	28 May 2011	Biomass burning	18	0.68	1.42
4	5 September 2011	Desert dust	29	0.50	0.75
5	18 September 2011	Biomass burning	10	1.02	1.81
6	17 November 2011	Biomass burning	22	0.92	1.43
7	3 June 2012	Desert dust	14	0.56	0.55
8	10 June 2012	Desert dust	21	0.31	0.58
9	23 august 2012	Biomass burning	54	0.52	1.42
10	26 August 2012	Biomass burning	23	0.76	1.67
11	19 November 2012	Desert dust	21	0.42	0.82

April 26 and September 5, 2011 produced high values of AOD$_{440}$ (0.58 on April 26 and 0.55 on September 5). They were considered to be desert dust due to the low values of the Ångström parameter ($\alpha = 0.43$ and $\alpha = 0.75$, respectively), to the predominance of the coarse mode and to the single scattering albedo increasing with wavelength (SSA$_{440}$ = 0.92 to SSA$_{1020}$ = 0.96 and SSA$_{440}$ = 0.91 to SSA$_{1020}$ = 0.97, respectively). The imaginary part of the refractive index was found in the range 0.003 ± 0.001. Similar optical properties of aerosols in June 3 and 10, and November 19 in 2012 indicate their desert origin as well. In order to explain the data, backward trajectories were analyzed using HYSPLIT model. Air masses trajectories were found to be oriented from northern Africa towards the South of Europe.

In 26 august 2012 was analyzed, when the average AOD is 0.76 at wavelength 440 nm and α is higher ($\alpha > 1.6$). The single scattering albedo value decrease with wavelength and the real part of the refractive index was found in the range 1.5±0.05; this means the predominance of the accumulation mode. From correlation between Ångström parameter computed in the spectral interval 440 – 870 nm and AOD at 440 nm for Timisoara, is was conclude that the atmosphere is loaded with particles from the biomass burning. Correlation between HYSPLIT model and MODIS show that the air masses trajectories are passing over the biomass burning sites and then towards Timisoara. The same pattern was found for other cases of pollution with biomass burning aerosol.

CONCLUSIONS

The aerosol properties including aerosol optical depth, Ångström parameter, single scattering albedo, volume size distribution and real part of refractive index were analyzed for Timisoara station by using the sun photometer measurements during 2011 and 2012. By analyzing these properties the aerosol type is determined. In this period several pollution episodes occurred, five of them with dust and six with biomass burning. Generally the pollution with aerosol pollution has a negative effect on solar irradiance, regarding the energy losses.

REFERENCES

Adler G., J. M. Flores, A. Abo Riziq, S. Borrmann, and Y. Rudich, (2011) Chemical, physical, and optical evolution of biomass burning aerosols: a case study, *Atmospheric Chemistry and Physics*, 11, 1491-1503.

Alizadeh Choobari O., Zawar-Reza P., Sturman A. (2014) The global distribution of mineral dust and its impacts on the climate system: A review, *Atmospheric Research*, 138, 152 -165

Calinoiu D., Paulescu M., Ionel I., Stefu N., Pop N., Boata R., Pacurar A., Gravila P., Paulescu E., Trif-Tordai G. (2013) Influence of aerosols pollution on the amount of collectable solar energy. *Energy Conversion and Management* 70, 76–82.

Dubovik O., Smirnov A., Holben B., King M.D., Kaufman Y.J., Eck T.F., Slutsker I. (2000a) Accuracy assessments of aerosol optical properties retrieved from AERONET sun and sky-radiometric measurements, *Journal of Geophysical Research*, 105, 9791 – 9806.

Dubovik O., and King M.D. (2000b) A flexible inversion algorithm for retrieval of aerosol optical properties from Sun and sky radiance measurements, *Journal of Geophysical Research*, 105, 673 – 696.

Dubovik O., Holben B., Thomas F., Smirnov A., Kaufman Y.J., King M.D., Tanre D., Slutsker I. (2002) Variability of absorption and optical properties of key aerosol types observed in worldwide locations, *Journal of the Atmospheric Sciences*, 59, 590 – 608.

Dubovik, O., Sinyuk A., Lapyonok T., Holben B.N., Mishchenko M, Yang P., Eck T. F., Volten H., Munoz O., Veihelmann B., W. J. van der Zande, Leon J.F., Sorokin M., and Slutsker I., (2006) Application of spheroid models to account for aerosol particle nonsphericity in remote sensing of desert dust, *Journal of Geophysical Research*, 111, 34.

Gustafsson, O., Krusa, M., Zencak, Z., Sheesley, R. J., Granat, L., Engstrom, E., Praveen, P. S., Rao, P. S. P., Leck, C., Rodhe, H., Brown (2009) Clouds over South Asia: Biomass or Fossil Fuel Combustion?, *Science*, 323, 495–498.

Mahowalda N., Albania S., Koka J.F., Engelstaederc S., Scanzaa R., Warda S., Flanner G.M. (2013) The size distribution of desert dust aerosols and its impact on the Earth system, *Aeolian Research*, Article in Press, Elsevier.

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ASSESSMENT OF DUST POLLUTION AND BIOTOXICITY SNOW COVER URBAN AREA (UFA, RUSSIA)

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ABSTRACT

Dust pollution of snow cover of an urban area is studied and the assessment of biotoxicity of tests of the snow which have been selected in industrial, inhabited, park zones and at highways is given.

Keywords: *Snow, dust pollution, biotoxicity, infusoria.*

INTRODUCTION

In recent years, much attention is paid to issues of air pollution. Shows the quantitative relationship between the concentrations of various pollutants in the atmospheric air and the population health indicators (Kuramshina et al., 2013). Snow cover is the convenient indicator of pollution of atmospheric air, it as the natural store registers the valid size of losses of polluting substances during a cold season. As is known, the pollution of snow cover occurs in wet and dry loss of pollutants from the atmosphere. For regional and global pollution fraction of dry deposition is usually 10-30%, but close to local sources with large emissions of the coarse aerosols fraction part of dry emissions may reach 70-80% (Vasilenko et al. 1985). The analysis of literature data shows that the usual information about the content of chemical substances in snow cover is clearly insufficient to assess the degree of toxicity and hazards to the environment, because in the combined effects of chemicals toxic effects may increase. In this connection, very informative methods are biological testing by sensitive organisms to evaluate the toxicity of water-soluble substances present in the snow.

The present work is devoted to the study of dust pollution of the snow cover, Ufa and assessment of biotoxicity of snow samples taken in the industrial, residential and green areas, at highways with heavy traffic, as well as with the background territories remote from urban areas in South-Western direction, opposite to the prevailing winds.

MATERIAL AND METHODS

Samples of snow were collected in industrial and Park zones in the forest and at highways with heavy traffic. As a control used samples of snow background of the region, remote from Ufa at a considerable distance, where there are no local sources of pollution. Samples of snow were taken in the spring before the melting of the pits prepared for all thickness of the snow cover. Thus recorded the size of the pit (length, width, depth), date of selection and duration of accumulation of snow cover. The time period of accumulation of atmospheric deposition was calculated from the date of stable snow cover up to the time of sampling. Samples of snow had thawed at room temperature, filtered for separation of solids deposition. After drying sludge weighed. Mass of sediment was determined by the total mass of dust falling on a unit area per unit time. The calculation was carried out according to the following formula: $m = m_s / S \cdot t$, where m is the mass of dust falling on a unit area per unit time ($kg/km^2 \bullet day$); m_s - mass of dust deposited snow, kg; S - area of the pit, km^2; t is the time interval between the date of stable snow cover and sampling of snow day (Vasilenko et al., 1985, Kuramshina et al., 2000).

Toxicological estimation of snow water samples obtained during thawing of snow samples were performed by the method of biotesting with the use of daily culture of infusoria of Stylonychia according to Fomin et al., 1992, Kuramshina N.G. et al., 2000. Assessment of the degree of toxicity were performed in the automatic mode using avtomehanizaciya with biodetection, engine positioning, computer and software complex analysis of toxicity (VNIRO, LLP "Biotest"). Biotoxicity test water was estimated by the change of the survival of the ciliates on exposure in the test water. Criterion toxicity was reduced survival of the ciliates 50% or more in the analyzed water in comparison with the control.

RESULTS AND DISCUSSION

Obtaining a detailed picture of pollution of atmospheric air of city territory is very difficult because of the large number of emission sources and complex spatial distribution of pollutants in urban conditions. Practically the only reliable source of data on the extent of urban pollution of the atmosphere is the study of pollution of the snow cover. The results of the study of the spatial distribution of dust pollution in the urban area in 2012 presented in table 1. For comparative analysis attracted our results obtained previously in 1995 (Kuramshina et al., 2000).

Table 1: Dust pollution of the snow cover, Ufa

Place of sampling	The mass of dust, mg		The area of the pit, m^2		Duration of snegostav,day		Dust load, $kg/km^2 \cdot day$	
	1995	2012	1995	2012	1995	2012	1995	2012
Industrial zone								
Khimprom	831,3	33,7	0,17	0,04	137	133	35,7	7,0
North area	199,0	123,3	0,27	0,35	134	135	5,5	2,6
Residential area								
Mr. Inors	495,1	82,1	0,12	0,07	134	131	30,9	8,6
Mr. Sipaylovo	152,9	165,3	0,12	0,04	127	135	10,0	30,6
Mr. Green grove	122,1	121,0	0,06	0,04	122	134	16,7	22,4
Mr. Nizhegorodka	462,5	27,1	0,12	0,12	121	134	31,9	1,7
Mr. Dema	107,3	110,2	0,085	0,14	125	136	10,1	5,8
City parks, suburban forests								
Park Gafuri	40,8	53,2	0,12	0,05	127	130	2,7	8,2
Park Kalinina	344,4	304,5	0,12	0,07	127	131	22,6	32,7
Park Yakutova	293,3	168,0	0,077	0,04	122	130	31,1	32,3
Lenin Park	5,7	141,8	0,12	0,07	130	132	0,40	15,4
North water diversion	153,3	79,2	0,06	0,04	134	133	19,1	14,9
R. of Sutolka (forest)	333,9	91,2	0,06	0,04	122	130	45,8	17,5
Park Demsky	419,4	197,6	0,12	0,10	125	132	27,9	14,7
Bridge Ufa-Dema	251,0	130,3	0,12	0,05	125	142	16,7	18,3
Road								
Ufa-Zaton	242,8	133,0	0,24	0,08	130	131	7,8	12,7
Ufa - Dema	100,6	118,4	0,20	0,07	125	139	4,0	12,2
Ufa-Kandry	189,4	201,0	0,07	0,05	125	138	21,6	29,1
Background territory								
Podymalovo village	96,6	78,6	0,14	0,10	128	134	5,4	5,9

The results presented in table 1, indicate that in the period 1995-2012, the level of dust load in most functional areas, Ufa declined significantly. However, it is not typical for transport zone and for some parts of the residential and green areas. The variations in the values of absolute and relative dust load in different functional zones of the city territory is presented in table 2.

Table 2: Absolute and relative values of the dust loadin various areas, Ufa (2012)

Functional area	Dust load	
	Absolute, kg/km^2·day	Relative
Industrial	2,6 – 7,0	0,4 – 1,2
Residential	1,7 – 30,6	1,0 – 5,2
Park	8,2 – 32,7	1,4 – 5,5
Transport	12,2 – 29,1	2,1 – 4,9
Background	5,9	1,0

From the results shown in Table 2 suggest that most of the urban territory observed exceeding the background level of dust pollution. The maximum values of the characteristic of the residential and park areas adjacent to industrial sites and urban thoroughfares. In assessing loss-dust decided to allocate four levels of contamination: low – 100-250; medium – 250-450; high – 450-850; very high – more than 850 kg/km^2 day. Studied urban area can be attributed to slightly polluted because the maximum level of dust load (32.7 kg/km^2·day) significantly lower than that (100 kg/km^2·day).

The results of the study of biotoxicity of snow samples taken in the spring of various functional zones, Ufa, presented in table 3.

Table 3: Biotoxicity samples of snow cover territory, Ufa

Place of sampling	Survival of the ciliates, %	Index toxicity (0-1)
Industrial zone		
Khimprom	31	0,69
North area	33	0,67
Residential area		
mr. Inors	39	0,61
mr. Sipaylovo	37	0,63
mr. Green grove	61	0,39
mr. Nizhegorodka	64	0,36
mr. Dema	67	0,33
City parks, suburban forests		
Park Gafuri	60	0,40
Park Kalinina	70	0,30
Park Yakutova	62	0,38
Lenin Park	65	0,35
North water diversion	66	0,34
R. of Sutolka (forest)	50	0,50
Park Demsky	68	0,32
Bridge Ufa – Dema (forest)	53	0,47
Road		
Ufa – Zaton	57	0,43
Ufa – Dema	59	0,41
Ufa – Kandry	61	0,39
Background territory		
Podymalovo village	80	0,20

From the results presented in table 3, it follows that higher values of the index of toxicity characteristic samples snow water industrial zones (0,67-0,69), two districts in the zone of influence of industrial Northern part of the city (0,61-0,63), and the territory adjacent to roads with heavy traffic (0,39-0,43).

The degree of toxicity of dust pollution snow is different. At similar dust load characteristic for a residential area adjacent to industrial sites (8.6 and 30.6 kg/km^2 day.) and parkland (8.2 and 32.7 kg/km^2 day) biotoxicity test snow water of habitable zone (0,61-0,63) significantly exceeds that of the park area (0.30-0.40).

CONCLUSION

Studies suggest regular biotesting of snow cover the urban area for assessing toxic pollution in winter period, the method of biotesting has advantages in comparison with a very time-consuming, complex geochemical measurements and allows in the integral form to evaluate the toxicity of the emissions.

LITERATURE

Kuramshina N.G., Imashev U.B. Geochemical, ecological and social condition of the main technological areas of Bashkortostan. – Ufa: Gilem, 2013. – 236 p.

Vasilenko V.N., Nazarov I.M., Friedman M.D. Monitoring of pollution of the snow cover. Gidrometeoizdat, 1985. – 180 p.

Fomin P.S., Checkin A.B. Water. Control of chemical, bacterial and radiation safety according to international standards: a Handbook. - M, 1992. – 600 p.

Kuramshina N.G., Kuramshin E.M., Verzakov M.S., Erkeev M.I., Lapikov V.V., Chukturidi V.I. Indication dust pollution snow cover of the territory of Ufa and assessment of biotoxicity samples of snow. Bashkir ecological bulletin, 2000. No. 2. C. 32-35.

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DYNAMICS OF THE STATE OF ENVIRONMENT IN THE CONDITIONS OF THE CITY

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ABSTRACT

Carrying out environmental monitoring allowed to define structure of atmospheric and soil pollution of regions of Belarus. The hygienic assessment of degree of danger of pollution of free air and the soil of the cities is given. Sources of emissions of polluting chemicals are defined.

Key words: *sity, atmosphere, soil, chemical pollutants, monitoring.*

INTRODUCTION

As a result of the emissions which are carried out by the enterprises of the industry, a reactive wastage of the main production, household garbage the composition of city free air which is one of factors of habitat of the person, capable to have negative impact on a population state of health significantly changes. In it the percent of the maintenance of a dust considerably increases, there are "trace quantities" substances, unrepresentative for environment.

FINDINGS AND DISCUSSION

Carrying out environmental monitoring allowed to find existence of atmospheric pollution of oxidizing type which are formed as a result of a chemical combination of jet hydrocarbons with nitrogen oxides under the influence of a sunlight. For example, in Vitebsk four areas on ecological trouble are allocated, in two of which the large production enterprises are concentrated. On value of a cooperative index the most polluted in the city is the area of the railway station where level of air pollution by the majority of controlled substances is 1,5 - 2 times higher, than in other territory. On this site average annual concentration of oxides of nitrogen and a dust makes 1-1,5 maximum concentration limits, formaldehyde of 3,3 maximum concentration limits [1].

The hygienic assessment of degree of danger of pollution of free air is defined by the cooperative index IZA (index of pollution of the atmosphere) considering frequency rate of excess of maximum concentration limit, a class of danger of substance, quantity collateral present pollutants in the atmosphere. As the most significant substances nitrogen dioxide, white damp, suspended matters, phenol and formaldehyde are emitted. The analysis IZA loudspeakers for the last 25 years in Minsk allows to determine particular consistent pattern. For example, the most adverse IZA was in 1980 - 1985 (3,4 - 5,5 points) that can be explained with a high level of industrial production. The period of recession of industrial production is characterized also by lower IZA (2,0 - 3,0 points). Since 1997 lifting of an index to 4,4 points and is observed above that is allegedly caused by sharp body height of vehicle fleet. Free air of. Minsk it is characterized by the high content of the formaldehyde which concentration at the level of maximum concentration limit is noted only in 1987. In other years level of formaldehyde is at the level of 1,2 - 3,3 maximum concentration limits. The content of dioxide of nitrogen, white damp, suspended matters and phenol was at the level of 0,1 - 0,75 maximum concentration limits.

The soil cover in an urban environment is one of the main components of the environment, carrying out a number of very important functions which set causes the main social function of city soils – comfort of accommodation of the person. Thus it is necessary to recognize that the soil cover of the city is the screen of absorption and accumulation of the toxic substances which are besieging from air, getting to it with a solid industrial and household waste. In the soil environment toxic substances partially decay and lose the activity, other part, interacting with each other and with a soil absorbing complex, increases reactivity, increasing the toxicity. Technogenic pollution of soils peculiar and not always coincides with pollution of other environments. Soils are an intermediate in pollution of the adjacent environments which are first of all surface and underground water, vegetation and free air.

According to the conducted researches [2-5], the economic complex of Mogilev is the main factor of negative impact on environment since technogenic pollution of soils through air-gas emissions of the production enterprises and vehicles is prevailing. It is noted that the structure and intensity of pollution of soils of the city not always correlates with sources existing now and levels of emissions of pollutants in the atmosphere. The maintenance of pollutants in soils – reflection of the anthropogenous influence long and changing in time. For example, till 1997 pollution of soils went mainly due to specific emissions of the enterprises (a methanol, a carbon disulfide, a hydrogen sulfide, etc.) . In bulk volume of emissions of 28 - 32% 10 - 15% – the power system enterprises, 25 - 59% – transport (without individual vehicles) fell to the share of the production enterprises. Now the total level of pollution is formed generally at the expense of the traditional pollutants which are thrown out by motor transport and combined heat and power plant. For example, in 2004 with emissions from stationary sources among which JSC Mogilevkhimvolokno, RUP "Mogilevliftmash", UERP "Mogilev Automobile Plant to them S.M. Kirova", JSC "Mogilev repair plant", in the atmosphere entered 10,427 t of the heavy metals (HM).

Geochemical researches testify to the composite ecological condition of a soil cover of Mogilev. The structure of pollutants is multidimensional and caused more by specifics of an economic complex. Data processing of the geochemical analysis with creation of statistical surfaces on a kriging-method for concentration of separate metals and for Z_c was carried out in the environment of GIS by means of expressly developed complex of programs so that classification of extent of pollution corresponded to provisions. All zonal statisticians given below have estimating character and are received by results of the analysis of statistical surfaces together with the card of use of territories from the Master plan of Mogilev (table 1) [5].

Table 1: Pollution of a soil cover of the functional zones of Mogilev and adjacent territories

The functional zone	The area, hectare	Zn	Cd	Pb	Mn	Cu	Square of the polluted lands, %
Public and housing multiroom estate	1543,8	8,8	21,6	8,2	0,2	0,8	31,7
Housing farmstead development of city type	2360,3	16,6	22,0	7,0	0,2	0,7	32,1
Housing farmstead development of rural type	350,1	-	-	-	-	-	-
Production and municipal and warehouse building	2309,7	6,9	7,1	7,1	1,7	-	20,9
The planted trees and shrubs public territories	1309,4	12,2	28,3	8,6	-	0,3	39,1
The planted trees and shrubs territories of a special purpose	386,6	7,5	4,6	4,2	-	-	13,8
Inundated territories	531,9	34,4	36,8	8,7	-	-	53,0
Turnpike and main streets and roads	667,0	10,8	18,4	7,4	0,1	0,6	29,7
Public railroad	298,4	3,4	5,7	17,5	1,9	0,1	25,3
Engineering constructions	12,0	40,5	40,0	12,3	-	-	54,9
Farmlands	2602,3	0,4	0,1	0,2	-	-	0,6

Forest area	1148,8	5,4	2,3	12,5	-	-	18,1
Open landscape	988,2	6,2	7,6	10,2	-	-	20,4
Other	152,5	-	-	25,3	-	-	25,3
In total	14661,1	7,3	10,6	6,3	0,3	0,2	19,3

The most priority among HM is cadmium which air-gas emissions are bound to work of power system and motor transport [6]. The average content of an element is 0,5 mg/kg of the soil at minimum value 0,02 and maximal – 1,8. Differentiation of a soil cover of the territory of the city on pollution by this metal looks as follows:

- 19,7% of the territory where the content of cadmium does not exceed two background values, are not polluted (the earth of agricultural residential suburbs);
- 69,7% of the territory where the content of cadmium in them comes nearer to the parameter of maximum loads, are admissible is polluted (mainly territories of the production and municipal and warehouse building, and also densely populated zones of multiroom building with a heavy-bodied transport network);
- 10,6% of the territory where the maintenance of a pollutant is in maximum concentration limit limits, are extremely dangerously polluted (the downtown and the floodplain of the Dnepr River a zone of accumulation of Cd which is washed away from the territory of a reservoir of a river basin).

Accumulation of Zn in the soil is bound to work of motor transport, objects of power system and metallurgy [6]. Average content it in soils makes 49,9 mg/kg of the soil at minimum value 6,2 and maximal – 512,0. Differentiation of the territory of the city on extent of pollution by Zn of is as follows: 53,2% of the area it is not polluted (generally farmlands of adjacent territories and in housing farmstead estate); about 40% of the territory of the city have admissible extent of pollution and represents a reserve of the next pollution of lands since the content of Zn in them comes nearer to the maximum concentration limits parameters (the earth of zones of city buildings, thoroughfares and floodplains of the city rivers); 7,3% of lands are extremely dangerously polluted (a flood plain of the Dnepr River).

Accumulation of lead in soils is bound to pollutions of products of combustion of fuel, especially when using motor transport on ethylated autogasoline [6]. Average content it in soils makes 15,4 mg/kg of the soil with fluctuations from 1,8 to 227,3. Differentiation of a soil cover on degree to pollution is noted:

- 87% of the territory where the content of lead does not exceed two hum noises, are not polluted or poorly polluted;
- 6,7% of the territory where the maintenance of a pollutant is ranging from two hum noises to maximum concentration limit, are admissible is polluted;
- 6,3% of the territory are extremely dangerously polluted (it is noted in territories of all functional zones, it is more in a flood plain of the Dnepr River, along transport highways, especially in right-bank and central part of the city).

Intensity of pollution is expressed by manganese much more weakly in comparison with other pollyutant. The average contents it in the selected soil tests makes 342,1 mg/kg of the soil at minimum value 20,5 and maximal – 3170,0. 80,4% of the territory of the city the maintenance of Mn has less than two background values, 19,3% of two values of a hum noise up to the size maximum concentration limit that is defined as admissible level. Polluted Mn of the soil (the contents is higher than maximum concentration limit) are noted on the area of 0,3% (the territory of steel works).

Pollution of soils by nickel is bound to pollutions by metallurgical production, in mechanical engineering, power industry of [6] and other productions. The average level of the contents it in soils of the city makes 6,4 mg/kg at minimum 1,3 and maximal 54,3. 91,2% of the area of soils have the content of nickel which is not exceeding two background sizes; 8,8% at level from two background

sizes to maximum concentration limit (knot of the enterprises of JSC "Mogilev Electromechanical Plant", RPUP "Mogilev plant "Strommashina", Elektrodvigatel plant, JSC "Volt").
Accumulation of copper in the soil is caused by air-gas emissions in the atmosphere in metallurgical production and mechanical engineering [6]. The average maintenance of this pollutant in the selected soil tests makes 10,4 mg/kg at minimum 2,6 and maximal 53,8. Differentiation of a soil cover according to the content of copper looks as follows: 98,1% of soils – the contents no more than two background values; 1,7% – from two background values to maximum concentration limit, 0,2% at the level of maximum concentration limit (RPUP "Mogilev plant "Strommashina", Elektrodvigatel plant, JSC "Mogilev Steel Works").

By researches it is established that chrome is not a factor of pollution of a soil cover of studied objects: the contents it in the selected soil tests does not exceed background values.

The index of a total score of pollution of a soil cover is one of very important indicator indexes of safety of conditions of accommodation of the person in the occupied place. It generalizes actions of all complex of pollutants on an ecological condition of a soil cover and gives an assessment of extent of their pollution. It is established that in the territory of Mogilev the area of the polluted soils makes 22,8%, level of their pollution is insignificant: $Z_c = 1,8$ that allows [8] to consider on the basis of existing standards a soil cover of the city insignificantly polluted.

CONCLUSIONS

Therefore, regulation of body height of the cities, town-planning actions, carrying out of "dirty" productions from the large centers, the corresponding changes of technological processes and inventory, improvement of cleaning of a wastage of productions, improvement of treatment facilities at the enterprises, development of waste-free productions the major solutions about improvement of quality of life in the large city.

REFERENCES

Прищепа И.М. Роль факторов внешней среды в возникновении и течении бронхиальной астмы и хронического бронхита в различных регионах Республики Беларусь: Автореф, дисс. на соиск. уч. степ. канд. мед. наук // НИИ вакцин и сывороток им. П.И. Мечникова. - 1997. – 15 с.

Марцинкевич Г.И., Шкарубо А.Д., Усова И.Л. Оценка загрязнения почвенного покрова г. Могилева тяжелыми металлами // Вестник БГУ. Серия 2. Химия, биология, география, 1/2005. – С. 86-91.

Справочно-статистические материалы по состоянию окружающей среды и природоохранной деятельности в РБ. - Мн.: БелНИЦ «Экология», 2005. – 60 с.

Мирончик А.Ф. Радиоактивное и техногенное загрязнение лесов пригородной зоны Могилева // Чернобыль: 20 лет спустя: сб. тезисов междунар. конф. – Гомель: РНИУП «Институт радиологии», 2006. – С. 202.

Феденя В.М., Матвеева В.И., Рыбак В.А. и др. Загрязнение почвенного покрова г. Могилева тяжелыми металлами//Вестник БРУ.-№4(13), 2006.– С. 235-240.

Какарека С.В., Хомич В.С., Кухарчик Т.И. и др. Выбросы тяжелых металлов в атмосферу: опыт оценки удельных показателей. – Мн.: институт геологических наук НАНБ, 1998. – 158 с.

Гигиеническая оценка почвы населенных мест / Инструкция 2.1.7.11-12-5-2004. - Мн., 2004. – 38 с.

Перечень предельно допустимых концентраций и ориентировочно допустимых концентраций химических веществ в почве / Гигиенические нормативы 2.1.7.12-1-2004. - Мн., 2004. – 28 с.

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NOX CONTROL OPTIONS FOR EXISTING COAL-FIRED POWER PLANTS IN ROMANIA

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ABSTRACT

This paper in a technical review of the fuel changes and technology options for existing coal fired power plants from Romania in response to new requirements in the amount of pollutants air emissions. Industrial Emissions Directive (Directive 2010/75/EU) aims to improve air quality in European countries and protection against health risks due to air quality. Additionally it aims to reduce the amount of acid, eutrophication and formation of ground level ozone to record a fall in concentration of pollutants such as sulfur dioxide, nitrogen oxides and particles in the air. To comply with these regulatory requirements, it is important to implement Best Available Techniques(BAT) NOx control technologies on coal fired boilers. The popular primary control technologies at large combustion plants in the EU are low-NOx burners and over-fire air. The secondary NOx technologies applied on EU coal-fired boilers are reburning, selective non-catalytic reduction (SNCR), and selective catalytic reduction (SCR).

Key words: *nitrogen oxides, urea, selective non-catalytic reduction, selective catalytic reduction, lignite fired boilers.*

INTRODUCTION

Over 35% [2] of the delivered power in Romania comes from the 20 GW of installed coal, natural gas and heavy oil power plants. As a Member State of the EU Romania agree at the Spring session of the European Council on 9 March 2007 to reduce until 2020 the emissions of greenhouse gases 20% compared to the levels of 1990 [3].

During the combustion of fossil fuels NOx is produced in the form of NO 95% and NO2 5%. But nitric oxide with oxygen from the air and under the influence of ultraviolet rays becomes a very toxic gas NO2 to humans and the environment.

NOx reducing technologies can be placed in two categories: primary control technologies and secondary control technologies.

Primary control technologies

The primary control technologies as the name says reduce the amount of NOx in the primary combustion zone, and the secondary technologies reduce the NOX in the flue gas away from the combustion zone. Also a secondary technology to reduce NOX such as reburning uses a second stage of combustion.

The most popular primary control technologies are low-NOx burners (LNB) and overfire air (OFA). Based on the capacity of the unit, fuel, and reducing requirements to achieve good performances from primary control technologies we can use one o both of these.

A LNB limits the NOx values by controlling the stoichiometric and temperature in the combustion process. This LNB are designed to regulate the aerodynamic distribution and mixing of the fuel and air, so modifying the operating conditions: reduces the availability of oxygen in primary flame zone, reduce the flame temperature and residence time of peak flame temperature [3]. Installed on existing coal-fired power plants modern air-staged LNB can achieve NOX reductions up to 50%. LNB flames are longer compared to regular burners. In case of rehabilitated boilers the flames can reach the furnace walls, this may require LNB adjustments thereby modifying the capacity of NOX reduction.

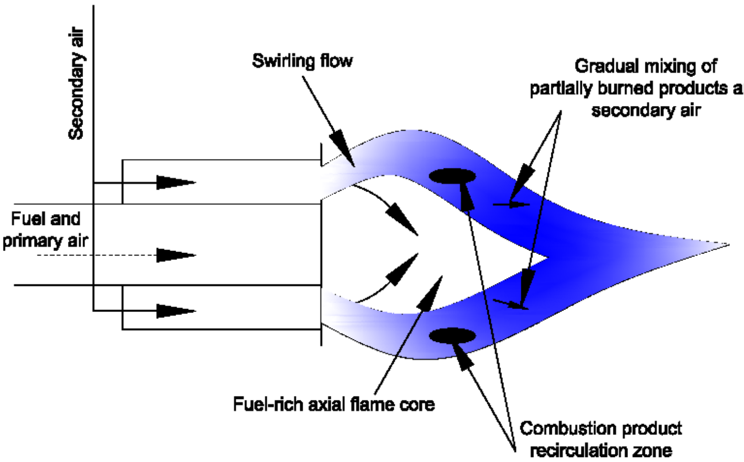

Figure 1. Low-NOX burner

Retrofitting of a boiler by adding OFA involves modification boiler walls and water tubes to create the necessary space for installing air nozzles and the addition of ducts, dampers and the wind box. The operating principle of this system is based on a lack of oxygen in the primary combustion zone and an excess of oxygen in the secondary combustion zone to ensure complete burn-out. Based on this principle the amount of oxygen in the combustion zone is reduced to 70-90%. Normally 15-30% of the combustion air needed for the burn-out is deviated and introduced through these air ports positioned above the primary combustion zone.

To comply with existing and future Nox regulations required by law at the level of 200 mg / m3N (in reference to 6 % O2) in the output flue gases, primary measures described above are not sufficient. Intervention is required such as secondary measures.

Secondary control technologies

The most popular secondary control technologies are reburning, SCR and SNCR. Reburning method is based on the introduction of fuel above the main combustion zone thereby creating a fuel-rich zone. In this area hydrocarbon fragments react with NOX to form hydrogen cyanide (HCN), isocyanic acid (HNCO), isocyanate (NCO), and other nitrogen-containing species [5]. These compounds of hydrogen are finally reduced to N2. To complete burnout of reburning fuel, air is introduced above the injecting area. Retrofitting of a boiler by adding fuel reburning is very important to know the fuel available, a balancing of capital versus operating costs, and boiler specifications. It is a very expensive method, in many plants in which these reburning technologies have been installed it does not work due to high costs of operation.

The first power plant that used reburning technology is a wet-bottom, wall fired 300MW Ladyzhin unit in Ukraine [5]. In general a NGR technology can achieve up to 60 % NOx reduction.

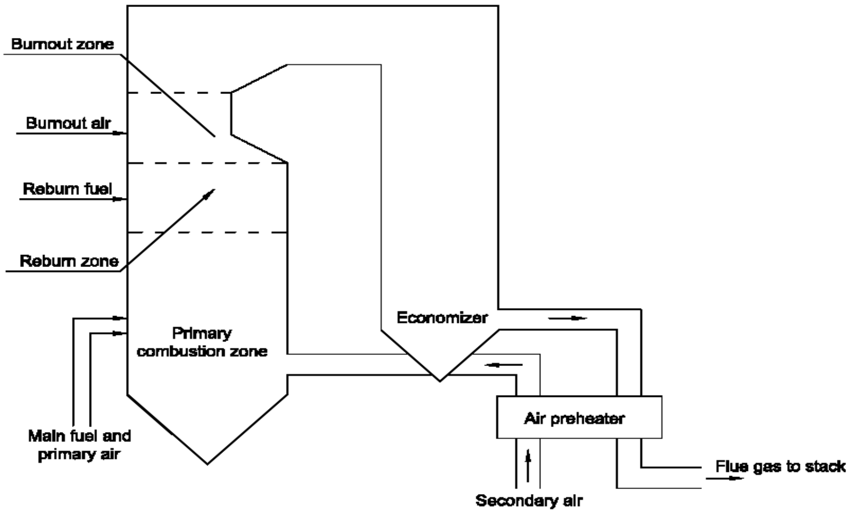

Figure 2. Boiler with reburning

Another method of reducing NOx is SCR, this is a post-combustion method. The operating principle of this installation is to introduce in flue gas path a reducing agent derivative of NH3, and then the flue gas in the presence of a catalyst form N2 and water. Depending on the location of the catalyst we order 3 installations:

- DeNOX → Dust removal → DeSOx: The catalyst is placed before electrostatic precipitator and desulphurization installation. The advantage is that the flue gases are at the desired temperature but has the disadvantage that the gases are not dedusted and desulfurized, which can be a disadvantage for the catalyst.

- Dust removal → DeNOX → DeSOx: The catalyst is placed after dedusting. Has the advantage that the gas stream is filtered but has the disadvantage that the flue gas must be reheated

- Dust removal → DeSOx → DeNOX: The catalyst was placed at the end of circuit of the flue gas cleaning. Flue gas reheating is required. The advantages are reduced exposure to abrasives and smaller dimensions catalyst.

Different types of catalysts are used depending on the flue gas temperature: between 300 and 450 °C uses titanium oxide, for temperatures between 300 and 600 °C uses porous aluminum silicate or zeolite and for temperatures between 100 and 220 °C particles of activated charcoal partially combined with inert material. Installed on existing coal-fired power plants SCR can achieve NOX reductions up to 90%. One of the main disadvantages is the space needed for the installation of facilities necessary for the functioning SCR. In the existing plants is almost impossible to find a section on the flue gas channel where the catalyst can be installed.

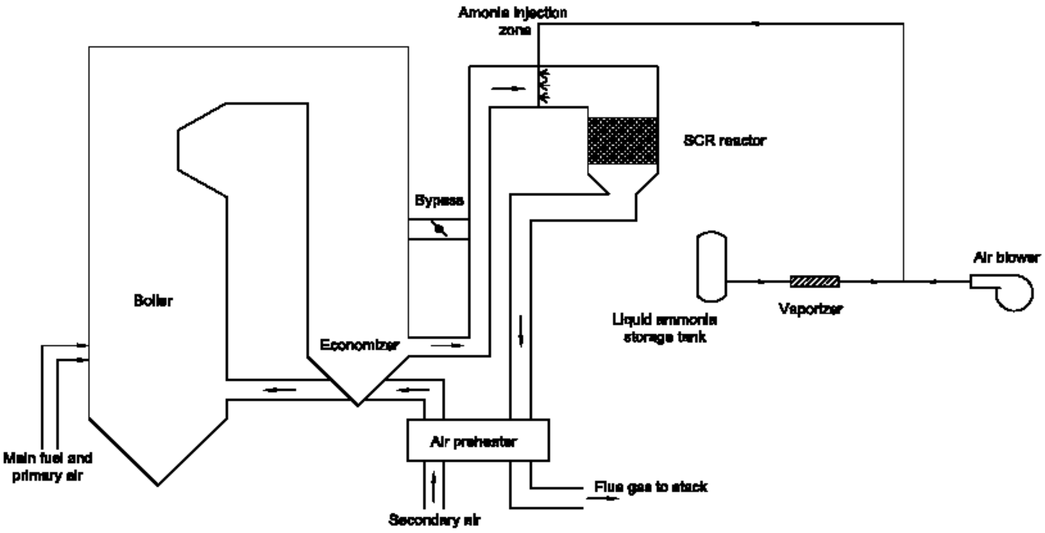

Figure 3. Boiler with SCR installation

Forty years after Lyon’s patent defining the conditions for selective non-catalytic NO reduction to N2 by ammonia (SNCR, excess air conditions, 850 to 1100º C) [1], there is continuing industrial interest in its use as a low cost and effective control technique. The main advantage of SNCR to SCR installations is that these systems do not require a catalyst.
SNCR reaction for urea and ammonia(NH3) are:

$$(NH_2)_2CO+2NO+1/2O_2 \rightarrow 2H_2O+CO_2+2N_2 \qquad (1)$$

$$2NH_3+NO+1/2O_2 \rightarrow 2N_2+3H_2O \qquad (2)$$

If the temperature in the area where is injected the reducing agent and reaction time are not appropriate non-reacted ammonia may pass through the stack. This amount of non-reacted ammonia is known as “NH3 slip”. High concentrations of NH3 slip can react with sulfuric compounds and form ammonium sulfates and bisulfates can cause plugging. Fly ash from a boiler with high NH3 slip is odorous and his marketability is reduced. Installed on existing coal-fired power plants SNCR can achieve NOX reductions ranged from 15- 60%.

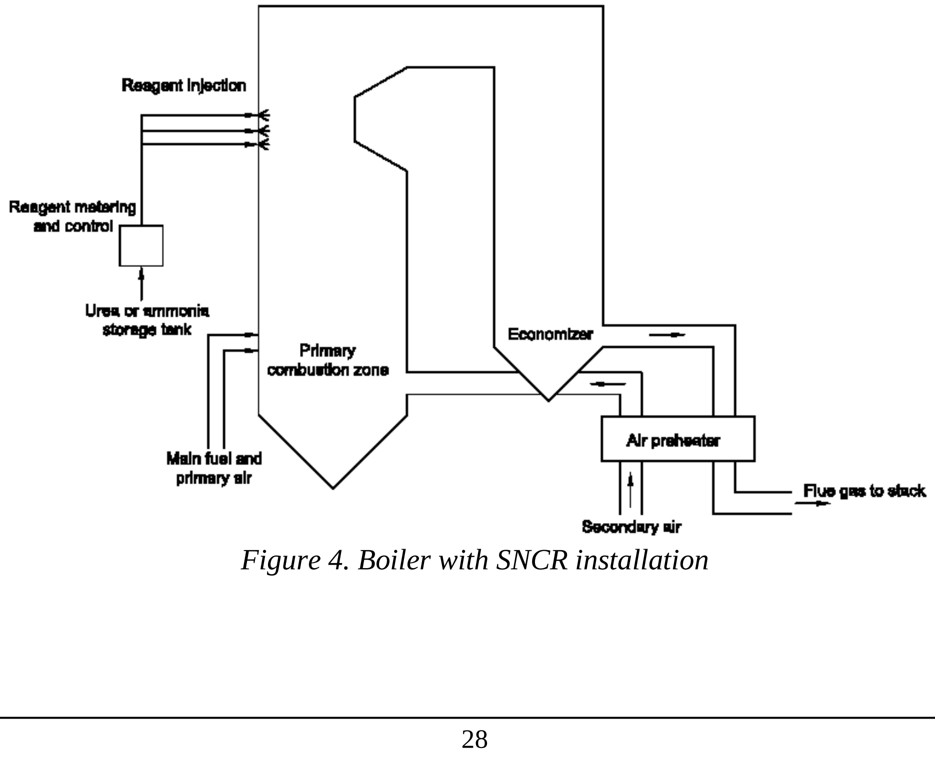

Figure 4. Boiler with SNCR installation

MATERIAL AND METHODS

The power plant studied

Power plant SUD, Timisoara, Romania is composed of the main equipment:

- Two hot water boilers of 100 Gcal / h (116.3 MWt) powered by coal and natural gas called CAF, CAF 2
- Three steam boilers of 100 t / h, 15 bar, 250 ° C powered by coal and natural gas called CAE1, CAE2, CAE3
- A steam turbine type R 19.7-1.4 / 0.3 to 1.2 bar backpressure and 19.7 MWe
- Three tubular heat exchangers for district heating capacity of 50 Gcal / h (58.15 MWt)
- Four steam boiler 10 t / h, 15 bar superheated steam, powered by natural gas maintained in cold reserve.

Currently, slag and ash deposit of power plant SUD Timisoara is the only one in Romania as Environmental requirements. It is located 1.5 km southwest of the village Utvin. Steam boilers of 100 t/h were originally intended for industrial use. These consumers have disappeared and 19.7 MW steam turbine is a very recent investment (commissioning in 2007), making it possible to ensure urban heat cogeneration.

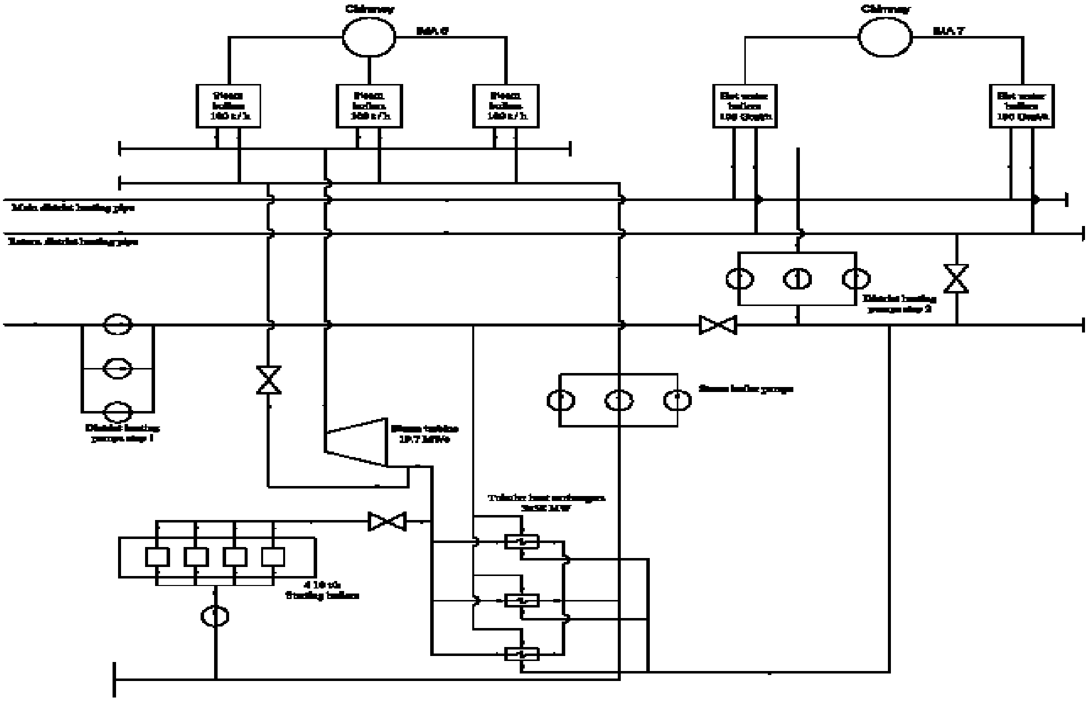

Figure 5. Power plant SUD thermo-mechanical simplified scheme

Table 1: Fuel properties in Romania [7]

Properties	Lignite	Coal	Heavy oil	Imported coal
Heating value Hu [kj/kg]	7.397 ÷ 8.617	15.330	39.500	27.026
Carbon C [kg/kg]	0,230 ÷ 0,191	0,388	0,845	0,671
Hidrogen H [kg/kg]	0,019 ÷ 0,016	0,030	0,094	0,0417
Fly ash [kg/kg]	0,211 ÷ 0,275	0,370	0,003	0,1871
Water [kg/kg]	0,423 ÷ 0,420	0,108	0,009	0,042
Nitrogen [kg/kg]	0,010 ÷ 0,034	0,008	0,003	0,007
Sulfur [kg/kg]	0,007 ÷ 0,006	0,014	0,033	0,0175
Oxygen [kg/kg]	0,100 ÷ 0,058	0,082	0,013	0,033

The reducing agent will be conveyed via circulation pipeline from the storage tank to the Mixing and Metering Module. The Module contains all necessary measuring equipment and valves for the injection of the reducing agent. The injection is situated in the combustion chamber at a temperature between 900 – 1,000 °C. The PLC for measuring and controlling is placed in a control cabinet. The separate control cabinet is located nearby the storage tank.

The SNCR process uses injection nozzles which assure the necessary size and velocity of the liquid droplets, correlated to both the boiler geometry and the flue gas conditions [2]. Each injection lance is equipped with one or more nozzles to ensure an equal distribution of the diluted reducing agent in the flue gas. Because of the easy handling, mostly compressed air instead of steam is being used for atomizing.

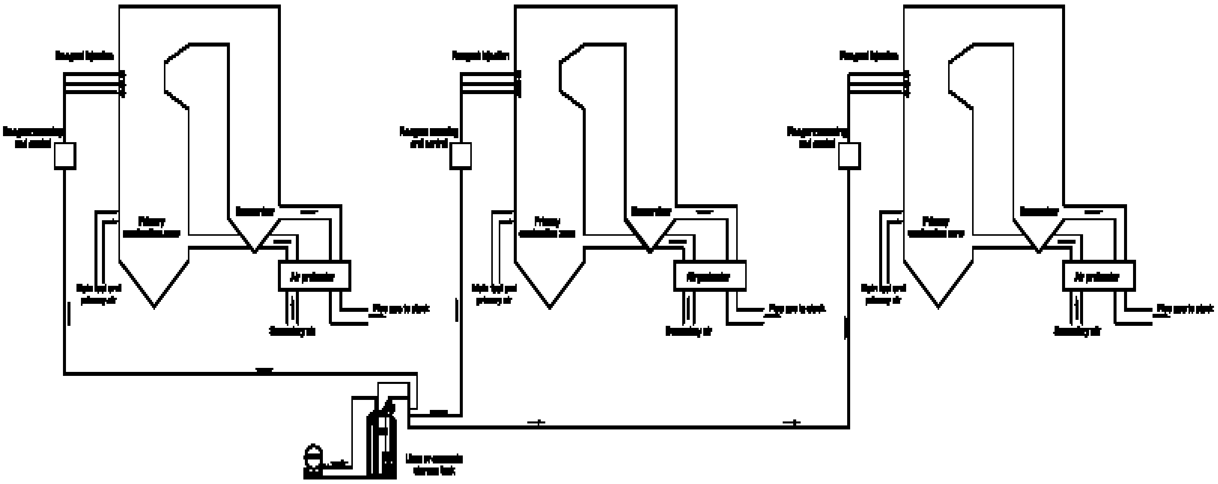

Figure 6. SNCR installation in Power plant SUD

Figures 3 and 4 represent the flow of the injection, generated at different levels. Depending on the temperature, the reducing agent will be injected in one of the injection levels. The injection takes place at the level of the optimal temperature range of 900 to 1,000°C. The quantity and positioning of the lances depends on the dimensions of the furnace cross section, the required NOx reduction and the operating conditions. The lances are equipped with an outer mixing chamber where the reduction fluid is atomized by pressurized air. The reduction fluid will pass one or more outlets at the lance tip. The quantity and direction of these nozzles are designed according the injection geometry. The media (air/reducing agent-water mix) are transported to the lances through flexible steel hoses.

Because of the time delay between the injection and the NOx concentration measurement at the stack, the necessary reducing agent flow has to be pre-calculated in order to follow the changing operating conditions as closely as possible.

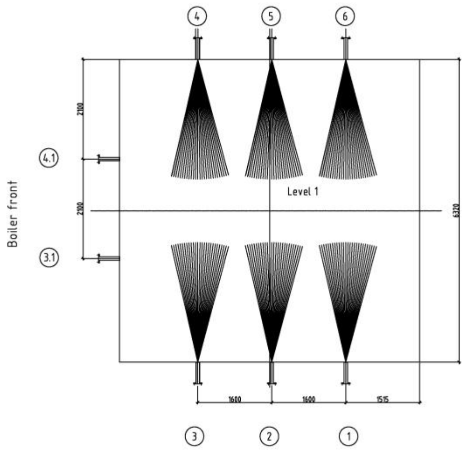

Figure 7. Injection Level 1 (Power plant CET Timisoara Sud) [7]

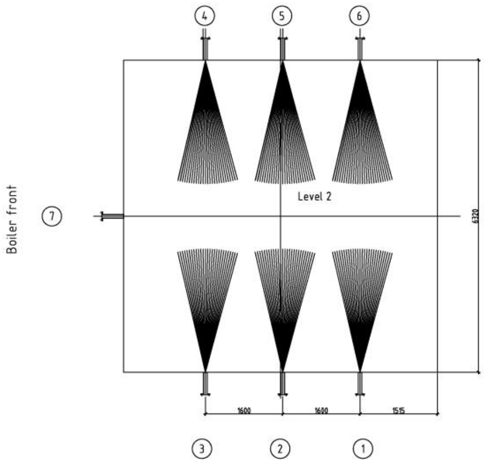

Figure 8. Injection Level 2 (Power plant CET Timisoara Sud) [7]

The reducing agent proposed is NOxAMID45 with the following characteristics [7]:

- Chemical characterization: 45 weight-% urea solution with additive
- Density: 1.126 kg/m3,
- pH: app. 9,
- Boiling temperature: 106 - 110 °C,
- Crystallization point: + 11 °C,
- Ignition point: not applicable,
- Explosion limit: not applicable,
- Color: colorless,
- Odor: slightly NH3 odor,
- Form: watery liquid,
- Water risk class according to WHG: Class 1 (WHG: Wasserhaushaltsgesetz; German water law),
- Consumption estimate of reducing agent for a line: 69 kg/h maxim.

Ecological aspects

After burning coal the quantity of nitrogen oxides, are 95% is the form of NO and 5% NO2. But nitrogen monoxide in the presence of oxygen from air and under the influence of ultraviolet rays becomes nitrogen dioxide a very toxic gas for people and the environment [4].

Given the low level of NO3 concentration required 200 mg / m3N (in reference to 6 % O2) by law in the output flue gases, the proposed SNCR system guarantees a NOX concentration in dry clean gas at stack outlet (referred to 6 % O2) as maximum daily average of 200 mg / m3N, at 100 t/h boiler load. The NH3 slip in dry clean gas at stack outlet (referred to 6 % O2) is presumed, according our calculations, by a daily average maxim at 100 t/h boiler load of 20 mg / m3N.

RESULTS AND DISCUSSION

With measurements made in 2010 before upgrading the NOX level exceeds the concentration required 200 mg/Nm3. There were instantaneous measurements of NOX 604 mg/Nm3.

Table 2: Emissions from Power plant SUD in 2010

Chimney	**SO2**		**NOx**		**Particles**	
	Emissions 2010		**Emissions 2010**		**Emissions 2010**	
	Concentration (mg/ m^3_N)	Amount (tons)	Concentration (mg/ m^3_N)	Amount (tone)	Concentration (mg/ m^3_N)	Amount (tone)
IMA 6	3444	1116	468	152	55	18
IMA 7	3436	1305	426	162	203	77

As a result of EU accession negotiations (Brussels, 31 March 2005) were imposed these quantities of pollutants for Power plant SUD:

Table 3: Quantities of pollutants allowed in Power plant SUD

Chimney	**Pollutant**	**2010**	**2011**	**2012**	**2013-2016**
IMA 6	**SO2 (tons)**	648	648	648	131
	NO_X (tons)	128	128	83	83
	Particles (tons)	22	22	22	22
IMA 7	**SO2 (tons)**	4116	823	823	823
	NO_X (tons)	531	531	531	344
	Particles (tons)	90	90	90	90

To achieve this environment conditions will require using primary and secondary control technologies to reduce NOX. As a primary control technology we recommend OFA and for secondary control technology we recommend SNCR. Measures proposed are BAT techniques as follows: OFA-BREF May 2005, section 3.4.1.2 SNCR- BREF, 2005, Section 3.4.2.2.

From the secondary air flow of the pulverized coal burners we will make a bypass by which the warm air will be fed with a set of ports positioned in the furnace walls in a section above the coal burners. Air by burners will be reduced to a level close to the stoichiometric. This will generate in the primary combustion zone a lower temperature level, which limits the rate of formation of NOX. Additional air is introduced through the ports; excess of oxygen in the secondary combustion zone will ensure complete burn-out. For this reason, the location of the ports is at a considerable distance from the top level of burners in the direction of the flue flow gas without exceeding the the distance limit to which air can participate in the combustion process.

The reducing agent is sprayed as an aqueous solution in a section upstream of the optimal zone, but in the immediate vicinity. As the load variation of the boiler system lead to changes in the temperature of the flue gas, the optimum injection zone "slip" at the top of the furnace. In these circumstances it is possible that the injection not be optimal over the entire heat load of the boiler. In order to avoid such a situation, the injection of the reducing agent is through a system of injectors placed in the two sections. Depending on the thermal load the boiler would be operated fuel injectors located in the optimum temperature.

The OAP aims to reduce NOX emissions from 540 mg / m3N at 400 mg / m3N. SNCR further will ensure reduction to 200 mg / m3N. Together will yield a reduction of more than 50%.

We monitored NOX in the flue load operation before retrofitting and after. Monitoring was done within 24 hours in 18.01.2013. In the first chart we can see the NOX level measured without SNCR installation.

Average amounts of NOx measured at the stack were 589.32 mg/m3N.

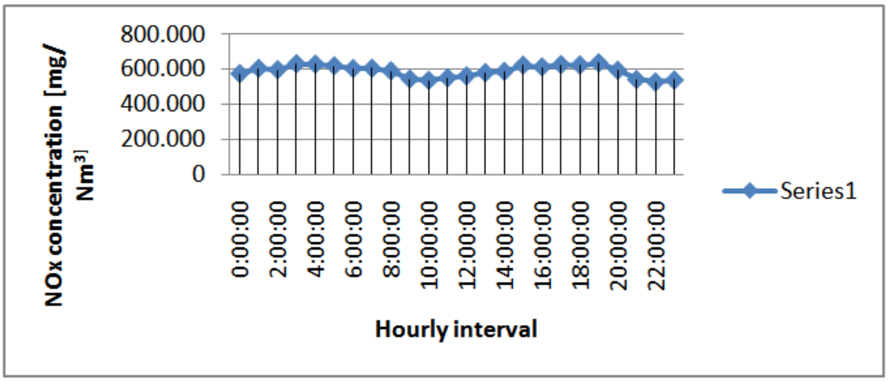

Figure 9. NOX measured at the stack (Power plant CET Timisoara SUD)

In the second chart one can see the NOx measured with OAP installation with boilers at full capacity. Average amounts of NOx measured at the stack was in one day 348.07 mg/ m3N. Also it is notable that OAP results register a removal rate around 40%.

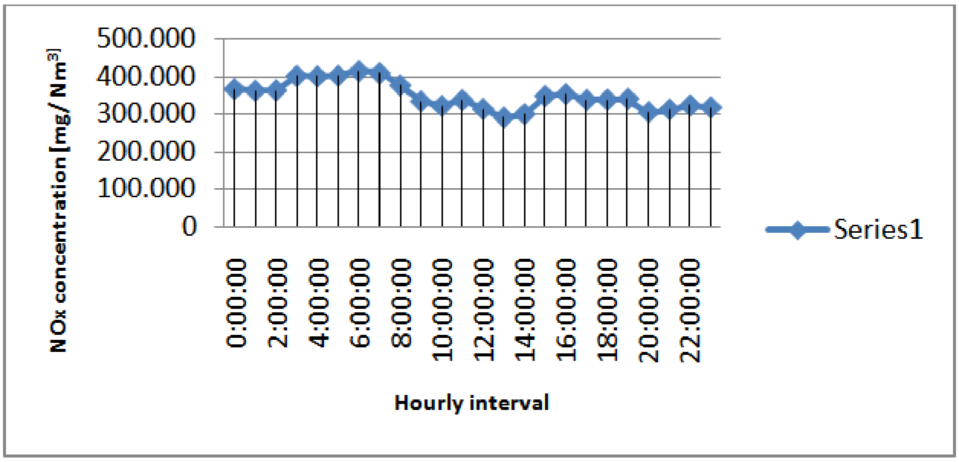

Figure 10. NOX measured at the stack with OAP (Power plant CET Timisoara SUD)

As we can see the primary measures are not enough. Given the low level of NOX concentration required 200 mg/ m3N (in reference to 6 % O2) by law in the output flue gases, the proposed SNCR system guarantees a NOX concentration below the limit imposed. In the next chart we can see the NOx level reached with the SNCR installation and the NOx level required.

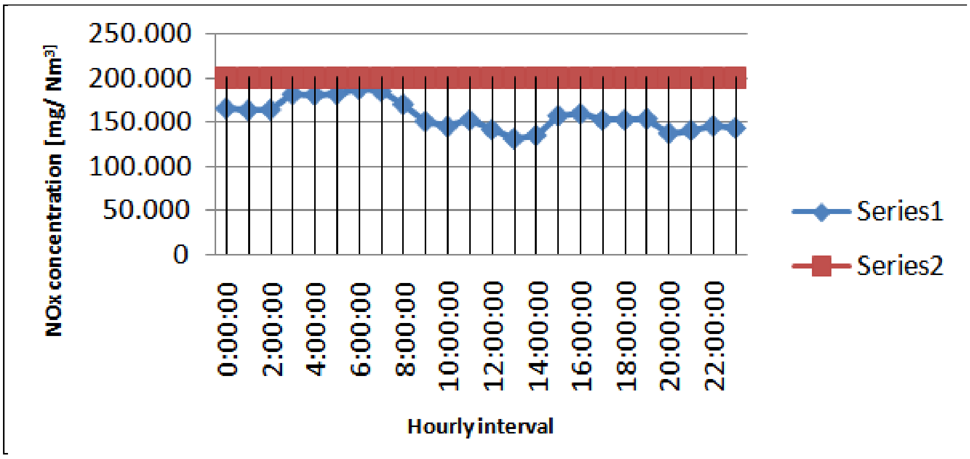

Figure 10. NOX measured at the stack with OAP and SNCR (Power plant CET Timisoara SUD)

Average amounts of NOx measured at the stack was in one day 156.6 mg/m3N. The removal rate of nitrogen oxides contained in the flue gas is around 70%.

CONCLUSION

In most cases the primary measures are not enough to reduce nitrogen oxides in the flue gas is recommended to use secondary measures.

For solid fuel fired boilers without large variations of load and a stable fuel quality, the SNCR technique is regarded as BAT to reduce NOx emissions as follows: SNCR-BREF May 2005, paragraph 3.4.2.2.[3] and OFA-BREF May 2005, section 3.4.1.2.

This research proved that engineers make efforts to optimize the SNCR system with other technologies for controlling NOX and other air pollutants and that this is possible.

The OAP and SNCR technologies aim to reduce NOx emissions from 540 mg/m3N at 200 mg/m3N.

We monitored NOX in the flue load operation before retrofitting and after. Monitoring was done within 24 hours and the average amounts of NOx measured at the stack were 589.32 mg/m3N.

After retrofitting the average amounts of NOx concentrations measured at the stack was in one day 156.6 mg/m3N. The removal rate of nitrogen oxides contained in the flue gas is around 70%.

After installation of dense slurry and desulphurization with this investment, Power plant CET Timisoara SUD will be the first power plant from Romania that meets all environmental conditions assumed in the EU accession.

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REFERENCES

R.K. Lyon. (1975) Method for the Reduction of the Concetration of NO in Combustion Effluents Using Ammonia U.S. Patent No. 3,900,554.

http://transelectrica.ro/web/tel/home

Romania Ministry of Environment and Sustainable Development. (2008) National sustainable development strategy Romania 2013 – 2020 – 2030,p. 40

EU Industrial Emissions Directive Best Available Techniques (BAT) Reference Document for the Large Combustion Plants (2010/75/EU), p. 108

Srivastava, R.K., Hall, R.E., Khan, S., Culligan, K., Lani, B.W., 2005. Nitrogen oxides emission control options for coal-fired electric utility boilers. Journal of Air and Waste Management Association 55, 1369–1388.

INSTITUTE OF CLEAN AIR COMPANIES (ICAC): Selective non-catalytic reduction (SNCR) for controlling NOX emissions, May pp 5, 11, 2000.

ISPE Timisoara. Detailed design, rehabilitation of the district heating in the city to comply with environmental rules on emissions to air and to increase efficiency in urban heat supply. Timisoara, 2012

EUROPEAN COMMISSION: Integrated prevention and control. Reference document on the Best Available Techniques for large combustion plants, July, pp 11, 2006.

Ionel, I., Genesis of the nitrous oxide formation during the SNCR of the flue gas, by using ammonia as reducing agent, Energetica, seria A, nr.5, 1994

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“ECOLOGY OF URBAN AREAS” 2014

THE STUDY OF TRACE METALS LEVEL BY USING VASCULAR PLANTS IN DURRES CITY

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ABSTRACT

Ligustrum lucidum, Fam: Oleaceae and Leandro plant, Nevium Oleander, Fam: Apocynaceae were collected from urban area of Durres city, Albania with different anthropogenic impact in the city. The tree leaves were sampled during the March 2013. 42 samples of leaves of four tree species were collected at 20 sampling sites among main streets of Durres city and a composite sample was prepared for the analyses of each tree sample. Concentrations of trace metals in leaves samples were analysed by furnace AAS. CVAAS was used for the determination of Hg. The trace metal contents were expressed as arithmetic means and standard deviation. The analytical data were subject to statistical analysis. Statistical analysis of the data was carried out using EXCEL and MINITAB-15 Package Programs. After statistical treatment of the data it's note:

- *the tendency for distribution of the elements listed in an ascending order of accumulation factor. For each elements the list is: Hg<Pb<Cu<Zn<Mn. Here we can distinguish more clearly the changes in concentration of different elements in various monitoring points.*
- *the area is mainly polluted by Pb, Mn, that represent a high accumulation factors and high values of the coefficient of variances.*

Pearson Correlation analysis ($p<0.05$) was carried out on the data set of heavy metals to describe their behavior and the association. Weak correlation ($R^2<0.45$, $p<0.05$) were found between Pb-Mn, Zn-Cu and Mn-Cu in leaves samples. Multivariate analysis (Cluster Analysis and Factor Analysis) were caried out to detect the groups of samples with similar patterns of element concentrations and the number of the groups and most important factors were discussed. Based on the similarity of the distribution of the elements at each sampling site, two main groups of elements are extracted. The data were also processed with factor analysis (FA) in order to identify the main source categories of the analysed samples regarding the site contamination and elements distribution. Two main factors were identified that cause the differences in the distribution of trace metals under investigation: the species of the plants and samples position.

Keywords: *Vascular plants, Ligustrum lucidum, Fam: Oleaceae and Leandro plant, Nevium Oleander, Fam: Apocynaceae, urban environment, air pollution.*

INTRODUCTION

Air pollution is an environmental problem, which is caused by domestic heating and all the human activities. In Durres city the heavy traffic is a factor that affects more in the level of pollution, especially during the summer tourist season. Automobile transport also affects in the spread of dust and increased concentration of different pollutants such as heavy metals into the air, coming mostly from traffic emissions. A major impact on pollution of these area has had and continues to have the Chemical Company in Porto Romano area, which was closed in 1990. Until it is closed it has produced Sodium Dichromate for leather processing as well as pesticides Lindane and Tiram. Based on the environmental report great contamination are in Currila and in Zhiron areas. Certainly, within residential areas, also affect the combustion of any organic substance of them (wood, trash, rubber, plastics..), as well as vapors of some production processes within urban areas, which contain gases and harmful substances. Based on the degree of exposure of the pollution that is most close to polluted areas, ages and their physiological condition bring an increase to the symptoms to effects of pollution on their health. So most exposed are the people that live near at dense traffic or at the crossroads, especially the people with health problems.

The aim of this study is to investigate the level of metal contaminants (Cu, Mn, Pb, Zn and Hg) in vascular plants in Durres area. We used many species of vascular plants to accumulate heavy metals. Thus, the concentration of these elements in vascular plants, collected from polluted areas is significantly higher, than the concentration of these elements collected from areas that are away from crossroads or dense traffic. The response of vascular plants depends on the species and the type of pollution. There are differences among species regarding the tolerance to heavy metals, but there also are difference within the same species found that Hg is the most toxic element.

MATERIAL AND METHODS

Sampling

Samples were taken during the last 10 days of March 2013, at 30 stations in Durres city, at about one week after rainy days. The monitoring stations are distributed along main streets of the city. A composite sample was prepared for the analyses of each tree sample. Types of vascular plants that were used for monitoring most commonly are : *Ligustrum lucidum, Fam: Oleaceae* and *Leandro, Nevium Oleander, Fam: Apocynaceae plants.*

Figure 1. Map of Durres city, where are taken the sample of vascular plant. Monitoring stations

The leaves of Ligustra, Ligustrum, Lucidum (St. 1,2,5,9,10,13,16,17,18,20,21,22,25,38,40,41), Ligustrum Sinense (St. 19,29,30,31,32,33,35,39) and Leandro. Nevrum Oleander (St. 7,27,28,42) tree species were collected in most sampling sites. The species different from this one are shown in Table 1.

Table 1: Monitoring stations in Durres city and species of vascular plant

Station	St. 3	St. 4	St. 6	St. 8	St. 11	St. 12	St. 14	St. 15	St. 23	St. 24	St. 26	St. 34	St. 36	St. 37	St. 43
Vacular plant	Hypaphae Thamnaiotes	Pyrochantha Coccinea	Ilqe, Quercus Ilex	Magiola,Magnolia Grandeflona	Quercus Ilex	Spirea Vanhuntei	Evonymus Japonicus	Pitospora Tobira	Catalpa Bignoniade	Vibuznumsp	Pittospora Tobira	Pittospora Tobira	Laurus Nobilis	Magnoli,Grandeflona	Pittospora Tobira

Preliminary treatment of samples

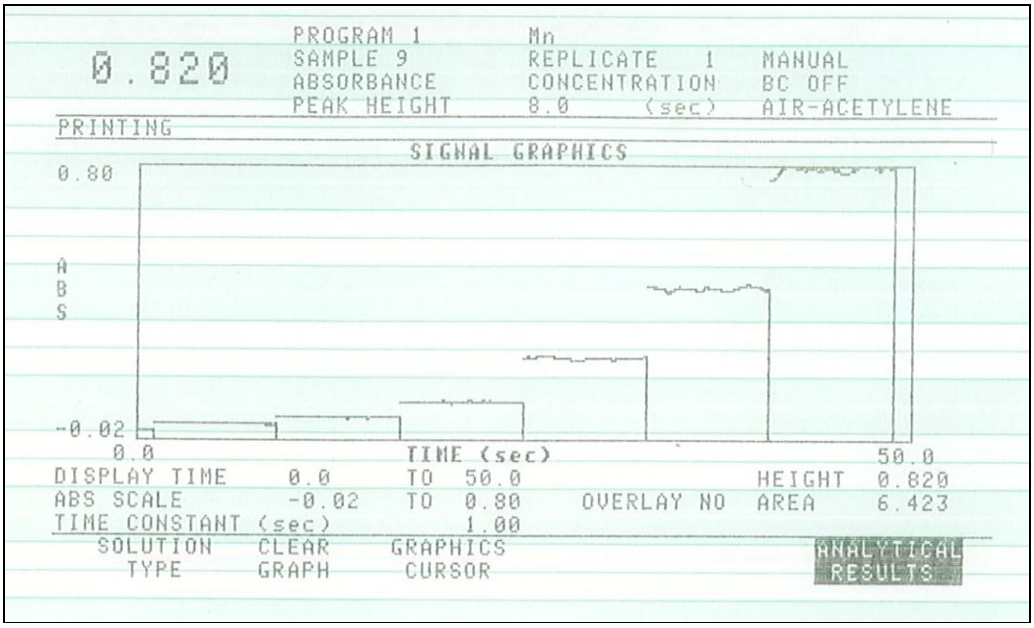
After the transportation of leaves sample in laboratory, leaves samples were dried at ambient air on sheets paper until a constant weight was reached. Then the dried leaves samples were homogenized to a fine material. The leaves crush is made by hand, wearing laboratory gloves without powder polyethylene.

Dried plant samples were digested with nitric acid (ultra pure, 65%) and deionized water (99 : 1) in Teflon tubes. The experiment dishes are cleaned with dilute nitric acid and are washed with distilled water. Elements standard solutions used for calibration curves were prepared by dilution of base standard liquids of 1000 mg /L.

Digesting sample technique was conducted in Teflon tubes with semi-pressure system. 0.5g of dry leaves of each sample were digested with 10 mL of nitric acid $HNO3$ (9:1). Teflon tubes closed and then were left at room temperature for 48 h, and digested for 3 hours at 80-90°C. Subsequently, the temperature was increased to 200°C for 1 hour to realize the full digestion. After cooling, the Teflon tubes were opened and left for evaporation of nitric acid to small volumes. Samples were then diluted with deionized water to a total volume of 50 mL. Vascular plant digests were analysed for Cu, Mn and Zn using AAS Atomic Absorption Spectrophotometry using air-acetylene flame. Determination of Pb metal was made using AAS with electro-thermal atomiser with graphite furnace. Mercury Hg was analysed using an Absorption Techniques with cold vapor (CV-AAS). This method is specific for mercury, since it is only metal that has high vapor pressure at ordinary temperature. If we keep inorganic mercury in water solution can be easily reduced with $SnCl2$ to metallic mercury in the form: Hg^0: $Hg^{+2} + Sn^{+2} \rightarrow Hg^0 + Sn^{+4}$

Calibration method

Linear calibration method that find the link between the analytical signal and the measured analyse concentration were used for obtaining the calibration curves of each element. Blank solution of each element was used. Heavy metal concentration in samples were calculated based on their analytical signal (value of absorbance and the relevant equations of calibration curves. The signals of standard solution of Mn and Hg are shown in Fig. 2.



```
            PROGRAM 1        Mn
  0.820     SAMPLE 9         REPLICATE     1    MANUAL
            ABSORBANCE       CONCENTRATION      BC OFF
            PEAK HEIGHT      8.0      (sec)     AIR-ACETYLENE
PRINTING
                    SIGNAL GRAPHICS

DISPLAY TIME      0.0      TO  50.0                  HEIGHT  0.820
ABS SCALE         -0.02    TO  0.80    OVERLAY NO    AREA    6.423
TIME CONSTANT (sec)            1.00
   SOLUTION    CLEAR     GRAPHICS                   ANALYTICAL
     TYPE      GRAPH     CURSOR                      RESULTS
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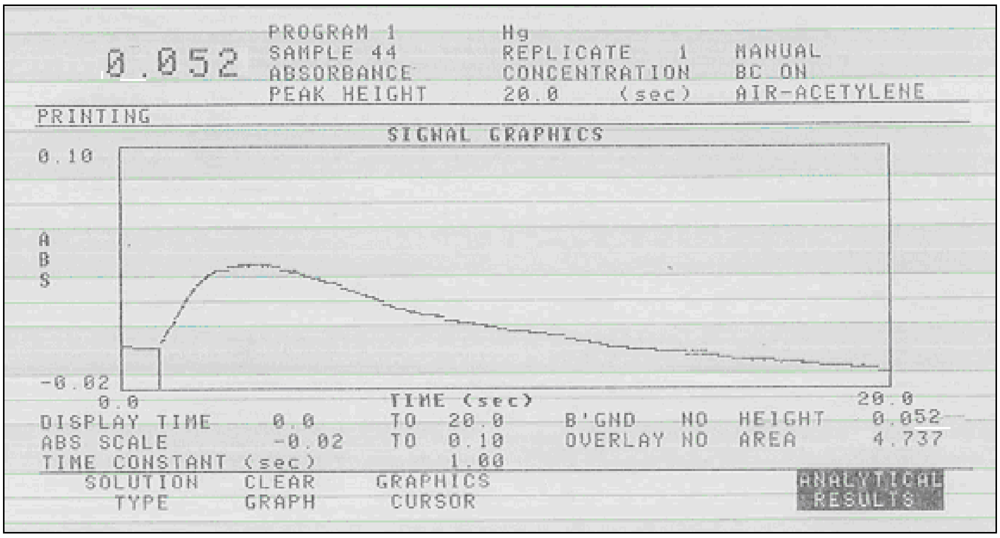

```
                  PROGRAM 1         Hg
   0.052          SAMPLE 44         REPLICATE    1    MANUAL
                  ABSORBANCE        CONCENTRATION     BC ON
                  PEAK HEIGHT       20.0    (sec)     AIR-ACETYLENE
PRINTING
                            SIGNAL GRAPHICS
DISPLAY TIME      0.0     TO  20.0      B'GND   NO   HEIGHT    0.052
ABS SCALE        -0.02    TO  0.10      OVERLAY NO   AREA      4.737
TIME CONSTANT (sec)            1.00
```

Figure 2. The signals of standard solution of Mn and Hg

RESULT AND DISCUSSION

In order to perform rapid and preliminary screening of element concentrations found in vascular plants samples in the different sites, a descriptive statistical analysis was carried out on the data sets as reported in charts below. The trace metal contents were expressed as arithmetic means and standard deviation. The analytical data were subject to statistical analysis. Statistical analysis of the data was carried out using EXCEL and MINITAB-15 Package Programs. In table 2 we note the tendency for distribution of the elements listed in an ascending order of accumulation factor. For each elements the list is: Hg<Pb<Cu<Zn<Mn. Here we can distinguish more clearly the changes in concentration of different elements in various monitoring points. Also we note that the area is mainly polluted by Pb, Mn, who not only represent a high accumulation factors, but also their interval of change for each element is relatively high.

Table 2: Results of statistical data processing (EXCEL, Descriptive Statistic) (mg/kg, DW)

Parameters	Hg	Pb	Zn	Mn	Cu
mean	0.29	1.75	39.22	68.56	8.95
median	0.23	1.42	39.61	46.08	9.30
Range of concentration	0.07-0.73	0.30	11.37	14.71	2.33
maximum	0.73	5.79	94.12	219.61	18.60

In table 3 we note that Mn has the highest values of max/min report. This fact means that the high level of pollution affected by anthropogenic origin pollution. For Pb and Zn elements, high values come also by anthropogenic origin pollution, especially from traffic emissions.

Table 3: Presentation of the report Mean / Median and Max / Min

Parameters	Hg	Pb	Zn	Mn	Cu
Mean/Med	0.96	1.23	1.49	6.77	0.99
Max/Min	8.00	**19.60**	**14.93**	**824.17**	8.28

Therefore to distinguish natural or anthropogenic origin of elements analysed in leaves samples was carried correlation analysis and analysis of elements in groups (Cluster Analysis) elements.

Correlation analysis ($p<0.05$) was carried out on the data set of heavy metals to describe their behavior and the association.

In Table 4 we note a weak correlation ($R^2<0.45$, $p<0.05$) were found between Pb-Mn, Zn-Cu and Mn-Cu in leaves samples. This speaks to their same origin may be of fine dust particles that come from road traffic. As for the correlation of Mn with Mg, we can say that they comes from dust deposited on plants.

Table 4: Correlation between elements Cu, Pb, Mn, Zn, Hg

```
          Cu       Pb       Zn       Mn
Pb     0.292
       0.058
Zn     0.302    0.191
       0.049    0.220
Mn     0.364    0.427    0.150
       0.017    0.004    0.338
Hg    -0.011   -0.003    0.022   -0.068
       0.943    0.987    0.890    0.663
Cell Contents: Pearson correlation
               P-Value
```

Multivariate analysis (Cluster Analysis, CA) were to detect the groups of samples with similar patterns of element concentrations and the number of the groups and most important factors were discussed (table 5).

Table 5: Cluster Analysis of Observations: Cu, Pb, Zn, Mn

```
Euclidean Distance, Complete Linkage
Amalgamation Step
Final Partition
Number of clusters: 6
                                         Average   Maximum
                                 Within  distance  distance
             Number of      cluster sum      from      from
          observations       of squares  centroid  centroid
Cluster1             6          2187.78   18.1760   25.2145
Cluster2             3           294.10    9.8487   11.1338
Cluster3            22          6685.73   16.3452   33.5839
Cluster4             3           675.69   13.4682   19.6086
Cluster5             7          3285.40   20.2338   34.4749
Cluster6             2           259.32   11.3869   11.3869
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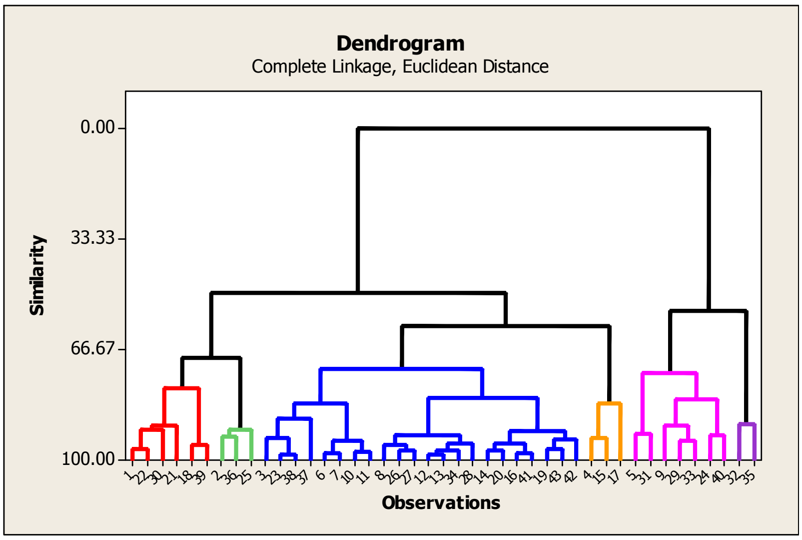

Figure 3. The dendrogram of the distribution of the stations classified on their esimilarity

Cluster 1: In this group we have these stations **1, 22, 30, 21, 18, 39**, where prevails Ligustrum plant, fam: Lucidum Ligusta which has very good accumulation abilities for heavy metals
Cluster 2: In this group we have the stations **2, 25, 36** where prevails Ligustrum plant, fam: Lucidum Ligusta which has very good accumulation abilities for heavy metals
Cluster 3: In this group we have these stations **3, 23, 38, 37, 6, 7, 10, 11, 8, 26, 27, 12, 13, 34, 28, 14, 20, 16, 41, 19, 43, 42**. These are located in the major crossroads where traffic is dense.
Cluster 4: In this group we have these stations **4, 15, 17**. These are located near the beach. This fact has a high impact in values.
Cluster 5: In this group we have these stations **5, 31, 9, 29, 33, 24, 40.** In the values of these stations affect has the location near the sea, also the type of plant.
Cluster 6: In this group we have these stations **32, 35** where prevails Ligustrum Sinensis plant. In the values of these stations affect has traffic emission.
The data were also processed with factor analysis (FA) in order to identify the main source categories of the analyzed samples regarding site contamination and elements distribution.

Factor Analysis: Cu, Pb, Zn, Mn, Hg

```
Factor Analysis of the Correlation Matrix

Rotated Factor Loadings and Communalities (Varimax Rotation)
Variable  Factor1  Factor2  Factor3  Factor4  Factor5  Communality
Cu          0.149   -0.126    0.004    0.966   -0.169        1.000
Pb          0.085   -0.967   -0.002    0.126   -0.206        1.000
Zn          0.985   -0.081   -0.012    0.141   -0.054        1.000
Mn          0.058   -0.210    0.037    0.172   -0.960        1.000
Hg          0.012   -0.002   -0.999   -0.004    0.033        1.000
Variance   1.0036   1.0011   1.0003   0.9983   0.9966       5.0000
```

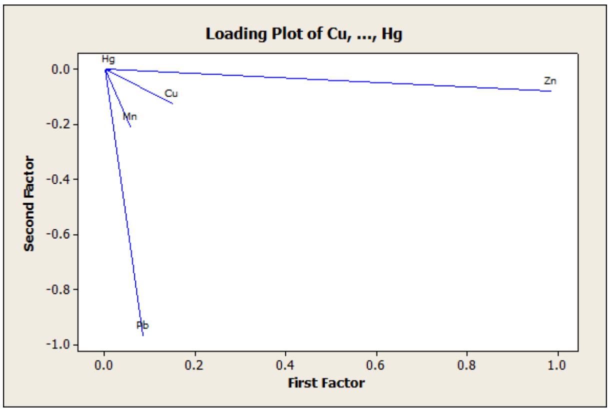

Figure 4. The diagrams of scree plot and loading plot of factor analysis

Two main factors were identified effecting differences in trace metals distribution: the species of the plants and samples position.

Factor 1: This factor is mainly loaded by high positive value of Zn. This factor is related with car emission due to dense traffic.

Factor 2: This factor is mainly effected by high negative loading of Pb. This factor is related with car emission due to dense traffic.

Factor 2: This factor is mainly effected by high negative loading of Hg. This factor is also related with car emission due to dense traffic. Negative values of this element are related with this factor that affect the reduction of this element in plants. The presence of Hg in this group make us to think that the pollution caused by anthropogenic origin pollution, especially from traffic emissions.

CONCLUSION

Symptoms caused by pollutants like heavy metals should be studied in different species, sensitive to that pollutant so their presence in different areas should be controlled. Durres city has a high level of pollution, especially in main roads or in the crossroads. We have to considerate that the concentration of the heavy metal we don't take only by the absorption from the air, but also through the roots. This fact make us difficult to distinguish when the concentration comes from the accumulation by the ground or from the air. From this study we note the tendency for distribution of the elements listed in an ascending order of accumulation factor. For each elements the list is: Hg<Pb<Cu<Zn<Mn. Here we can distinguish more clearly the changes in concentration of different elements in various monitoring points. Also we note that area is mainly polluted by Pb, Mn, who not only represent high accumulation factors, but also their interval of change for each element is relatively high. For Pb and Zn elements, high values come also by anthropogenic origin pollution, especially from traffic emissions. Weak correlation ($R^2<0.45$, $p<0.05$) were found between Pb-Mn, Zn-Cu and Mn-Cu in leaves samples. This speaks to their same origin may be of fine dust particles that come from road traffic. As for the correlation of Mn with Mg, we can say that the deals comes from dust deposited on plants. Types of vascular plants that were used for monitoring most commonly are: *Ligustrum lucidum, Fam: Oleaceae* and *Leandro, Nevium Oleander, Fam: Apocynaceae plant.*

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REFERENCES

Baker, A. J. M. 1989: Accumulators and excluders- Strategies in the response of plants to heavy metals. J. Plant Nutr., 3: 643-654.

Alloway, B. J. 1995. Heavy Metals in Soils. Blackie Academic & Professional. London. SecondEdition, p. 11-57, 122-205, 284-305.356.

Azimi S., Rocher V., Garnaud S., Varrault G., Thevenot D.R. (2005). Decrease of atmospheric deposition of heavy metals in an urban area from 1994 to 2002 (Paris, France). Chemosphere 6, 645-651

Barnes D, Hamadah MA & Ottaway JM (1976). The lead, copper and zinc content of tree rings and bark: A measurement of local metallic pollution. The science of the Total Environment 5

Fergusson, J.E. 1990. The heavy elements: chemistry, environmental impact and health effects.

Gjoka, F., Felix-Henningsen, P., Wagener Hans-R 2002. Heavy metals in soils of vicinity ofindustrial Site of Laç, Albania. Balkan Ecology, Vol. 5, Nr. 3, 301306. Sofie-Bulgaria

N. Rascio, Metal accumulation by some plants growing on zinc-mine deposits,Oikos 29 (1977) 250–253.

R.D. Reeves, Hyperaccumulation of trace elements by plants, in: J.L. Morel, G.

Echevarria, N. Goncharova (Eds.), Phytoremediation of Metal-Contaminated

Soils, NATO Science Series: IV: Earth and Environmental Sciences, Springer,NY, 2006, pp. 1–25.

M.R. Macnair, The hyperaccumulation of metals by plants, Adv. Bot. Res. 40(2003) 63–105.

N. Caille, F.J. Zhao, S.P. McGrath, Comparison of root absorption, translocation and tolerance of arsenic in the hyperaccumulator Pteris vittata and thenonhyperaccumulator Pteris tremula, New Phytol. 165 (2005) 755–761.

Akosy, A. (2008). Chicory (Cichorium intybus L.): A Possible Biomonitor of Metal Pollution.

Akosy, A.; & Sahin, U. (1999). Elaeagnus angustifolia L. as a Biomonitor of Heavy Metal Pollution. Turkish Journal of Botany, Vol.23, No.2, (1999), pp. 83-87, ISSN 1300-008X

Beerling, D. J. & Franks, P. J. Plant science: The hidden cost of transpiration. *Nature* 464, 495-496 (2010).

Brodersen, C. R. *et al*. The dynamics of embolism repair in xylem: In vivo visualizations using high-resolution computed tomography *Plant Physiology* 154,1088-1095 (2010).

Canadell, J. *et al*. Maximum rooting depth of vegetation types at the global scale. *Oecologia* 108, 583-595 (1996).

Kenrick, Paul & Peter R. crane. 1997. The origin and Early Diversication of Land Plants: A Cladistic Study.

Pryer, K. M.: Schneider, H.: Smith, AR: Cranfill, R: Wolf, PG: Hunt, JS: Sipes, SD (2001). Horsetails and ferns are a monophyletic group and the closest living relatives to seed plants. Nature 409 (6820) 618-622

Abercrombie, Hicken & Johnson. 1966. A Dictionary of Biology.

(penguin Booksu Greger M (1999) Metal availability and bioconcentration in plants.

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USE OF GIS TECHNOLOGY IN THE ASSESSMENT OF THE SPREAD OF AIR POLLUTION

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ABSTRACT

Large changes in microclimate in the Kostolac basin are the result of the negative impact of Kostolac power plants and "Drmno" coal mine. Thermal power plants Kostolac A and Kostolac B emit large amounts of SO_2, NO_x (NO_2), CO, ash and slag into the atmosphere. Bearing in mind that there are models developed to analyse the dispersion of gaseous substances from stationary sources in accordance with the available technical resources, the data from the monitoring of the thermal power plant Kostolac have been analysed. Analyses were performed using the VSMOKE model. VSMOKE is a computer based model used to predict the concentration of pollution for certain types of gaseous substances resulting from the combustion process. This model has been modified to allow for an integrated use of a GIS tool to enable the display of spatial context of prediction calculations. Bearing in mind the limitations on the time interval of observation, the analysis was based on data for the first six months of 2012.

Key words: *thermal power plants Kostolac, air pollution, flue gases, microclimate, VSMOKE.*

GEOGRAPHICAL POSITION AND PHYSICAL-GEOGRAPHICAL FEATURES

In the broadest sense, Kostolac mining and energy basin belongs to the area between the Great Morava River in the west, Golubac Mountains to the east, the Danube in the north and Mlavski basin in the south. Basic morphostructural elements of the terrain are Stig, Podunavlje (the Danube region) and Donje Pomoravlje (the Lower Morava region) as representatives of lowland terrain, and Sopotska greda and Bozevacka greda, low hills with elements of the terrace features. Stig plain is a relief unit with pronounced border, to the east in the form of Bozevacka kosa and Sopotska greda in the west. The southern border is the beginning of the middle course of the Mlava river, while it is connected with the Danube basin in the north without any visible morphological transition (Stepanovic, 2011).

In the narrow sense, Kostolac coal basin covers an area of approximately 100 square kilometres, with the town Kostolac in the centre (44°43′N 21°14′E), and the wider area of the entire mining-energy basin, which is approximately 400 square kilometres, within which reserves of lignite, brown coal and hard coal are explored. (Đorđevic-Miloradović, 2012). Production of Kostolac coal mines is mainly used for thermal power plants, and a smaller part for mass consumption. For the smooth operation of four blocks of the thermal power plants in Kostolac, with the total power of almost 1,000 MW, if we include 500 000 t of coal pieces for mass consumption, the production of 9.5 million tons is required. The Government of Serbia has made the decision to build a S_1 block and in this regard has already signed an agreement with the Chinese company "CMEC" to build a new block of 350 MW, which will cause an increase in annual coal production to 12 million tons. Production in 2012 amounted to about 9.700.000 tons. (Company "Thermal Power Plants and Mines Kostolac", Business Report, 2013).

Mining and energy basin Kostolac, in addition to coal mines, consists of two thermal power plants, Kostolac A and Kostolac B, which produce about 12% of the total electricity production in the system of the Electric Power Industry of Serbia. Thermal power plant Kostolac A, is located in the town Kostolac, and is composed of two blocks; A_1 and A_2, with a total installed capacity of 281 MW (100+281). The thermal power plant Kostolac B, known as Drmno is located on the right bank of the river Mlava, near the village of Drmno and about 5 kilometres from the right bank of the Danube. To the east of the thermal power plant, at a distance of approximately one kilometre, is an open pit with the same name, which supplies the power plant with coal. Like Kostolac A, the thermal power plant Kostolac B consists of blocks B_1 and B_2 with the installed capacity of 2h348,5 MW. Annual energy production of all four blocks of Kostolac power plants is near 6 billion KWh. (Company "Thermal Power Plants and Mines Kostolac", Business Report, 2013)

Table 1: Production of electricity in Kostolac thermal power plants in 2012

A_1	A_2	B_1	B_2	Total gross MWh
759.999	1 537.146	2 561.225	790.296	5 648 666

Figure 1. Orthophoto geotopographic representation of the position of the thermal power plants Kostolac A and Kostolac B

CONDITION OF THE ENVIRONMENT

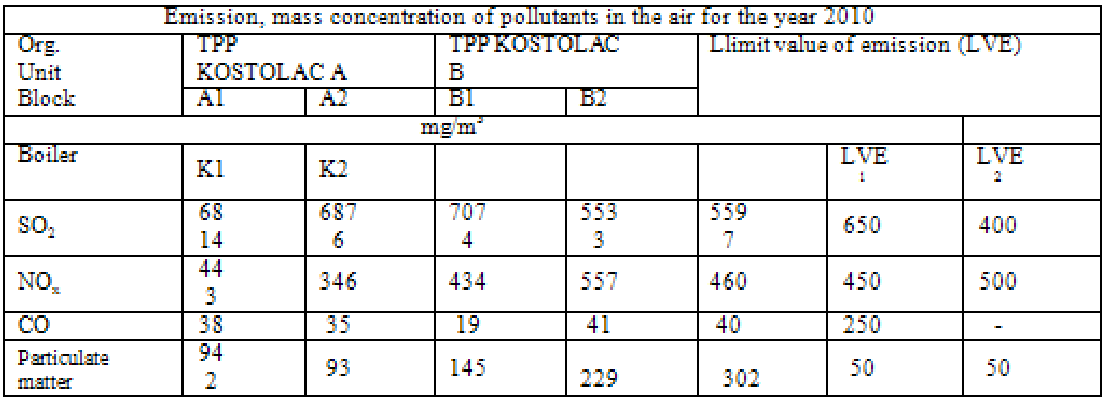
Condition of the atmosphere and the quality of the environment in Kostolac basin are largely a consequence of the industrial facilities of the company Thermal Power Plants and Mines Kostolac. Combustion of coal in boilers of thermal power plants, creation of dust from surface mines Drmno, Cirikovac and Klenovik and slag and ash landfills are major modifiers of the microclimate of the area. Combustion of about 9 million tons of coal and disposal of more than 2 million tons of ash per year creates the conditions for a change in air, surface and underground water. The biggest changes are caused by the emission of fumes, particulate matter and production of ash and slag.

By rapid combustion of coal in thermal power plants’ boilers, at high temperatures, over a period of a few tens of seconds, a large amount of gases such as CO_2, SO_2, NO_2, CO, O_3, particles of soot and ash (particulate and suspended matter PM), with traces of minerals and metals, are released into the atmosphere. These gases are known as factors of the greenhouse effect and contribute to the destruction of the ozone layer. When it comes to the quality of the environment, special attention is given to the group of gases known as sulfur oxides (SOx) and nitrogen oxides (NOx). Their influence on the microclimate changes manifests in increasing concentrations of ground-level ozone in the atmosphere, creation of acid rain, changes in the chemical composition of soil and water ecosystems, deforestation and the creation of smog. It is known that the combustion of coal at temperatures higher than 15000 ^{0}C leads to rapid oxidation of sulfur and nitrogen compounds to sulfur dioxide (SO_2) and nitrogen suboxide oxidize immediately after leaving the chimney to sulfur dioxide (SO_2) and nitrogen dioxide (NO_2). In the atmosphere, sulfur dioxide combines with other gases such as ozone (O_3) or water and transfers to a sulfuric or sulfurous acid, and nitrogen dioxide to nitrous or nitric acid. At the ground layers, further chemical processes lead to the formation of ozone and smog (Djordjevic-Miloradović, 2012). Today, there are different opinions about the further movement of nitrate oxides in the atmosphere. Due to a large impact of these elements on the condition and quality of the environment, restrictions on the concentration of sulfur dioxide are reduced to 150 μg/m^3, nitrate oxide 85 μg/m^3 and particulate matter 50 μg/m^3 at the ground layer of air. The total annual damage caused by air pollution and greenhouse effect in our country is estimated between 0.45 and 1.37 billion Euro, or between 1.8% and 5.5% of GNP.

The thermal power plants Kostolac, with the emission of pollutants, primarily flue gas and ash, are the dominant source of atmospheric pollution. Flue gas is a combustion product of fuel, in this case coal, and is a mixture of gases (sulfur dioxide, nitrogen oxide, carbon monoxide, fluoride, and chloride), the concentration of which depends on the characteristics of the fuel. In addition to gases, flue gas also contains solid particles that are a product of an incomplete combustion of fuel, such as soot, and the influence of mineral components in a fuel (ash). The most abundant element in flue gas is sulfur dioxide making up about 97%.

We analysed the data of pollutant emissions for the year 2010.

Table 2: Emission of pollutants in thermal power plants Kostolac in 2010 (Company „Thermal Power Plants and Mines Kostolac", ecological program of monitoring, 2013)



Emission, mass concentration of pollutants in the air for the year 2010							
Org. Unit Block	TPP KOSTOLAC A		TPP KOSTOLAC B		Llimit value of emission (LVE)		
	A1	A2	B1	B2			
mg/m^3							
Boiler	K1	K2				LVE 1	LVE 2
SO_2	6814	6876	7074	5533	5597	650	400
NO_x	443	346	434	557	460	450	500
CO	38	35	19	41	40	250	-
Particulate matter	942	93	145	229	302	50	50

It can be seen from Table 2 that the emission of SO_2 in flue gases of power plants Kostolac A and Kostolac B exceed significantly the maximum allowed values defined in the national and EU regulations. Measured values vary from 5758-6582 mg/Nm^3.

The thermal power plant Kostolac A emitted tenfold higher amount of particulate matter than the allowed amount. In recent years, the operation of electrostatic precipitators of the thermal power plant Kostolac A has been improved. After the reconstruction of the B_2 boiler in the thermal power plant Kostolac B, the concentration of particles emitted by the power plant is about 200 mg/m^3, but there are occasional overdrafts that up to 700 mg/m^3. Regardless of the high efficiency electrostatic precipitators they cannot absorb particles smaller than 10 microns, which are very dangerous for plant and animal organisms. It is necessary to reconstruct the existing electrostatic precipitator installations with the aim to achieve more effective protection and reduction of particle concentrations up to 50 mg/m^3, which is required by the EU Directive (Jovovich, 2010).

Radioactivity of the ash is also a potential risk caused by ash from thermal power plants. Coal is mainly composed of organic matter, while some elements present in traces are radioactive. Among these elements are uranium (U) and thorium (Th), including their decay products of radium (Ra) and radon (Rn). During coal combustion, most of U and Th and their decay products leave their structure and are distributed between the gas phase and solid combustion products. Almost the total amount of radon in coal is transformed into gas when burned and released through the emission. On the opposite side, less gaseous elements such as thorium and uranium and most of the products of their disintegration are retained in the solid waste, i.e. ash and slag. (Kisić, 2012). Measurements conducted by the Laboratory for Radiation Protection and Environmental Protection, the Vinca Institute (2006), showed no increased radioactivity due to the operation of the thermal power plants Kostolac.

MODELLING AS A METHOD FOR CALCULATION OF CONCENTRATION OF AIR POLLUTION

Mathematical modelling is one of the scientifically accepted methods for calculating the spread of gaseous substances from stationary sources. By applying the mathematical model based on the data on the stationary source, topographic, climatic and urban features of the studied area, through a variety of scenarios, the dispersion of gaseous matter can be observed (Brode, 1988). Based on the modelling categories applied, the modelling which does not specify the impact can be used, by applying a limited number of parameters with different values in order to estimate the effects. These modelling categories are applied regardless of the actual conditions and events in the analysis of events that have already occurred or hypothetical situations. The second category of modelling is the modelling of actual or accidental events in order to monitor the spread of gaseous substances in real time, based on which a valid decision can be made. The third category consists of models that analyse the effect over a given period of time to determine the assessment activities in the period covered, such as period occurring during the year. The number of parameters and the model used for the evaluation of effects of dispersion of gaseous substances can vary depending on the category of modelling that is used (Example Air Quality Analysis Checklist, 2013).

The paper analyses the impact of various scenarios of emissions of harmful substances from the blocks B_1 and B_2 of the thermal power plant Kostolac B on the air quality in the area. Ground-level concentrations of pollutants at different distances were calculated. The Gaussian statistical model for estimating ground dispersion of gaseous substances was applied to certain values of emissions of gaseous substances and parameters related to the outdoor environment. The basis of this model is the assumption that the impurities emitted by a continuous point source form a smoke column in which symmetrical distribution of particle concentration in relation to the axis of the smoke column is observed. The main equation of the statistical Gaussian model is composed of two probability functions of the normal distribution law and has the following form (Lazaridis, 2011):

$$C(x,y,z) = \frac{Q}{2\pi\sigma_y(x)\sigma_z(x)\bar{u}} \exp\left(-\frac{y^2}{2\sigma_y^2(x)}\right)\left\{\exp\left[-\frac{(z-H)^2}{2\sigma_z^2(x)}\right] + \exp\left[-\frac{(z+H)^2}{2\sigma_z^2(x)}\right]\right\} \tag{1}$$

where Q is the mass flow; C-impurity concentration at a given point of space; $\sigma_y(x)$, $\sigma_z(x)$ diffusion dispersions in the direction of the corresponding axis, which depend on the weather conditions and the distance that particles travel from the source to the point with the coordinate x, where it is assumed that the direction of the axis $0X$ coincides with the direction of the wind vector; $\bar{u}$ − mean wind speed at the level of measurement; H-effective height of the source.

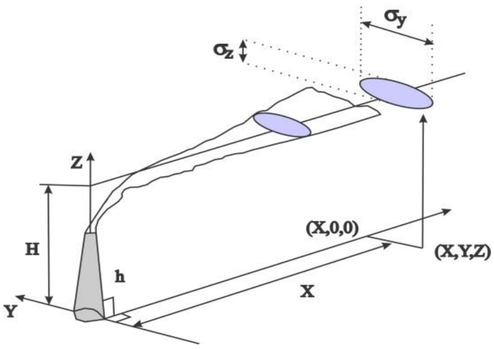


Figure 2. Graphical representation of the dispersion of smoke column from the source (Jaćimovski, 2013)

In the equation (1), σ_y, σ_z are the horizontal and vertical dispersion of the distribution of impurities. For the determination of these dispersions the following relations are used (Vnukov, 1992):

$$\sigma_y = Ax^a ; \sigma_z = Bx^b \qquad (2)$$

where A, a, B, b are the coefficients that depend on atmospheric stability and terrain surface and are determined experimentally. Atmospheric stability is determined through the Pasquill-Gifford's stability classification system, which distinguishes six classes of stability, ranging from A (very unstable) to F (very stable).

Table 3: Parameters for calculation of dispersion (Lazaridis, 2011)

		A	a	B	b
very unstable	A	0,527	0,865	0,28	0,90
unstable	B	0,371	0,866	0,23	0,85
slightly unstable	C	0,209	0,897	0,22	0,80
		A	a	B	b
neutral	D	0,128	0,905	0,20	0,76
stable	E	0,098	0,902	0,15	0,73
very stable	F	0,065	0.902	0 12	0,67

In order to enable geospatial representation of the spread of gaseous substances from the thermal power plant Kostolac B, a model for the process of preparing spatial data covering the analysed area up to 50 kilometres has been defined, although the calculation includes somewhat larger distance and the area up to 10 kilometres (Figure 2). Presented results refer to a specified radius, where the distance is 0 meters, the source of emission, i.e. chimney, while the 50 km i the maximum distance from the pollution source. For modelling, in order to calculate the ground concentrations of air pollution, we used data from the Table 4.

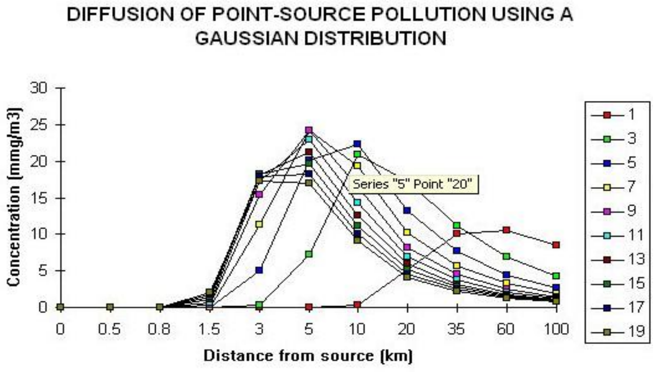


Figure 3. Model of spread of the concentration of pollutants, depending on the distance from the source of pollution

Bearing in mind the capabilities of the applied model for the analysis of spatial data, geotopographic elements are taken from the raster topographic and topographic map, orthophotos, digital topographic maps, categorized soil maps and vector content of the labelled locations of emission sources of the thermal power plant Kostolac B. By using the existing models for the analysis of the dispersion of gaseous substances from stationary sources, which are automated to a certain level, and available technical data, an analysis of available solutions, in accordance with the possibilities of the **VSMOKE** model (Brode, 1992) compared to the integrated use in the **ArcGIS** tool, which was used for modelling and the spatial representation of the results of analysis of monitoring data of the thermal power plant Kostolac B. It should be noted that there were limitations on the time interval that was analysed, because the data were available for the first 6 months of 2012.

Table 4: Value of emissions at the measuring station Kostolac for 2012

Date	Sulfur dioxide SO_2	Nitrogen dioxide NO_2	Nitrogen monoxide NO	Total nitrogen NO_X	Carbon monoxide CO	Wind speed	Wind direction	Air temperature	Relative air humidity	Atmosph. pressure
	μg/m^3	μg/m^3	μg/m^3	μg/m^3	μg/m^3	m/sec	degree	^{0}C	%	hPa
January	52,67	10,13	4,06	11,20	0,14	2,27	215,91	1,92	81,34	1009,58
February	65,10	13,07	2,76	11,85	0,71	2,05	203,13	-3,15	79,42	1012,40
March	28,15	17,71	5,83	18,25	0,52	1,60	203,18	8,36	56,52	1014,36
April	16,60	11,53	2,36	10,37	0,27	2,01	196,68	14,32	64,97	997,67
May	17,07	11,31	2,29	10,12	0,37	1,69	204,03	17,34	72,99	1003,46
June	19,80	8,45	1,34	7,19	0,34	1,80	186,44	23,96	59,86	1003,46

VSMOKE is a computer model for calculation of the spatial concentration of pollution of certain types of gaseous substances resulting from the combustion process. The model was made in 1990 by Lavdas (Forest Service, Southern Research Station) and then was modified to allow for the integrated use with the GIS tools in order to display the spatial coverage of the contamination calculation obtained by applying the VSMOKE model (Lavdas, 1996).

The analysis included a digital terrain model, whose impact on the coverage of pollution can have a major effect and be the subject to further analysis. When using VSMOKE (Ambient Impact Analysis Guideline, 2009) model, it has to be borne in mind that it is intended for the plains and hilly areas, which completely corresponds to Kostolac basin. The plants are in the valley of the river Mlava, known as the Stig, which is in the east bordering with the valley of the river Pek and, and in the west by 20 kilometres wide valley of the Great Morava river. The northern border is the Danube, which further north leans on the Pannonian plain. This means that within the distance of 20 kilometres, there are no significant elevations that would stop or slow down pollutant emissions from sources. It should be emphasized that elevations in the terrain may lead to increased concentrations of harmful substances, especially in terms of stable atmospheres. Bearing in mind that the zone of the study area and the elements that are observed obtained data which are primarily determined by the lowland terrain, which means that in this case there is no significant influence of the terrain.

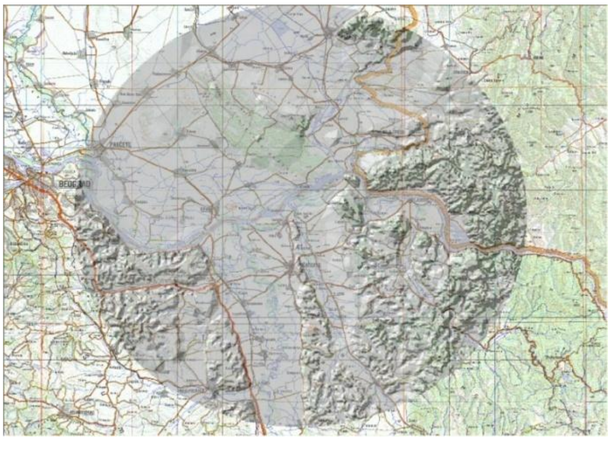
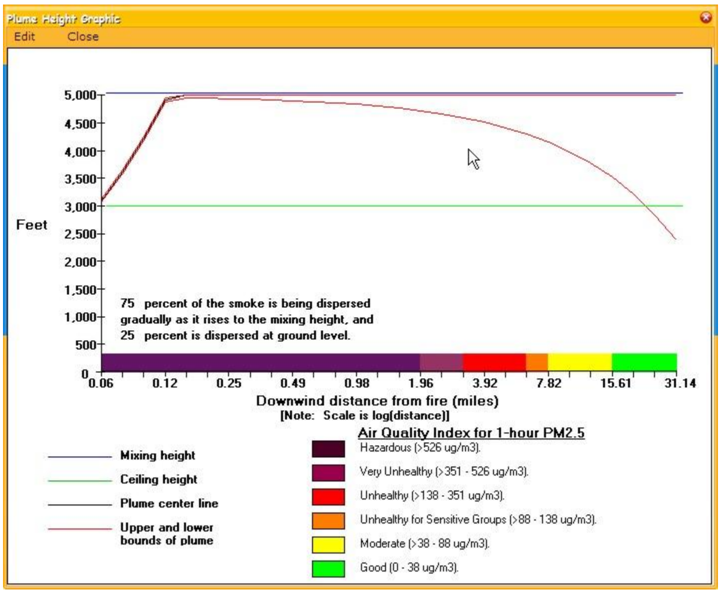


Figure 4. The digital terrain model that is influenced by Kostolac

Based on average annual values of the parameters analysed and the parameters which determine the stationary source emissions of gaseous substances at the thermal power plant Kostolac B, there was a direct application of the Gaussian model, and the results are shown in the graphs. The analysis of the dispersion model of gaseous substances was carried out for the precise location of the thermal power plant Kostolac B. Measurements were made in March 2012 for a period of 1500 hours.



75 percent of the smoke is being dispersed gradually as it rises to the mixing height, and 25 percent is dispersed at ground level.

Figure 5: Index of dispersion and emissions of suspended particulate matter PM-2.5

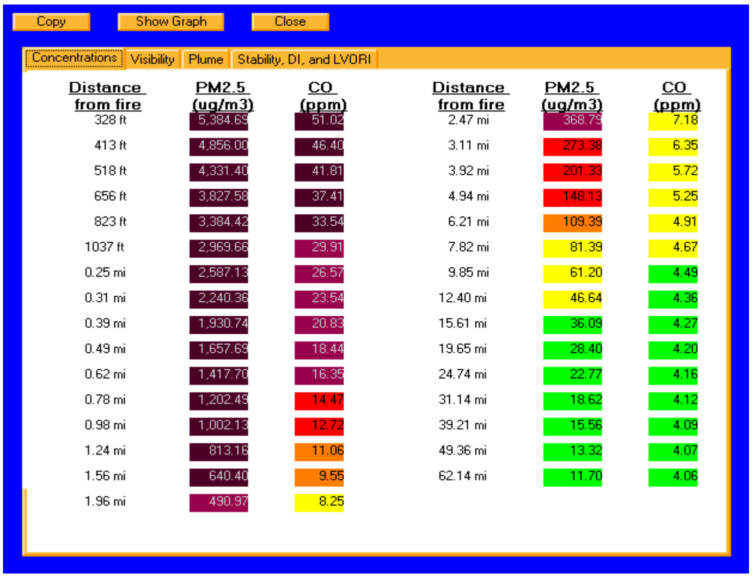
VSMOKE model provides three types of results. It determines the stability of the atmosphere and its ability to disperse pollutants, the concentration of PM-2.5 and CO, the distance from the source and calculates visibility (Long 2011). The dispersion index is an estimated ability of the atmosphere to dispel or absorb pollutants to acceptable low average concentration. According to the calculation, an acceptable concentration index should be higher than 30 at maximum operation of the power plant. The estimated dispersion index was in this case 34 on the basis of which it is estimated that the atmosphere has an average good dispersion capacity of pollutants. By combining the dispersion index and the value for relative humidity, the probability whether pollution affects the reduction of visibility and thereby creates fog can be estimated. The risk index for reduced visibility ranges from 1 to 10, and should be less than 4. One is considered an occurrence, when in 1.000 cases polluters in one case contribute to the occurrence of fog. In this analysis, the risk of reduced visibility was equal to one and is marked on the line (Turpin, 2001).

The measurements presented in the graph show that the emissions of PM-2.5 is extremely high> 526 μg/m^3 (Exposure LV for 24 hours 150 μg/m^3, the annual average 50 μg/m^3), it extends up to 3 km from the source of pollution and is a dangerous path to human health. A very dangerous air pollution with particulate matter concentration of 351-526 μg/m3 stretches up to 5 km from the source. Unhealthy atmosphere with the concentration of suspended particles 138-351 μg/m^3 extends to 9.6 km from the chimney of the thermal power plant. The air that adversely affects people with sensitive respiratory system has a concentration of suspended particles of 88-138 μg/m^3 and is felt up to 12.5 km. Variable contamination affected by winds and stability of the atmosphere, the concentration of suspended particles of 38-88 μg/m^3, and extends according to the model to 25 km. At the distance of 25 km from the source of pollution the air quality is good.

The graph shows the height zoning of pollutants and the influence of the atmosphere on their disposition. Emissions of pollutants are mixed with the atmosphere up to 5000 feet (1524m). VSMOKE model provides data on the percentage of disposition of gases and particles in high altitude areas. In this case 25% of the level of pollution is situated on the topographic surface, and 75% is covered by the turbulent motion of the atmosphere in the higher layers. Obtained values are related to atmospheric stability class D (neutral) and E (slightly stable).

VSMOKE model program, based on the parameters emitted by a stationary source, made a table with concentrations of suspended particulate matter PM-2.5 and CO of the sources and their impact on the health of the population.

Table 5: Particulate emissions PM-2.5 and CO from the chimney of Kostolac B



Distance from fire	PM2.5 (ug/m3)	CO (ppm)	Distance from fire	PM2.5 (ug/m3)	CO (ppm)
328 ft	5,384.69	51.02	2.47 mi	368.79	7.18
413 ft	4,856.00	46.40	3.11 mi	273.38	6.35
518 ft	4,331.40	41.81	3.92 mi	201.33	5.72
656 ft	3,827.58	37.41	4.94 mi	148.13	5.25
823 ft	3,384.42	33.54	6.21 mi	109.39	4.91
1037 ft	2,969.66	29.91	7.82 mi	81.39	4.67
0.25 mi	2,587.13	26.57	9.85 mi	61.20	4.49
0.31 mi	2,240.36	23.54	12.40 mi	46.64	4.36
0.39 mi	1,930.74	20.83	15.61 mi	36.09	4.27
0.49 mi	1,657.69	18.44	19.65 mi	28.40	4.20
0.62 mi	1,417.70	16.35	24.74 mi	22.77	4.16
0.78 mi	1,202.49	14.47	31.14 mi	18.62	4.12
0.98 mi	1,002.13	12.72	39.21 mi	15.56	4.09
1.24 mi	813.16	11.06	49.36 mi	13.32	4.07
1.56 mi	640.40	9.55	62.14 mi	11.70	4.06
1.96 mi	490.97	8.25			

High concentration of fine particles PM-2.5 and carbon monoxide may have a negative impact on human health. Agency for Environmental Protection has developed a colour monitoring system called the Air Quality Index in order to help the population to understand the degree of concentration of air pollution that can affect their health. The most dangerous pollution with suspended particles PM-2.5 extends up to 2.5 km from the source, and the concentration of CO up to 250 meters. Highly polluted atmosphere with a touch of suspended particles PM-2.5 of 490.97526 µg/m^3 extends up to 4 km 3154, and the concentration of CO with the same impact on the health of the population up to one kilometre. Atmosphere polluted with suspended particles was recorded almost up to 8 kilometres away from the source, the CO emission up to 1600 meters. All pollutions marked with brown, purple and red have impact on the health of all residents. Pollution represented in orange is a problem for certain populations, such as children, the elderly and those with chronic heart and lung diseases. Other people are not likely to be threatened by the level of pollution. A concentration of up to 109, 39 µg/m^3 is felt up to 10 km from the source, and the concentration of CO in this class of pollution is up to 2500 meters. Variable pollution caused by the state of the atmosphere and winds, suspended particles PM-2.5, extends 20 kilometres from the chimney of the thermal power plant, CO up to 12.6 kilometres. Good air quality, the allowed amount of suspended particles, is in the area located more than 25 kilometres from the source of pollution and the acceptable CO emission is 16 kilometres from the source.

By applying the VSMOKE model, integrated with the GIS tool, the direction and spread of concentrations of gaseous substances is obtained, with respect to the geotopographic content, which was used for the analysis, and the coverage of the area. With the model, it is also possible to analyse the spread of gaseous substances, night and day, bearing in mind that during the night the humidity level increases.

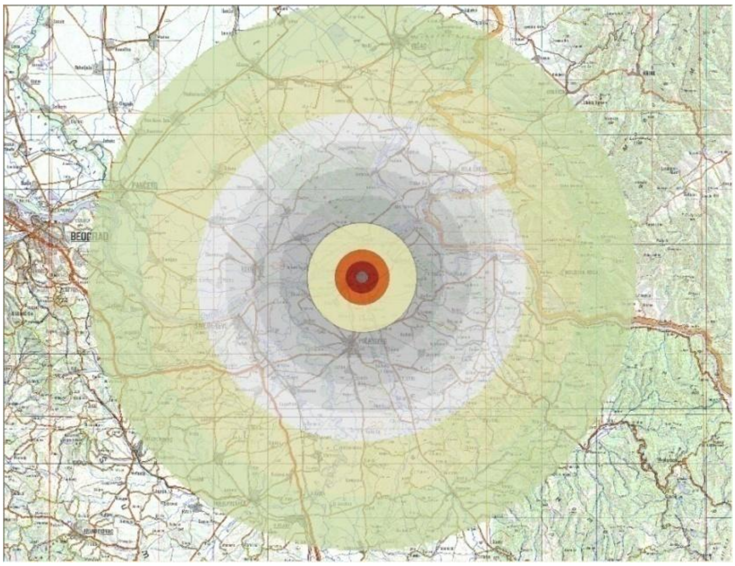


Figure 6. Concentration of the spread of gaseous substances of the thermal power plant Kostolac B in relation to geotopographic content for the first six months of 2012 (Table 4)

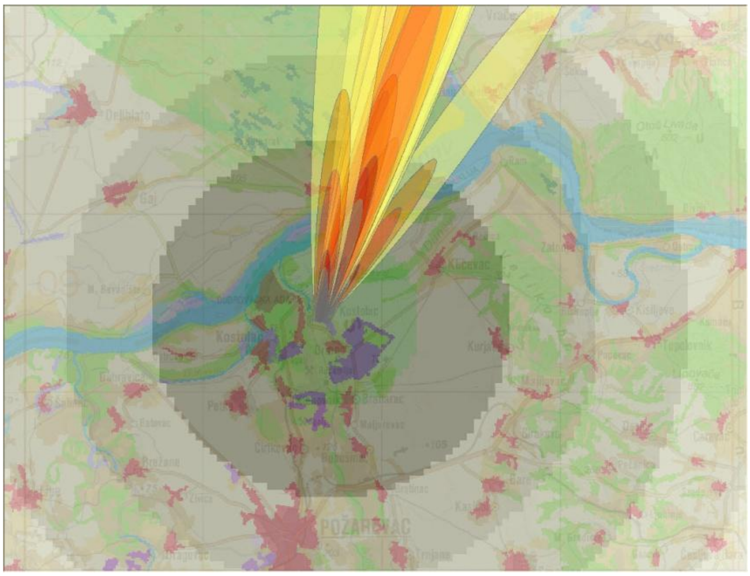
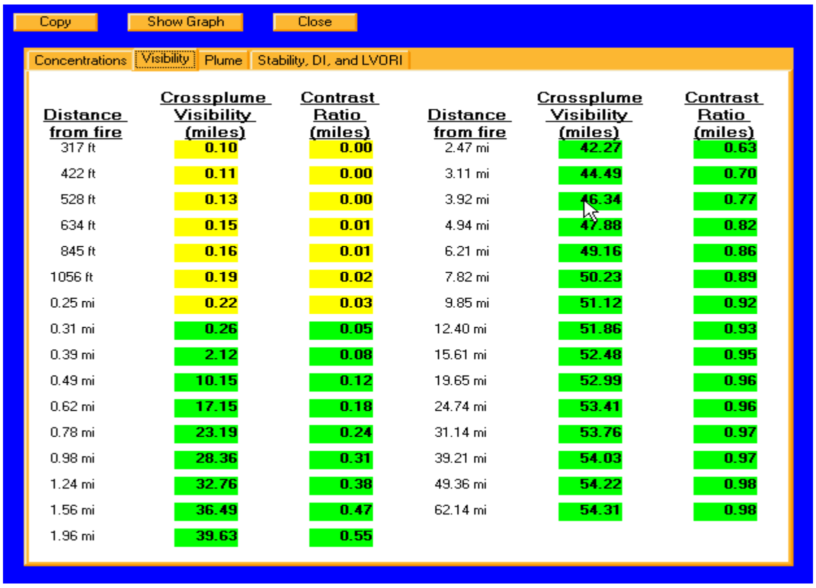


Figure 7. Degree of pollution and the impact of pollution on human health

By applying the VSMOKE model, integrated with the GIS tool, the direction and spread of concentrations of gaseous substances is obtained, with respect to the geotopographic content, which was used for the analysis, and the coverage of the area. VSMOKE model can provide with a combination of particle dispersion index and the values of relative humidity an assessment of the risks of reduced visibility due to the spread of pollutants. Gases and particles in the atmosphere have a significant influence on the degree and the distance of visibility. Fine particles have the ability to refract and absorb sunlight which may have an impact on reducing visibility. Estimated visibility obtained by calculations of the VSMOKE model is valid in conditions where the atmospheric humidity is less than 70%.

Table 6: Estimated visibility depending on the distance from the source



Distance from fire	Crossplume Visibility (miles)	Contrast Ratio (miles)	Distance from fire	Crossplume Visibility (miles)	Contrast Ratio (miles)
317 ft	0.10	0.00	2.47 mi	42.27	0.63
422 ft	0.11	0.00	3.11 mi	44.49	0.70
528 ft	0.13	0.00	3.92 mi	46.34	0.77
634 ft	0.15	0.01	4.94 mi	47.88	0.82
845 ft	0.16	0.01	6.21 mi	49.16	0.86
1056 ft	0.19	0.02	7.82 mi	50.23	0.89
0.25 mi	0.22	0.03	9.85 mi	51.12	0.92
0.31 mi	0.26	0.05	12.40 mi	51.86	0.93
0.39 mi	2.12	0.08	15.61 mi	52.48	0.95
0.49 mi	10.15	0.12	19.65 mi	52.99	0.96
0.62 mi	17.15	0.18	24.74 mi	53.41	0.96
0.78 mi	23.19	0.24	31.14 mi	53.76	0.97
0.98 mi	28.36	0.31	39.21 mi	54.03	0.97
1.24 mi	32.76	0.38	49.36 mi	54.22	0.98
1.56 mi	36.49	0.47	62.14 mi	54.31	0.98
1.96 mi	39.63	0.55			

With the model it is also possible to analyse the spread of gaseous substances, night and day, bearing in mind that during the night the humidity level increases.

Further analysis can focus on impact assessment in relation to the types and categories of land and populated areas.

CONCLUSION

In the paper, by using the mathematical model, we have established the condition of air pollution, simulating the spread of harmful substances for different assumed emission intensities in the known topographic, urban and meteorological situation. The method provides a realistic picture regarding the dispersion of pollutants, which can serve as a basis for assessing potential hazards and technical resolving of protection systems.

The analysis of available solutions is performed in accordance with the possibilities of **VSMOKE** model compared to the integrated use in **ArcGIS** tool that is used to model the spatial representation of the results of analysis of monitoring data of the thermal power plant Kostolac B. These results are consistent with earlier results obtained using the United States Agency for Environmental Protection SCREEN VIEW 3.5.0 application (Jaćimovski, 2014, Screen 3, 2002).

Application of laws dealing with environmental protection implies harmonization of our legislation with the EU regulations. One of the priority tasks is to adopt policies and procedures for the protection of air quality by reducing emissions of hazardous substances at the source of pollution. If we take into account the threshold limit values for emission of SO_2 in the flue gas, Kostolac power plants with respect to the installed power, have to reduce the output concentration of SO_2 for more than 94%, in order to reach the value lower than 400 mg/Nm^3, at full capacity of blocks and during the combustion of worst quality coal. The greatest impact on air pollution, taking into account the spread of sulfur dioxide emissions, is around the thermal power plant Kostolac, at a distance of 15 km from the source in the direction of the dominant wind. Apart from Pozarevac, nearby places such as Kostolac, Cirikovac, Bradarac, Klenovik and Petka also have increased levels of pollution (Environmental impact assessment – Desulfurization of flue gas at the thermal power plant Kostolac B, 2010).

For now, emission of nitrogen oxides does not exceed the allowed value. However, it should be noted that the European Union is already preparing the adoption of stricter regulations for which the maximum allowed emission of NOx will be decreased to a value of 200 mg/m^3 from the currently permitted 400 mg/m^3 starting from 1 January 2016. With the current emission of nitrogen oxides, the thermal power plants Kostolac exceeds the new limits and therefore has to seek solutions to reduce the emission as the current projects for flue gas desulfurization do not predict the reduction of nitrogen oxides.

Electric Power Industry of Serbia is obligated to find a solution to reduce sulfur dioxide emissions on existing blocks by the year 2015. A feasibility study "Directions for optimal reduction of sulfur oxides from thermal power plants of the Electric Power Industry of Serbia" was conducted, and the first power plant which will have a desulfurization system installed is the thermal power plant Kostolac B. As protection measures, the existing chimneys of Kostolac thermal power plants had the electrostatic precipitators for purification of flue gas from particles installed, but no measures were taken to reduce emission of sulfur oxides, and from the accompanying table, we see that they are several times higher than the allowed values. Some of the features of Kostolac lignite extracted in the open mine "Drmno" are small thermal power, relatively high humidity and ash content and total sulfur content of about 1.3%. (The choice of the optimal technical solution for the plant desulfurization of flue gas at the Kostolac B, 2010). The use of such fuels is the cause of high concentrations of SO_2 in the flue gas, which ranges between 5000-7000 mg/m^3 in the thermal power plant Kostolac B, and the specific emission of sulfur is about 30 kg/MNJh, which was one of the most important criteria for the choice of Kostolac B as the first thermal power plant in the Electric Power Industry of Serbia to have the desulfurization system installed. The project of the system of desulfurization was done by the consortium: Faculty of Mechanical Engineering and Faculty of Mining and Geology, University of Belgrade, Worley Parsons Company from the United States and Energoprojekt-Entel from Belgrade. The system for desulfurization consists of a plant for purification of flue gas using wet scrubbing, the so-called „gas scrubbing“ with limestone suspension, which is performed in the part of the plant which is referred to as an absorber.

Gas scrubbing is carried out in a way that the current of flue gas is introduced in the absorber in which limestone suspension is also introduced in the form of rain or droplets. In the process, sulfur dioxide binds to calcium from the limestone and results in gypsum in the form of a suspension. Gypsum is then transported to the landfill and prepared for later use, and the purified gases are released into the atmosphere. Gypsum suspension, which is a product of desulfurization by using the wet limestone processes, is a potential raw material for gypsum. If a good quality of gypsum is required, it is necessary to incorporate a high quality electrostatic precipitator in order to reduce the amount of particulate matter in the flue gas. The plant is large and consists of several parts such as absorber, heater of flue gas, the system for preparing limestone suspensions, limestone preparation, pumping stations, a system for waste water treatment system for drying plaster, gypsum storage system (Stojiljkovic, 2009). The planned production increase by 30% will surely affect the increase in pollution correspondingly.

In addition to modern technological solutions, we should not ignore the possibility that plants contribute to green technology with absorption, which includes growing of forest plantations in the vicinity of pollutants and shelterbelts next to towns.

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REFERENCES

Ambient Impact Analysis Guideline A Guideline for Performing Stationary Source Air Quality Modeling in Connecticut, State of Connecticut, Department of environmental protection (2009), http://www.ct.gov/deep/lib/deep/air/compliance_monitoring/modeling/ambientimpactanalysisguidelines.pdf

Brode R.W. (1988), Screening Procedures for Estimating the Air Quality Impact of Stationary Sources, U.S. Environmental Protection Agency, http://nepis.epa.gov/Adobe/pdf/2000J3ER.pdf, 20.07.2014. : 22.18

Brode R. W. (1992), Screening Procedures for Estimating the Air Quality Impact of Stationary Sources, Revised, U.S. Environmental Protection Agency, http://www.epa.gov/oppt/exposure/presentations/efast/usepa_1992b_sp_for_estim_aqi_of_ss.pdf , 20.07.2014. : 22.20

Đorđević-Miloradović J., Savić N. (2012), Rekultivacija i ozelenjavanje deponija, pepelišta i jalovišta u Kostolcu RIO Kostolac str. 72-84

Example Air Quality Analysis Checklist (2013), http://itepsrv1.itep.nau.edu/itep_course_downloads/AirPollutionModeling_2013/Modeling5-13Final/SampChcklstAppen.pdf, 20.07.2014. : 22.25

Jaćimovski S., Miladinović S., Radovanović R., Ilijazi V. (2013), Distribution of the concentration of sulphur dioxide into the atmosphere from point source, International conference Ecology of urban areas 2013, Zrenjanin, Univerzitet u Novom Sadu, Tehnički fakultet „Mihajlo Pupin“ str. 50-58

Jaćimovski S., Miladinović S. (2014) Microclimate changes in basin in Kostolac as a consequence of negative influence of Kostolac thermal power plants, Thematic Conference Proceedings of International Significance "Archibald Reiss Days" Academy of Criminalistic and Police Studies, Belgrade

Jovović A. i dr.,: (2010), Studija o proceni uticaja na životnu sredinu: Odsumporavanje dimnih gasova TE Kostolac B, Beograd

Kisić D. i dr. (2012): Prirodna radiaktivnost uglja i letećegg pepela u termoelektrani „Nikola Tesla B“, Elektroprivreda Srbije, Beograd

Konzorcijum; Mašinski i Rudarsko-geološki fakultet Univerziteta u Beogradu, WorleyParsons, Energoprojekt – Entel (2010), Studija o proceni uticaja na životnu sredinu –Odsumporavanje TE Kostolac B, Beograd str. 15-42, 86-114

Lazaridis M. (2011), *First principles of Meteorology and Air Pollutant*, Springer, New York, pp.201-232

Lavdas, L. G. (1996), Program VSMOKE—User's Manual. General Technical Report SRS-6. Asheville, NC: USDA Forest Service, Southern Research Station. Available for download www.treesearch.fs.fed.us/pubs/1561.

Long, A. Matthews, D. Stratton, Smoke Prediction with VSMOKE (2011), http://www.southernfireexchange.org/SFE_Publications/factsheets/2011-6.pdf

Privredno društvo "Termoelektrane i kopovi Kostolac", izveštaj o poslovanju, 2013

Screen3 Stationary Source, Modeling Guidance, Colorado Department of Public Health and Environment, Air Pollution Control Division, Technical Services Program (2002), (updated 28.12.1005), http://www.colorado.gov/airquality/permits/screen.pdf , 20.07.2014. : 22.20

Stepanović D. M. (2011), Savremene geomorfološke promene u Stigu , doktorska disertacija u rukopisu, Univerzitet u Novom Sadu, Prirodno-matematički fakultet, Departman za geografiju, turizam i hotelijerstvo, Novi Sad

Stojiljković D. i dr. (2009), Izbor optimalnog tehničkog rešenja postrojenja za odsumporavanje dimnih gasova TE „Kostolac B“ , Stručni rad UDK :622.992.84:620.92 Termotehnika , XXXV, 3-4, str. 231–249, Beograd

Turpin R., Angelis G.D., Groulix P. (2001), Air Plume Modelin Planning or Diagnostic Tool, http://www.ofcm.gov/atdworkshop/proceedings/session1/campagna.pdf

Внуков А.К. (1992), Защита атмосферы от выбросов энергообъектов:Справочник, Энергоатомиздат, Москва, стр. 134-138.

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EFFECTS OF TOBACCO STALKS BRIQUETTES COMBUSTION ON AIR POLLUTION

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ABSTRACT

Unlike the fossil fuels, in process of biomass combustion emissions of NOx and SOx gasses are almost negligible. Comparing with standard coils, mostly used in Serbia, emission of CO_2 for most of the biomass samples is less, due too higher heating value of biomass. If it is taking into account fact that yearly production of biomass in Serbia is estimated on 12.5 million tons, it can be concluded that wider use of biomass can affect on air pollution. Among the common biomass, tobacco stalks are particularly interesting. According to the official classification tobacco stalks belongs to the green agricultural waste. Yearly production of tobacco stalks is about 70 000 tons, which can totally cover all energy needs in processes of drying. Compared with other biomass, content of nitrogen in tobacco stalk is higher, which is result of fertilization in the cultivation. In order to decrease NOx gasses, tobacco stalks are mixed with corn cob in this study. Ultimate analysis is experimentally determined, and based of these data briquette samples are determined. Analysis of NOx gasses is theoretically performed. Results of analysis shows that air pollution can be significantly decreased with combustion of tobacco stalks and various combinations with other biomass.

Key words: *Tobacco stalks, combustion, briquette, NOx and SOx emission.*

INTRODUCTION

Excessive use of fossil fuels in last decades leads to its irreversibly spending. Main consequence of this is greenhouse gases emissions which strongly affects on climate change and non sustainable development. Use of low heating coal such is lignite in most of combustion processes like is electricity production and central heating results with high level of CO_2, NOx and SOx gasses emission. From the other side, problems that may arise in the supply of fossil fuels, as is the case currently in the Republic of Serbia caused by floods, impose the need for finding alternative sources of energy.

A low developed economies, which is situation present in Western Balkan countries, are mainly oriented on agriculture. Any agricultural activity strongly needs fuel, and in the same time agriculture produces great amount of waste which can be successfully implemented in energy consumption. In present situation in Republic of Serbia, according to the official statistic, yearly production of agriculture waste is about of 12.5 million tons. Assuming that only 25 % of this amount could be taken as energy source it would be possible to replace 1.4 million tons of oil, and this biomass could cover all energy need in agriculture sector (Jovanovic and Parovic, 2009).

Using of biomass in combustion process instead of low heating coal or oil, for any purpose would have strong environmental impact (Lazariou, 2012). It is known that in biomass combustion processes emission of SOx and NOx gasses is almost equal to zero, and this is one of the main advantages of using biomass. From the other side, moisture contents in biomass for combustion for briquette or pellet production need to be less than 15%, which leads to higher heating values comparing with standard using coil. In more complex analysis it could be easily shown that emission of CO_2 is also lower with biomass combustion.

Among the standard biomass such is wheat, corn, barley or oat, tobacco is of the main agricultural product in Republic of Serbia. Yearly production of all species of tobacco stalks (Virginia and Burley mainly) in Republic of Serbia is about 70 000 tons. More interesting for energy purposes is fact that tobacco stalks have no economic value since they are not taken in any serious energy consideration yet. According to the Waste Catalogue issued by the Ministry of Environment and Spatial Planning and the Agency for Environmental Protection of the Republic of Serbia (Waste catalogue, 2010), tobacco is placed in the waste that is non-toxic. Nicotine level, which is appeared as main obstacle for tobacco stalk wider usage, is very low (Peseski et al.,2010) and this leads to conclusion that implementation of tobacco stalks briquettes and pellets is ecologically accepted. Tobacco stalks could also be used in various production, such are pulp of paper, bioethanol, biogas or inorganic fertilizer (Radojicic et al., 2009, Radojicic et al.,2014, Sun et al.,2002, Chaturvedi, 2008).

Unlike the other common types of biomass, tobacco stalk have greater amount of nitrogen and sulfur, which affect with increased SOx and NOx gasses in combustion. These increased values are result of fertilization from one side, and consequence of acid rains from the other side. Comparing with other biomass types, wheat straw also have greater amount of nitrogen, but corn cob have nitrogen level on minimum. These facts impose conclusion that mixing tobacco stalks with corn cob for example can lead to generate very effective renewable fuel which can have satisfactory heating level and in the same time low generation of toxic gasses.

The aim of this research is to show generally decreasing of NOx and SOx gasses emission in biomass combustion processes. Further more, implementation of tobacco stalks as renewable energy source could be more effective in combustion instead of standard coils which are usually used. Low heating value of mostly used biomass is greater that coal heating value, and imposes logical conclusion that in the same time and CO_2 emission would be less.

THEORY

Calculation of solid fuels combustion products volumes can be made based on knowledge of the ultimate analysis of the fuel, using the stoihiometric combustion equation. Fuel composition can write in the form (Zivkovic and Djordjevic, 2001):

$$C + H + S + O + N + W + A^p = 100\% \tag{1}$$

Symbols C, S, O, N, W and A^p represents the percentage content of carbon (C), hydrogen (H), sulfur (S), oxygen (O), nitrogen (N), humidity (W) and mineral impurities (A) in the fuel.

Volumes of combustion gasses in Nm^3/kg can be calculated as follows:

$$V_{CO_2} = 1{,}867 \cdot \frac{C}{100} \tag{2}$$

$$V_{SO_2} = 0{,}7 \cdot \frac{S}{100} \tag{3}$$

$$V_{H_2O} = 11{,}2 \cdot \frac{H_2}{100} + 1{,}24 \cdot \frac{W}{100} \tag{4}$$

For NO2 and O2 volumes it is necessary to calculate minimal amount of oxygen (O_{min}) for combustion, and accordion to this amount minimal amount of needed air for combustion (L_{min}).

$$O_{min} = \frac{1}{100} \cdot \left[1{,}867 \cdot C + 5{,}6 \cdot \left(H - \frac{O}{8}\right) + 0{,}7 \cdot S\right] \tag{5}$$

$$L_{min} = \frac{O_{min}}{\lambda} \tag{6}$$

where λ is coefficient of excess air.

$$V_{N_2} = 0{,}8 \cdot \frac{N_2}{100} + \frac{79}{100} \cdot L_{min} \tag{7}$$

$$V_{O_2} = (\lambda - 1) \cdot L_{min} \tag{8}$$

where λ is coefficient of excess air.

For better analysis of combustion gasses amount in real condition it is better to compare amount of gasses in order to achieve same heating energy for biomass samples. For this reason, low heating energy value (LHV) have to be calculates for every biomass sample. This value can be calculated from (Demirbas, 1997, Moka, 2012):

$$LHV = 340 \cdot C + 1200 \cdot \left(H - \frac{O}{8}\right) + 105 \cdot S - 25 \cdot W \ \left[\frac{kJ}{kg}\right] \tag{9}$$

METHOD

Burley tobacco stalks, variety P-5 from Čoka production area, and Virginia tobacco stalks, variety H-9 from Šabac production area and corn cob hybrid F38 from Stara Pazova production area, are used for this examination. For theoretical prediction of combustion gasses species ultimate analysis is necessary. Biomass samples taken in this investigation are wheat straw, corn cob, barley, Burley and Virginia tobacco stalks. Burley tobacco is particularly interesting due to fact that leaves and stalks are dried in the same time without any energy consumption (natural during technique). All samples were taken with 10% initial moisture. After the sample collection, preparation of the samples for the analysis of chemical composition was performed in the standard manner. After grinding, the stalks are milled and sieved to a series of vibrating sieves. The fractions of particle size of 0.5 - 1.0 mm were taken for the analysis of the chemical composition. In the context of the analysis of the chemical composition the following were done: determination of the moisture content of the samples (NREL/TP-510-42621, 2008), extractive substances soluble in a mixture of organic solvents (NREL/TP-510-42619, 2008, NREL/TP-510-42618, 2008) and the determination of the ash content (NREL/TP-510-42622, 2005). Based on the moisture content, the results of the analysis of the chemical composition of all samples are expressed relative to the dry weight of the samples. Within the elementary analysis, the determination of carbon, hydrogen and oxygen was carried out. Unlike fossil fuels, biomass is characterized by a low content of sulfur and nitrogen in trace amounts. Therefore, we considered that for the calculation of the combustion gasses emission based on the elemental composition it is the most important to take into account the content of C, H and O. These elements are detected with elemental analyzers. Approximately 200 mg of a sample is burned in an oxygen atmosphere at 900^0C, and C is converted into CO_2, and H in H_2O. The components are quantitatively determined by using IR (infrared) detector (Solar Energy Research Institute, 1991).

After the ultimate analysis determination, composition of combustion gasses in theoretically determined. For better results interpretation, and understanding of environmental impact of biomass combustion, combustion gasses amount is compared in term of equal fuel weight.

FINDINGS AND DISCUSSION

For this study Virginia and Burley tobacco stalks and corn cob were selected for briquette samples. Corn cob is selected for mixing with tobacco stalk because of relativly low content of nitrogen and sulfur and close heating value with the same moisture content. Mixed briquettes are made from equal mass of tobacco stalks and corn cob in order to find average values of gasses emission between two biomass samples. Table 1 presents results of ultimate analysis and chemical composition of briquettes. Analyses were performed in five replicates, but for clearly reasons in Table 1 are given only average values.

Table 1: Ultimate analysis of biomass briquettes samples

Biomass	Element content						
	C	H	N	S	O	A	W
	[%]						
Virginia	39,57	6,17	0,43	0,77	38,12	4,94	10
Burley	39,62	6,31	0,80	0,49	38,94	3,81	10
Corn cob	41,92	5,28	0,42	0,01	40,91	1,46	10
Mix Virginia-Corn cob	40,77	5,79	0,61	0,25	39,92	2,66	10
Mix Burley-Corn cob	40,74	5,72	0,42	0,39	39,51	3,12	10

Variation in content of particular element can be result of various parameters which are related to the land composition, land cultivation, irrigation and fertilization. Characteristic of biomass could also vary depending on the origin or geographical region in which it is formed (Garcia et al.,2014, Gurel and Senel, 2012). These variations are also acceptable within the one plant culture in different years of cultivation. Although the nitrogen content in biomass samples is almost negligible, due to excessive fertilization it can be increased, which can be seen in Burley sample in Table 1. In the same manner, sulfur content in virginia sample from Table 1 is result of acid rains in the area where plants had been grown. All these variation would affect in ammount of NOx and SOx gasses in combusion.

Based on ultimate analysis, for selected briquettes are calculated volumes of combusion gasses according to the theory given from (1) to (8). Emission of CO_2 for selected fules is given on Figure 1. From Table 1 it can be seen that tobacco stalk have smaller amount of carbon, and result of this is decreased volume of CO_2 in combusion gasses for tobacco stalks compared with corn cob. Variation bettewen samples is about 6%, and it can be concluded that all samples have similar volumes of CO_2 in combusion gasses. In briquettes which are made from mixing biomass emission of CO_2 was almost the same.

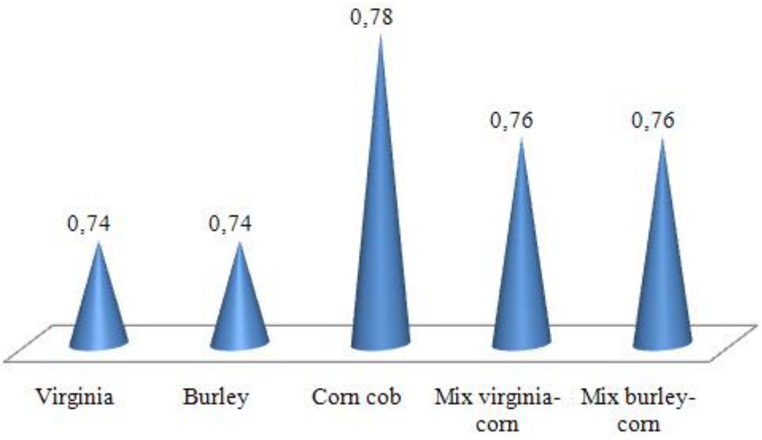

Figure 1. CO2 emission for selected biomass briquettes

Volumes of SO_2 in combustion gasses for briquettes samples are given in Figure 2. As it was mentiones before, due to land contamiantion in area where selected Virgnia tobacco plants were grown, content of SO_2 is the greates. Comparing with corn cob, briquettes made from Virginia tobacco stalk have almost 90% greater SO_2 emission. In briquettes made from biomass mixture, this emission can be decreased up to 40% comparing with tobacco stalks briquettes.

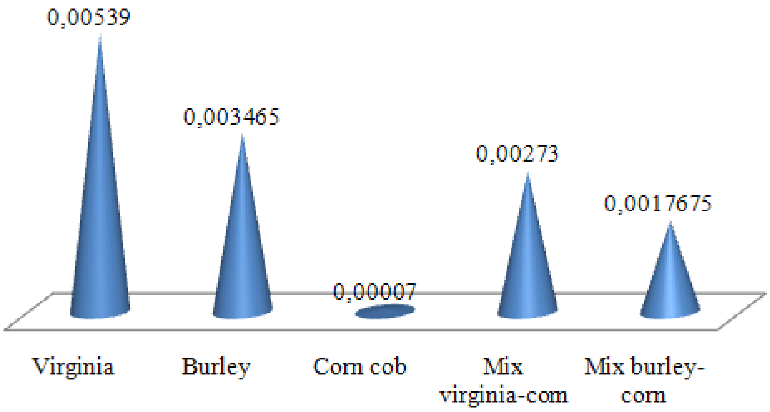

Figure 2. SO_2 emission for selected biomass briquettes

Volume of NO_2 in combustion gasses is given on Figure 2. For clarity reasons, on Figure 3 is only shown content on nitrogen from biomass. Nitrogen content from air needed for combustion is neglected. As it was mentioned, in case of Burley tobacco, nitrogen from fertilizer binds to plant and this affect with increased amount of NO_2 in gasses. Comparing with corn cob, it is almost 50% greater NO_2 emission. In case of briquettes made from biomass mixture, this can be decreased from almost 30%.

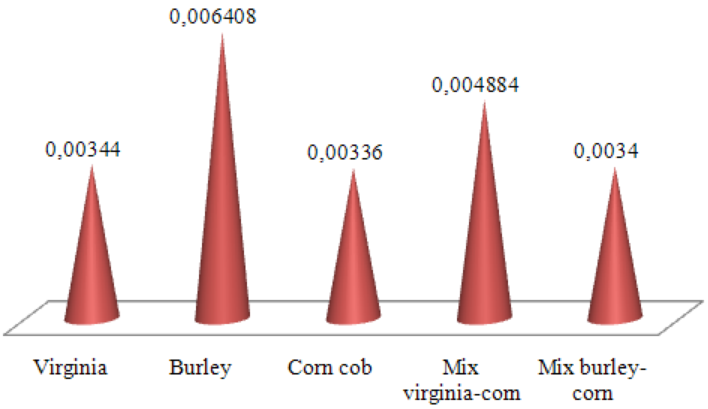

Figure 3. NO_2 emission for selected biomass briquettes

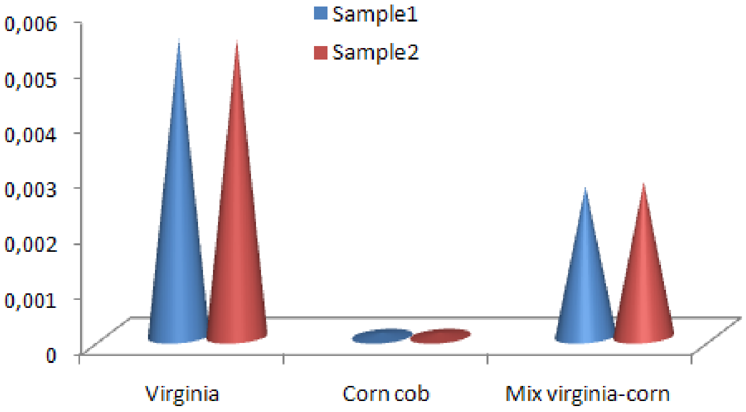

Figure 4. SO_2 emission for selected biomass briquettes for 1 kg fuel, and for the same heating value

Comparison between Virginia tobacco stalks, corn cob and mixture briquettes in case of SO_2 emissions are given in Figure 4. With Sample 1 is mark out emission in case of combustion of 1 kg of biomass, and with Sample 2 is mark out amount of biomass which is equal to heating value of Virginia tobacco stalks. Calculated from (9) lower heating value of Virginia tobacco stalks briquettes is 14,97 MJ/kg, and for corn cob is 14,2 MJ/kg. Since content of sulfur in corn cob is almost negligible, it is obvious that volume of SO_2 in case of corn cob briquettes shall be on minimum, what is mentioned before. In case of briquettes made from mixture, emission of SO_2 could be decreased up to 50% comparing with pure Virginia tobacco stalks briquettes.

On the same way, NO_2 emissions for Virginia tobacco stalks, corn cob and mixture briquettes are given on Figure 5. Although in case of corn cob briquettes NO_2 emission is smaller relative to Virginia tobacco stalks briquettes, in order to obtain same energy value in combustion, it would be necessary greater amount of corn cob briquettes. This would increase NO_2 emission for almost 10%, and it can be concluded that tobacco stalks briquettes in order of same energy delivery would have better NO_2 emission. In case of mixture briquettes, emission would be almost equal.

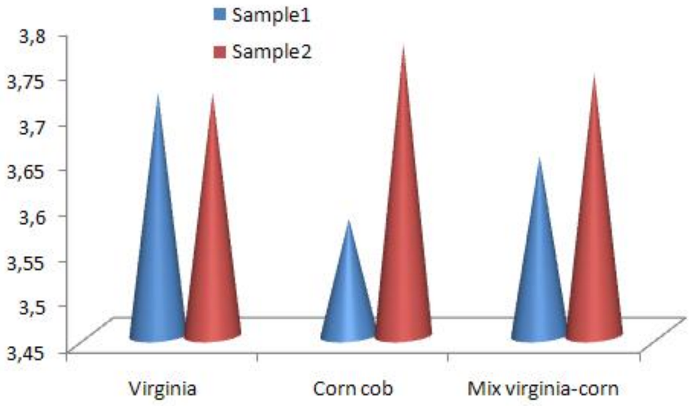

Figure 5. NO_2 emission for selected biomass briquettes for 1 kg fuel, and for the same heating value

In case of Burley tobacco stalks, corn cob and mixture biomass briquettes, comparison in SO_2 emission are given on Figure 6. Considering the fact that sulfur content in corn cob is almost 90% smaller than Burley tobacco stalk, in case of biomass mixture briquettes this emission could be decreased up to 50% regardless if is compared per 1 kg of biomass or same energy delivered. Briquettes made from Burley tobacco stalks have 15,01 MJ/kg lower heating values which is more than any other biomass samples. From Figure 6 it can be seen that there is no significant difference for SO_2 emission in case of biomass mixture briquettes in case of 1kg fuels combustion and combustion for the same energy delivered.

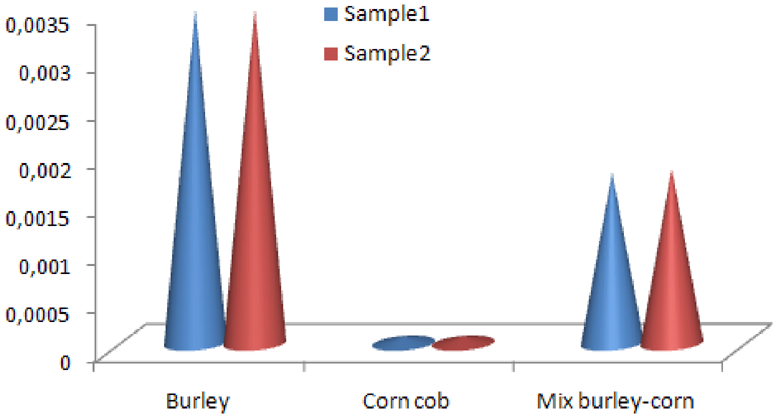

Figure 6. SO_2 emission for selected biomass briquettes for 1 kg fuel, and for the same heating value

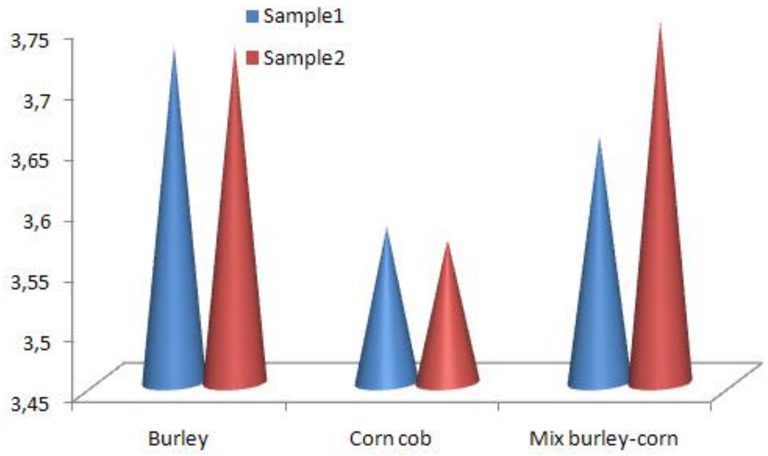

Figure 7. NO_2 emission for selected biomass briquettes for 1 kg fuel, and for the same heating value

Unlike Virginia tobacco stalks briquettes, in Burley sample nitrogen level was higher, which was explained previous. Results of higher nitrogen value are decreased NO_2 emission in combustion gasses. Difference between Burley and corn cob briquettes is about 50%, which is evident in case of combustion 1 kg fuel. For briquettes made from biomass mixture, in case of same energy delivered it was noted higher value of NO_2 emission. According to these data, it can be concluded that mixing Burley tobacco stalks with other types of biomass samples could not significantly decrease level of NO_2 emission.

CONCLUSIONS

Of total available renewable energy in Republic of Serbia, biomass is accounted with almost 63%. This amount is more than sufficient to cover all energy needs in agriculture sector, which is not presents situation. It can be concluded that in moment, very small amount of biomass is in use in agriculture. Biomass generally has available heating value and it can successfully replace fossil fuels. It is shown that tobacco stalks are suitable for using in energy purposes, and they are classified as non-toxic biomass. Particularly, in case of Burley tobacco stalks there is no need for energy in biomass drying process. Since tobacco stalks have not any value in tobacco industry, they are more than suitable as renewable energy source.

Based on presented results, it can be concluded that tobacco stalks have smaller content of carbon which affect in decreased level of CO_2 emission than other biomass. These data are calculated for the same moisture level for all biomass samples. Generally, CO_2 delivered from biomass combustion is organic and more acceptable because it is needed for plants growing. There is no significant difference in level of CO_2 emission for pure substance briquettes and biomass mixture briquettes, which is shown in results.

According to the samples used in this analysis, level of sulfur in Virginia tobacco stalks was detected on higher level. It was explained that level of sulfur can vary due to phenomenon of land contamination by acid rains, which was in case of used samples. This fact caused higher level of SO_2 volumes in combustion gasses for Virginia tobacco stalks briquettes than in other samples. Mixing with other types of biomass samples can significantly decrease level of SO_2 in emission gasses. For Burley tobacco stalks briquettes lower level of SO_2 emission was detected, and it can be concluded that emission of SO_2 is significantly decreased.

The highest level of nitrogen in ultimate analysis was detected in Burley tobacco stalks, which is result of using nitrogen fertilizers for plants growing. As it was expected, the highest volumes of NO_2 in emission gasses were calculated for Burley tobacco stalks briquettes. In briquettes made from biomass mixture level of NO2 is decreased, but in case of same energy delivered biomass made from mixture would have almost the same level of NO_2. This can be explained with difference in lower heating values between Burley tobacco stalks and corn cob. For Virginia tobacco stalks, briquettes made from biomass mixture could decrease level of NO_2 emission.

According to the results presented in this paper, generally it can be concluded that using of tobacco stalks as renewable energy source is acceptable from the ecological point. Plants growing conditions can significantly affect of amount of certain elements in biomass samples. Emission of toxic gasses such are SOx and NOx gasses is shown in level of acceptance. Furthermore, briquettes made from biomass mixtures can decrease level of toxic gasses emission.

REFERENCES

Chaturvedi S, Upreti DK, Tandon DK Sharma A, Dixit A.(2008) Bio-waste from tobacco industry as tailored organic fertilizer for improving yields and nutritional values of tomato crop. Journal *of Environmental Biology*; 29: 759-763.

Demirbas A. (1997) Calculation of higher heating values of biomass fuels. *Fuel*; 76(5): 431–239

García R., Pizarro C., Lavín A.G., Bueno J.L, (2014) Spanish biofuels heating value estimation. Part I: Ultimate analysis data, *Fuel*, Volume 117, Part B, , 1130-1138

Gurel A., Senel Z.(2012) Global Climate Change and Adaptations in Agriculture. *Journal of Environmental Protection and Ecology*, 13 (1), 56-60.

Jovanovic B, Parovic M. (2009) Conditions and development of biomass in Serbia. Belgrade; *http://www.jeffersoninst.org/sites/default/files/Biomass.pdf*

Lazaroiu Gh, Oprea I., Mihaescu E., Prisecaru T., Pisa I., Negreanu G., Mocanu C. R.(2012) Biomass Briquettes from Pitcoal-Wood: Boiler Test Facility Combustion Case Study. J Environ Prot Ecol, 13 (2A), 1070

Moka VK. (2012) Estimation of calorific value of biomass from its elementary components by regression analysis. BTech thesis;

NREL/TP-510-42618(2008) Determination of Structural Carbohydrates and Lignin in Biomass Laboratory Analytical Procedure

NREL/TP-510-42619 (2008) Determination of Extractives in Biomass.

NREL/TP-510-42621 (2008) Determination of Total Solids in Biomass and 251 Total Dissolved Solids in Liquid Process Samples

NREL/TP-510-42622 (2005) Determination of Ash in Biomass.

Pesevski M, Iliev B, Zivkovic D, Jakimovska-Popovska V, Srbinoska M, Filiposki B. (2010) Possibilities for utilization of tobacco stalks for production of energetic briquettes. *Journal of Agricultural Sciences*; 55 (1): 45-54

Radojicic V., Ecim-Djuric O., Djulancic N., Srbinoska M., Kulic G., (2014) The possibility of using burley tobacco stalks as biomass, *XXII International Conference "ECOLOGICAL TRUTH" Eco-Ist'14*, Proceedings, 284-290.

Radojicic V, Milosevic M, Tomasevic B. (2009) Tobacco waste management in Serbia. *Ecological truth* 09, Proceedings; pp 218 -221.

Solar Energy Research Institute, (1991) Methods of Analysis Biomass for Fuels and Chemicals. Solar Energy Research Institute. Golden, Colorado, USA

Waste Catalogue (2010) Ministry of Environment and Spatial Planning and the Agency for Environmental Protection of the Republic of Serbia [in Serbian]

Živković N., Đorđević A.**(**2001) Zaštita vazduha-teorijske osnove predviđanja zagađenosti vazduha sa primerima rešenih zadataka, Fakultet zaštite na radu, Niš,, CIP 504. 3. 054; ISBN-86-80261-31-9

IV International Conference
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AIR QUALITY IN BANAT AREA. ENVIROBANAT PROJECT OBSERVATIONS

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ABSTRACT

This paper presents the results obtained during the IPA Romania-Serbia Cross Border Cooperation Programm, project ENVIROBANAT, MIS-ETC 1425. The data collected and analyzed during the project implementation were acquired from the Romanian National Air Quality Monitoring Network and National Automatic Air Quality Monitoring System of the Republic of Serbia. The data were collected starting with November 2013 and the presented analysis covers a fourth month period, from November 2013 to February 2014.

Key words: *air quality, Banat, cooperation.*

INTRODUCTION

Air pollution knows no political boundaries and pollution management and joint effort by the governments to control and reduce the impact of pollutants on a regional basis, for fully integrated and cooperative approach of air quality issues are needed. According to the ambient air quality assessment and management standard in the EU expressed by Air Quality Framework Directive 96/62/EC a specific contribution must be enhanced, especially in border regions. Entering partnerships with regional Universities to help establishing commuting plans and find alternative ways to preserve the common history and touristy sites from pollution is the contribution of the project to UN Treaty on long-distance trans-boundary air pollution. Presently the European Pollutant Release and Transfer Register was created. Project data will complete it, contributing to transparency and public participation in environmental decision-making.

Anthropogenic pollution is mainly caused by industry. The Banat region is heavily industrialized on both sides (Romania and Serbia) with major mining industry, shipyards, rubber industry, copper and iron industry, all with high pollution potential. This makes the industry our target group. The best way to reduce the cross-border pollution is to involve the industry in environmental aspects of life and to make them understand that a better economic situation is insufficient if not completed with a better environment in order to have a better life.

Trans-boundary pollution is a natural phenomenon, specific to vicinity regions, generated by national sources, under the influence of shared climate. The specific target regions (two counties) share the footprint of both nations and are of joint interest concerning raising the environmental awareness.
During the ENVIROBANAT project, air quality data were collected from air quality monitoring station located in several important regional cities, as Zrenjanin, Timisoara, Pancevo, Resita, Kikinda, a.o. Timisoara was first mentioned as a place in either 1212 or 1266. The territory later to be known as Banat was conquered and annexed by the Kingdom of Hungary in 1030. Timisoara grew considerably during the reign of Charles I, who, upon his visit here in 1307, ordered the construction of a royal

palace. Timisoara’s importance also grew thanks to its strategic location, which facilitated control over the Banat plain. John Hunyadi established a permanent military encampment here, and moved here together with his family. In 1552, Ahmed Pasha conquered the city with a 16,000 Ottomans and transformed it into a capital city in the region. Timisoara was the first mainland European city to be lit by electric street lamps in 1884. It was also the second European and the first city in what is now Romania with horse drawn trams in 1867. Gustave Eiffel, the creator of the Eiffel Tower in Paris, built one of Timisoara’s footbridges over the Bega River. According to the last Romanian census, from 2002, there were 317,660 people living within the city of Timisoara, making it the fourth most populous city in Romania. However, today Timisoara is the second important industrial and economic node, after Bucharest.

Zrenjanin is a city and municipality located in the eastern part of Serbian province of Vojvodina. It is the administrative center of the Central Banat District of Serbia. In 2002, the city's population was 79,773, while the Zrenjanin municipality had 132,051 inhabitants. Zrenjanin is the largest city in the Serbian Banat, the third largest city in Vojvodina (after Novi Sad and Subotica) and the sixth largest city of Serbia. Economical, scientific and cultural cooperation between Zrenjanin and Timisoara is at highest level and the two cities are officially recognized as “sister cities”. In 2007, it was declared the City of the Future and, in 2008, the World Bank ranked it first among the cities/towns in Serbia with regard to the overall organization of its business environment. Its development has lasted for almost seven centuries, because, as a settlement under the name of Becskerek, it was first recorded in historical documents way back in 1326. Numerous branches of industry are developed and the most significant ones are the following: Food industry, Textile and leather industry, Metal industry, Chemical industry, Oil and natural gas production, Civil engineering, Traffic / Transport.

RESULTS

During the ENVIROBANAT project implementation the data on air quality were collected from the Romanian National Air Quality Monitoring Network and National Automatic Air Quality Monitoring System of the Republic of Serbia. The data were collected starting with November 2013 and the presented analysis covers a fourth month period, from November 2013 to February 2014. However, on the project webpage the AQM database of the Banat area are available from November 2013 to June 2014. www.envirobanat.ro.

The CO, NO, NO2, O3, SO2, PM10, Benzene, Toluene, Xylene (O-xylene, M-xylene, P-xylene), Etilbenzene concentrations in ambient air are measured and available at 1 hour mean concentration.
A view of the Banat area and AQM station coverage is presented in figure 1.

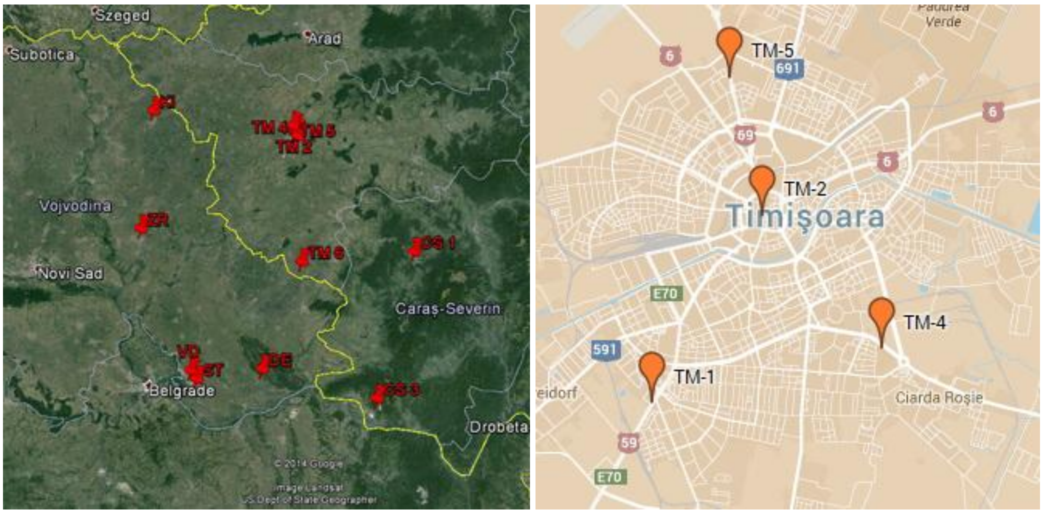
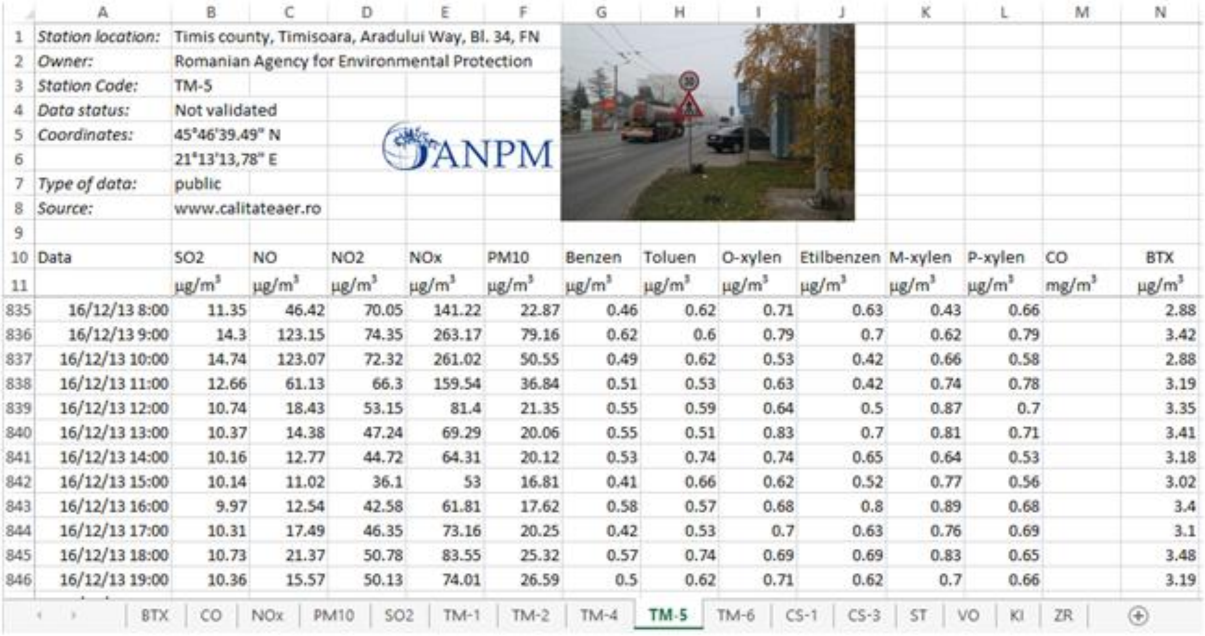


Figure 1. Locations of Romanian and Serbian air quality monitoring stations & view of Timisoara AQM stations

In the printscreen below, a representation of the developed ENVIROBANAT database is presented, in the view the TM-5 Timisoara station air pollutant criteria measurements. However, on the www.envirobanat.ro all the data from all the AQM stations can be downloaded at user disposal, in adobe acrobat extension files.



Station location: Timis county, Timisoara, Aradului Way, Bl. 34, FN
Owner: Romanian Agency for Environmental Protection
Station Code: TM-5
Data status: Not validated
Coordinates: 45°46'39.49" N
21°13'13,78" E
Type of data: public
Source: www.calitateaer.ro

	Data	SO2	NO	NO2	NOx	PM10	Benzen	Toluen	O-xylen	Etilbenzen	M-xylen	P-xylen	CO	BTX
		µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	mg/m³	µg/m³
835	16/12/13 8:00	11.35	46.42	70.05	141.22	22.87	0.46	0.62	0.71	0.63	0.43	0.66		2.88
836	16/12/13 9:00	14.3	123.15	74.35	263.17	79.16	0.62	0.6	0.79	0.7	0.62	0.79		3.42
837	16/12/13 10:00	14.74	123.07	72.32	261.02	50.55	0.49	0.62	0.53	0.42	0.66	0.58		2.88
838	16/12/13 11:00	12.66	61.13	66.3	159.54	36.84	0.51	0.53	0.63	0.42	0.74	0.78		3.19
839	16/12/13 12:00	10.74	18.43	53.15	81.4	21.35	0.55	0.59	0.64	0.5	0.87	0.7		3.35
840	16/12/13 13:00	10.37	14.38	47.24	69.29	20.06	0.55	0.51	0.83	0.7	0.81	0.71		3.41
841	16/12/13 14:00	10.16	12.77	44.72	64.31	20.12	0.53	0.74	0.74	0.65	0.64	0.53		3.18
842	16/12/13 15:00	10.14	11.02	36.1	53	16.81	0.41	0.66	0.62	0.52	0.77	0.56		3.02
843	16/12/13 16:00	9.97	12.54	42.58	61.81	17.62	0.58	0.57	0.68	0.8	0.89	0.68		3.4
844	16/12/13 17:00	10.31	17.49	46.35	73.16	20.25	0.42	0.53	0.7	0.63	0.76	0.69		3.1
845	16/12/13 18:00	10.73	21.37	50.78	83.55	25.32	0.57	0.74	0.69	0.69	0.83	0.65		3.48
846	16/12/13 19:00	10.36	15.57	50.13	74.01	26.59	0.5	0.62	0.71	0.62	0.7	0.66		3.19

Furthermore, in the graphs below the comparative results are presented for criteria pollutants. The graphs were compiled with available data from all air quality monitoring stations, depending on data availability.

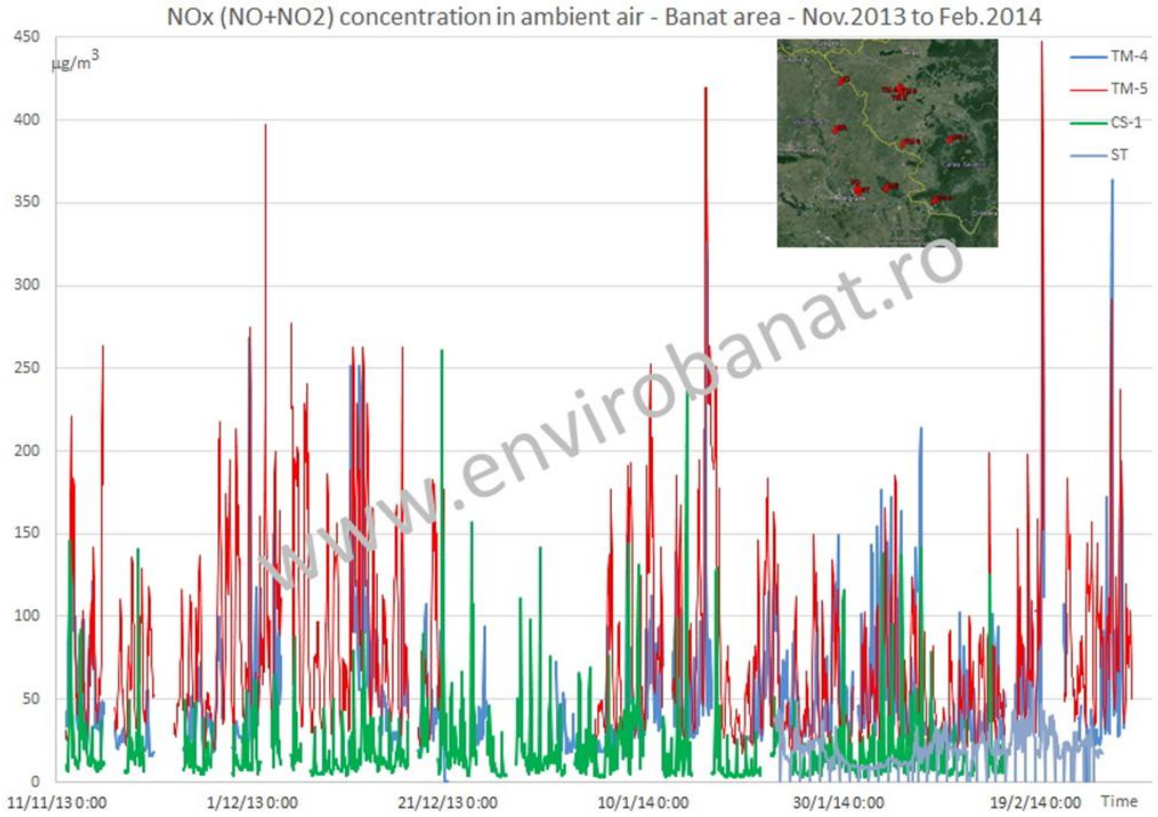


Figure 2. Nov.2013 – Feb.2014 comparative results for NOx concentrations

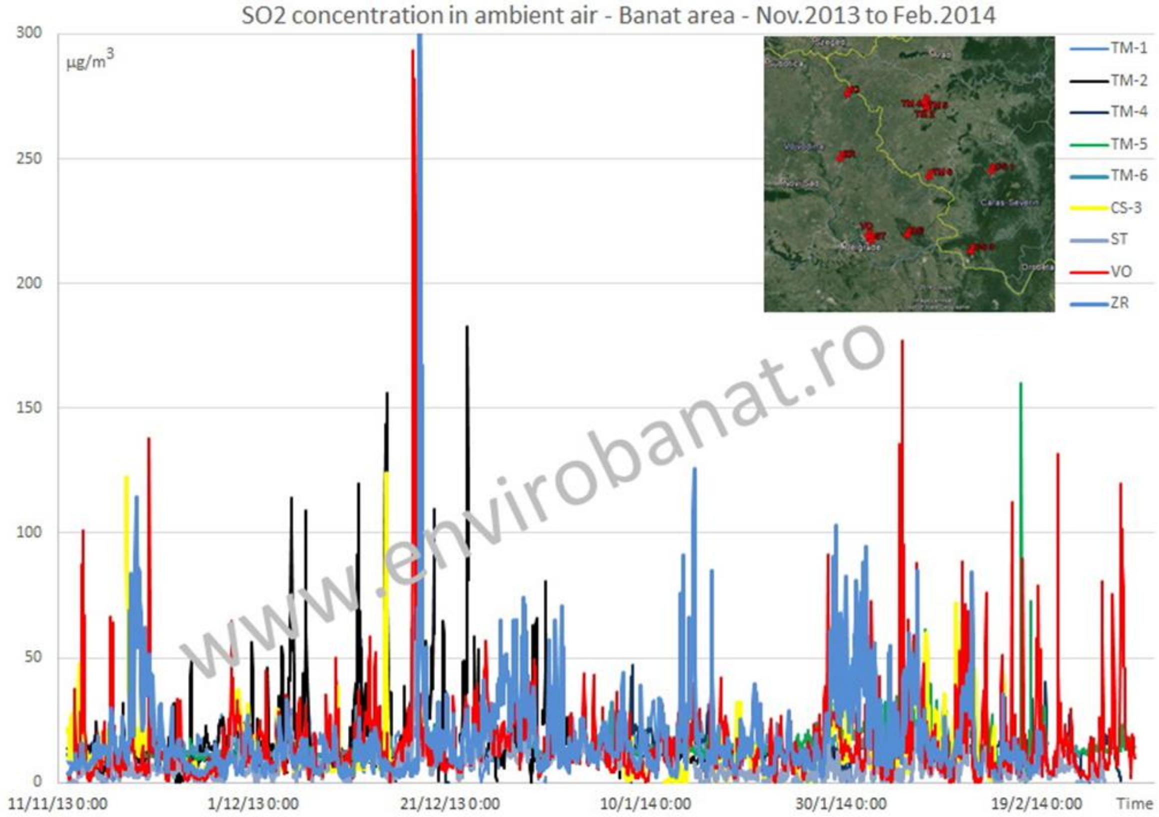


Figure 3. Nov.2013 – Feb.2014 comparative results for SO2 concentrations

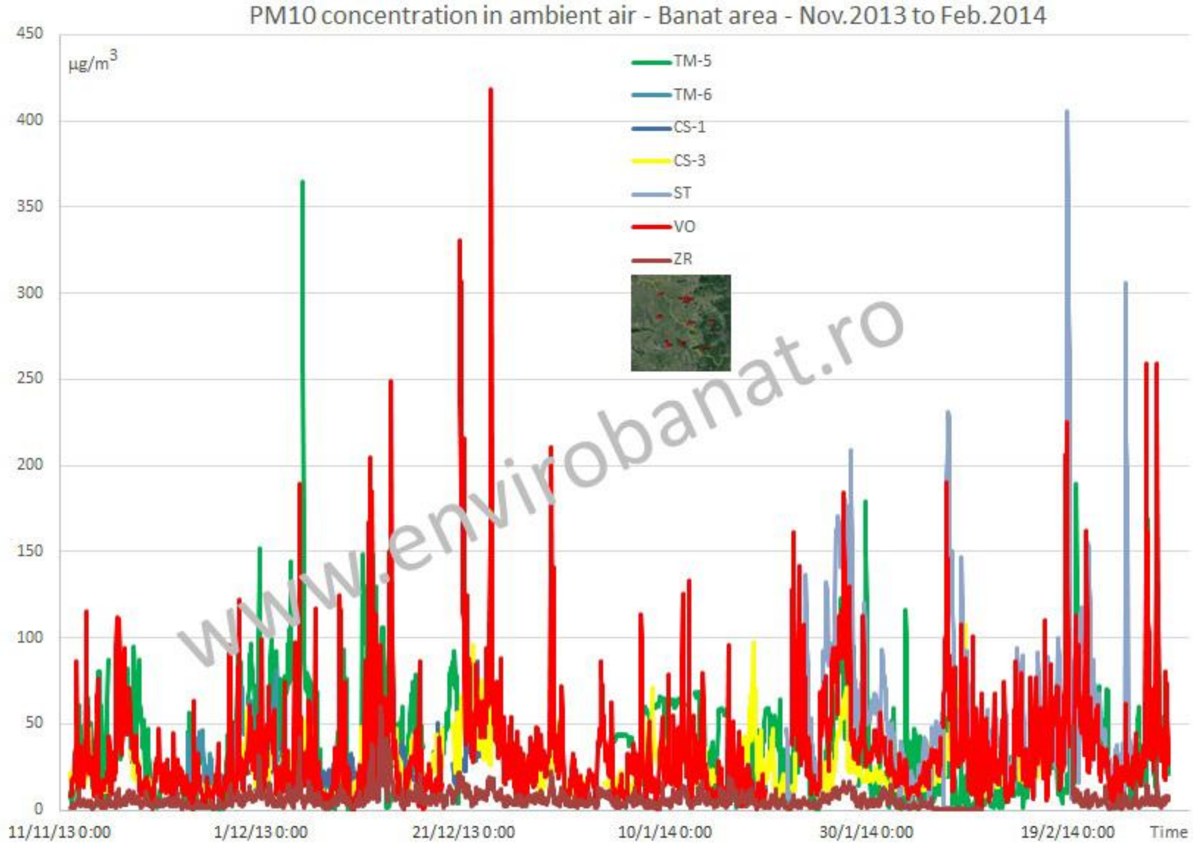


Figure 4. Nov.2013 – Feb.2014 comparative results for PM10 concentrations

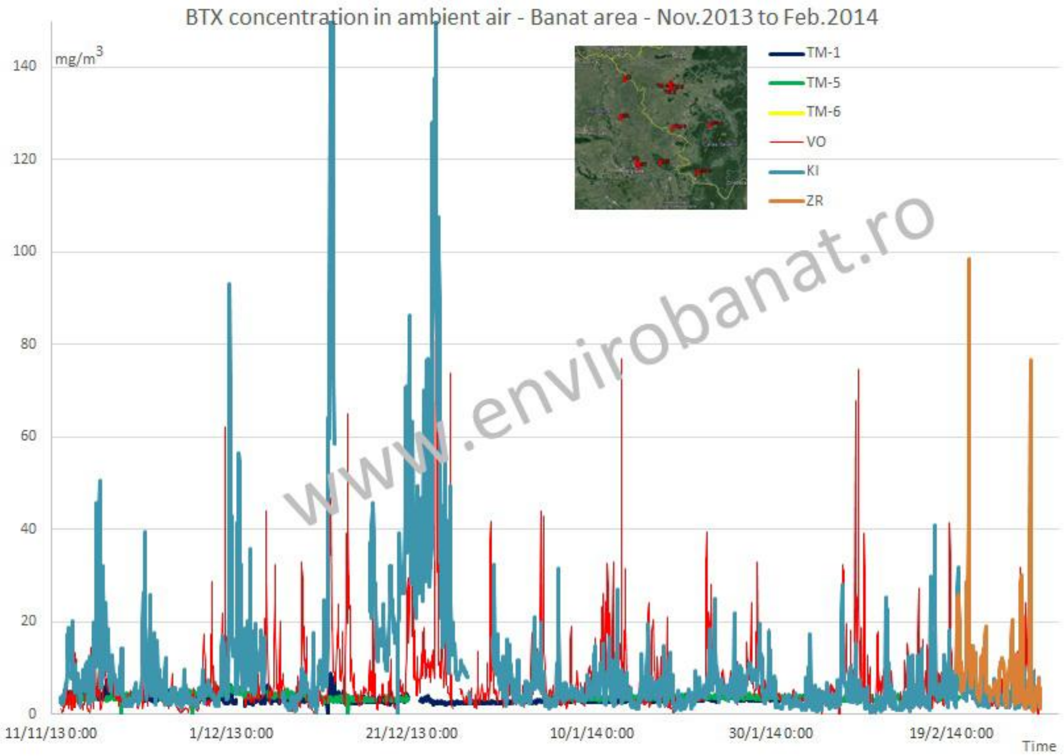


Figure 5. Nov.2013 – Feb.2014 comparative results for BTX concentrations

CONCLUSIONS

To conclude, one can observe that during the ENVIROBANAT - Sustainable development of an research center in Banat region and Danube flow area through scientific research and environmental simulation tools to asses and evaluate potential threats – project the joint research team (Romanian and Serbian scientists) manage to collect and analyze the one hour mean concentrations for criteria air pollutants in the Banat region. The CO, SO2, NO, NO2, (NOx) O3, SO2, PM10, Benzene, Toluene, Xylene (O-xylene, M-xylene, P-xylene) and Etilbenzene concentrations in ambient air were analyzed and all the data made available for any interested parties by means of project webpage www.envirobanat.ro. Analyzing the obtained graphics one can observe that there are some issues regarding the Banat environment. Most important seems to be the concentrations of BTX and PM10 in ambient air. The BTX (benzene-toluene-xylene) high emissions release occurs frequently in the Banat region with large refineries and petrol based industry. Action plans for BTX emission reductions are enforced on both sides of Danube and one can hope that the reduction measures planed will be successfully implements, for a better Banat environment and increased quality of life.

Several exceedances of PM10 concentrations in ambient air (above 50 μg/m3) were noticed on many of the AQM stations monitored. Part of the PM10 concentrations are caused by industrial activity and road traffic, however, looking at entire Balkan Peninsula (www.ec-europa.eu) one can observe that the PM10 issue is generalized at the entire peninsula. More studies and research should be conducted, as its seems to be a more complex problem and probably the PM10 (dust in general) concentrations are influenced by natural conditions and environment of Balkan area.

ACKNOWLEDGMENT

This work was supported by the IPA Romania-Serbia Cross Border Cooperation Programm, project Sustainable development of an research center in Banat region and Danube flow area through scientific research and environmental simulation tools to asses and evaluate potential threats, acronym ENVIROBANAT, MIS-ETC 1425, www.envirobanat.ro.

REFERENCES

Popescu F., Pavlovic M., a.o., (2014), EnviroBanat. Water and air quality in Banat area and Danube tributaries, Timisoara, Romania, ISBN 978-973-0-17234-8, www.envirobanat.ro, 2014
http://en.wikipedia.org/
www.calitateaer.ro, Romanian National Air Quality Monitoring Network
www.merz.gov.rs/en, National Automatic Air Quality Monitoring System of the Republic of Serbia
http://www.eko.vojvodina.gov.rs/index.php?q=2ZRA-Zrenjanin_automatske_stanice

IV International Conference
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COMPARATIVE STUDY FOR THE DEGRADATION PROCESS ON TWO TYPES OF BIOMASS AT LABORATORY SCALE

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ABSTRACT

Nowadays, the studies involving the use of renewable sources of energy are in a continuous stage of development in regard to different theoretical and experimental ways of approach. In the context of global crisis it is imperative to obtain solutions connected with new ways of capitalization of existing sources (wind, hydro, solar, biomass). In this context, biomass residues are of great potential connected with different used technologies, one of them being biogas production in during the anaerobic fermentation process. Degradation is an important part during the process of obtaining biogas and because of this the presented study underlines some of the characteristics of two different sorts of vegetal biomass, in regard to their physical and chemical properties and behavior during the anaerobic fermentation process.

Key words: *anaerobic fermentation, biomass residues, degradation process.*

INTRODUCTION

The use of biomass has for millennia helped human society to fulfill many of its fundamental energy needs, such as for the production of goods, cooking, domestic heating and the transport of people and goods (Chen et. al, 2008).

Biomass is rich in carbon but is not yet a fossil material. All plants and animals in the ecological system belong to biomass. Furthermore, nutrients, excrement, and bio waste from households and industry is biomass (Deublein, 2008).

The International Energy Agency (IEA) has projected an increase in primary energy demand of 1.6 per cent per year until 2030, when the cumulative increase will be equal to half of current demand.

At the same time, concentrations of greenhouse gases (GHGs) in the atmosphere are rising rapidly, with fossil fuel-derived CO2 emissions being the most important contributor. In order to minimize related global warming and climate change impacts, GHG emissions must be reduced to less than half of global emission levels of 1990. Another important global challenge is the security of energy supply, because most of the known conventional oil and gas reserves are concentrated in politically unstable regions. In this context, biogas from wastes, residues, and energy crops will play a vital role in future (Weiland, 2009).

Anaerobic digestion is considered to be the process of decomposition of organic matter by a microbial consortium in an oxygen-free environment. It is a process found in many naturally occurring anoxic environments including watercourses, sediments, waterlogged soils and the mammalian gut. It can

also be applied to a wide range of feedstock including industrial and municipal waste waters, agricultural, municipal, food industry wastes, and plant residues (Ward et. al, 2008).
The biogas is formed during the decomposition process of the organic substrate with the help of different types of bacteria (Eder et. al, 2007).

Biogas can be produced from nearly all kind of biological feedstock types, within these from the primary agricultural sectors and from various organic waste streams from the overall society (Holm - Nielsen et. al, 2009).

Biogas is produced in different environments, e.g., in landfills, sewage sludge and biowaste digesters during anaerobic degradation of organic material. Methane, which is the main component of biogas, is a valuable renewable energy source, but also a harmful greenhouse gas if emitted into the atmosphere. Methane, upgraded from biogas, can be used for heat and electricity production or as biofuel for vehicles to reduce environmental emissions and the use of fossil fuels (Rasi et. al, 2007).

The biogas production process is complex and sensitive since several groups of microorganisms are involved. The important processes in anaerobic digestion are hydrolysis, fermentation, acetogenesis, and methanogenesis, where hydrolysis is subject to the fermentation process, while acetogenesis and methanogenesis are linked (Karellas et. al, 2010).

Related with the industrial applications of this process, in Romania there are not in use today any biogas plants for vegetable waste (cellulose) in the absence of technology, not the raw material that is available in considerable quantities.

EXPERIMENTAL

The research was made on a small scale installation designed and created for experimental studies related to the behavior of different types of biomass residues during the process of anaerobic fermentation.

In this paper there will be presented two types of materials, corn cobs and barley, with some determined chemical and physical properties and their behavior, during the influence of the main parameters of the process (temperature and pH) from the point of view of the degradation process. Images were carried out in order to visually determine the evolution of the degradation during time over a period of 40 days for each batch of material.

In Figs. 1 and 2 there are presented the materials used for the batches.

Figure 1. Corn cobs

Figure 2. Degraded barley

Table 1 presented the chemical characteristics of the two types of biomass residues.

Table 1: Chemical characteristic of the two types of biomass

No	*Sample*	*Water content [%]*	*Ash content (db) [%]*	*Net calorific value (db) [MJ/kg]*
1	Corn cobs	19,7	3,6	17,2
2	Degraded barley	12,4	3,2	16,9

In Fig. 3 there is presented the schematics for the small scale installation.

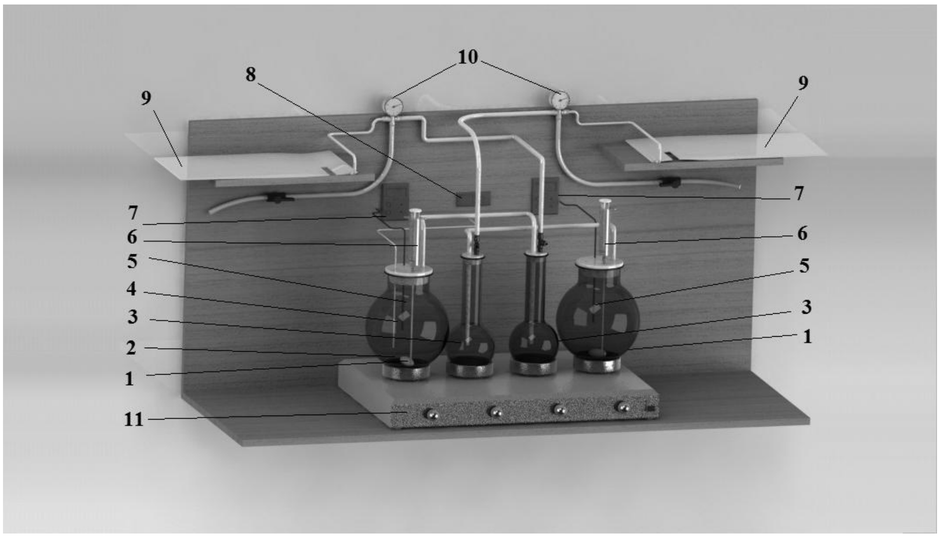


Figure 3. Schematics of the small scale installation

1 – glass reactor with a total volume of 6 l; 2 – magnet placed on the bottom of the 6l glass reactors for magnetic stirring; 3 – small glass reactor for biogas washing with water, with a total volume of 500 mL; 4 – thermocouple; 5 – pH sensors; 6 – system for pH correction and sample collecting; 7 – pH controllers; 8 – temperature controller; 9 – gas bags for biogas samples; 10 – pressure gauges; 11 – heating system.

In the next part, the process involved inside the installation is presented: inside the glass reactors (1) are inserted a semi-fluid suspension composed from fine-granulated biomass and water. Each glass reactor has on the bottom part a magnet (2) used for the magnetic stirring process in order to have a relatively homogenous material. From the glass reactors, the formed biogas will pass into the smaller glass reactors (3) half filled with water in order to “wash” the impurities of the biogas.

Each of the glass reactors (1) has inside a pH sensor (5) which is controlled with pH controllers (7), and also a thermocouple (4) controlled with the help of a temperature controller (8) in order to assure the necessary temperature for the process. The installation is equipped with special gas bags (9) in order to take samples if necessary and pressure control with the help of pressure gauges (10) in case of overpressure.

The temperature regime is assured with the help of the heating device (11) which allows 2 batches to be analyzed separately. The installation was built in order to support two batches of material under the same temperature conditions in order to better observe and make comparisons over the general particularities of each used material.

RESULTS AND DISCUSSION

During the anaerobic fermentation process, the main reaction having as a result the biogas production is given by the microbial degradation of the formed biomass during the photosynthesis from solar energy (Weiland, 2009).

$$6CO2 + 6H2O + Es \text{ (solar energy)} \rightarrow C6H12O6 + 6O2 \qquad (1)$$

The process converts plant metabolic compounds in the following products:

- Carbohydrates - starches, insulin, cellulose, sugar, pectin
- Fats - fats, fatty acids, oil, phosphates, carotene, waxes
- Protein - Protein, nucleoprotein, phosphoprotein
- Other - Vitamins, enzymes, resins, toxins, essential oils.

During the anaerobic fermentation process there was studied the variation of the main parameters (temperature and pH). In Figs. 4 and 5 there are presented daily variation for those parameters.

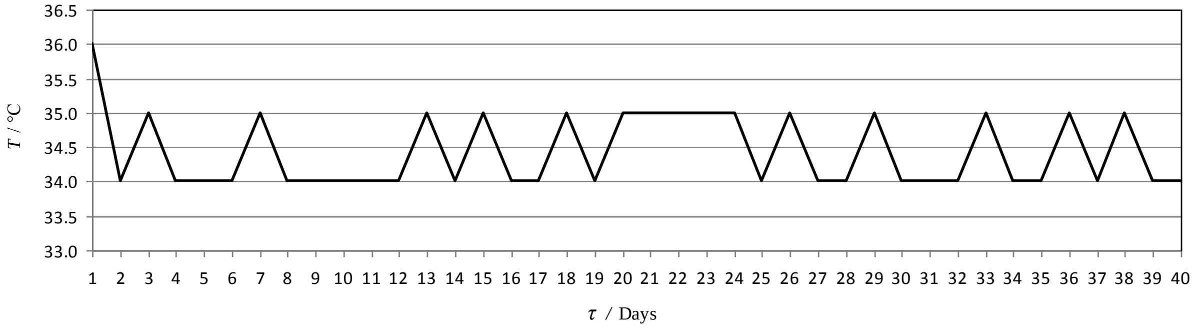


Figure 4. Temperature variation during the anaerobic fermentation process

From Fig. 4 it can be observed that the average value for temperature is approximately 35 ºC, the chosen temperature regime being the mesophilic one (30 – 37 ºC).

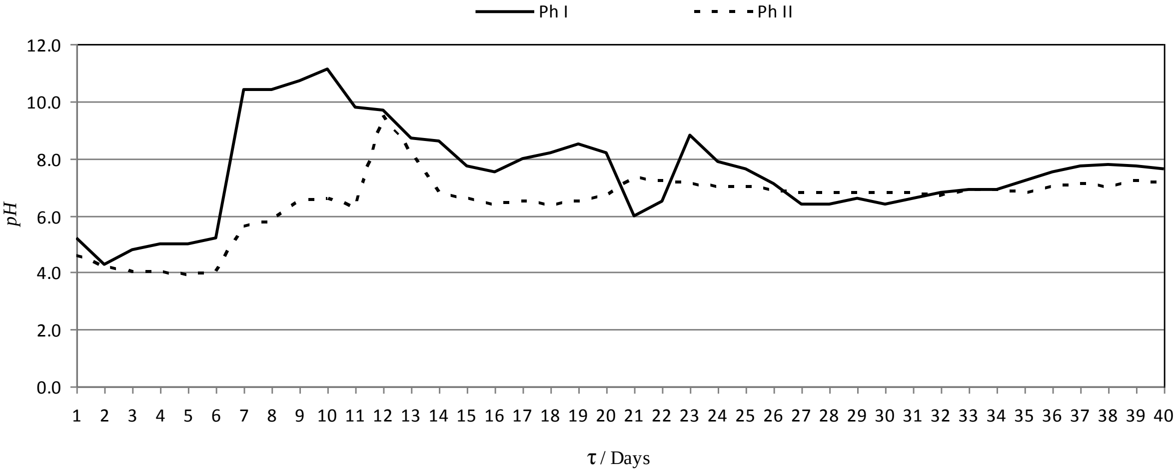
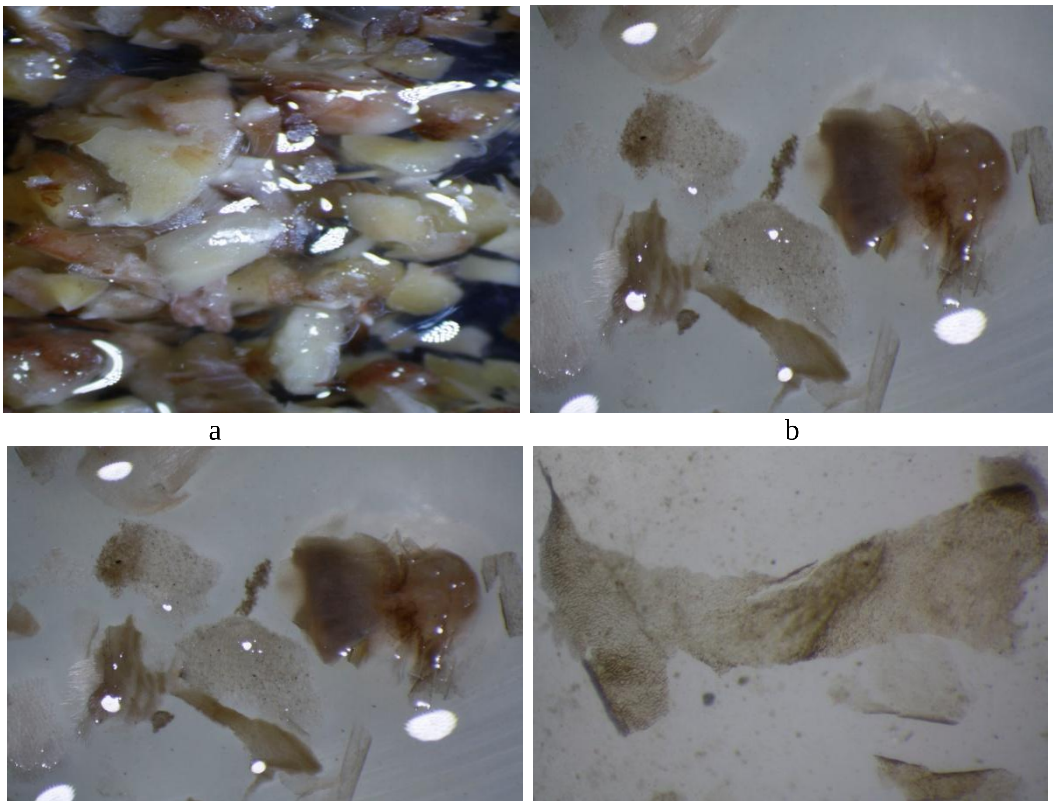


Figure 5. pH variation for the two batches of material

Related to Fig. 5 it can be observed that the pH variation has a different pattern for each batch with peaks varying from 4 to 11, implying the necessity of adding correction liquid in the first phase (because of the general tendency for an acid regime) and also during the stabilization process for having a value between 6.5 and 8 for each batch of the material. After the first 15 – 20 days the process is relatively stable in the neutral zone of interest.

In Figs. 6 and 7 there is presented the degradation process during a 40 days period for the two analyzed batches through the means of visual observations with the help of a microscope.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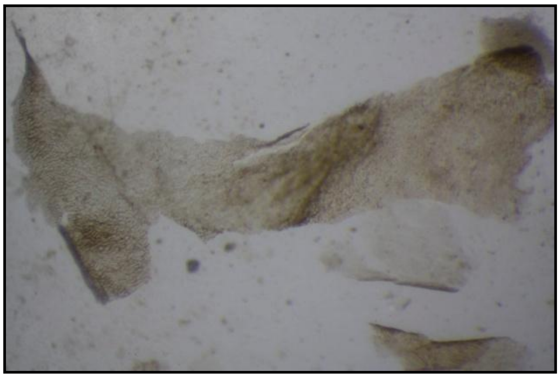
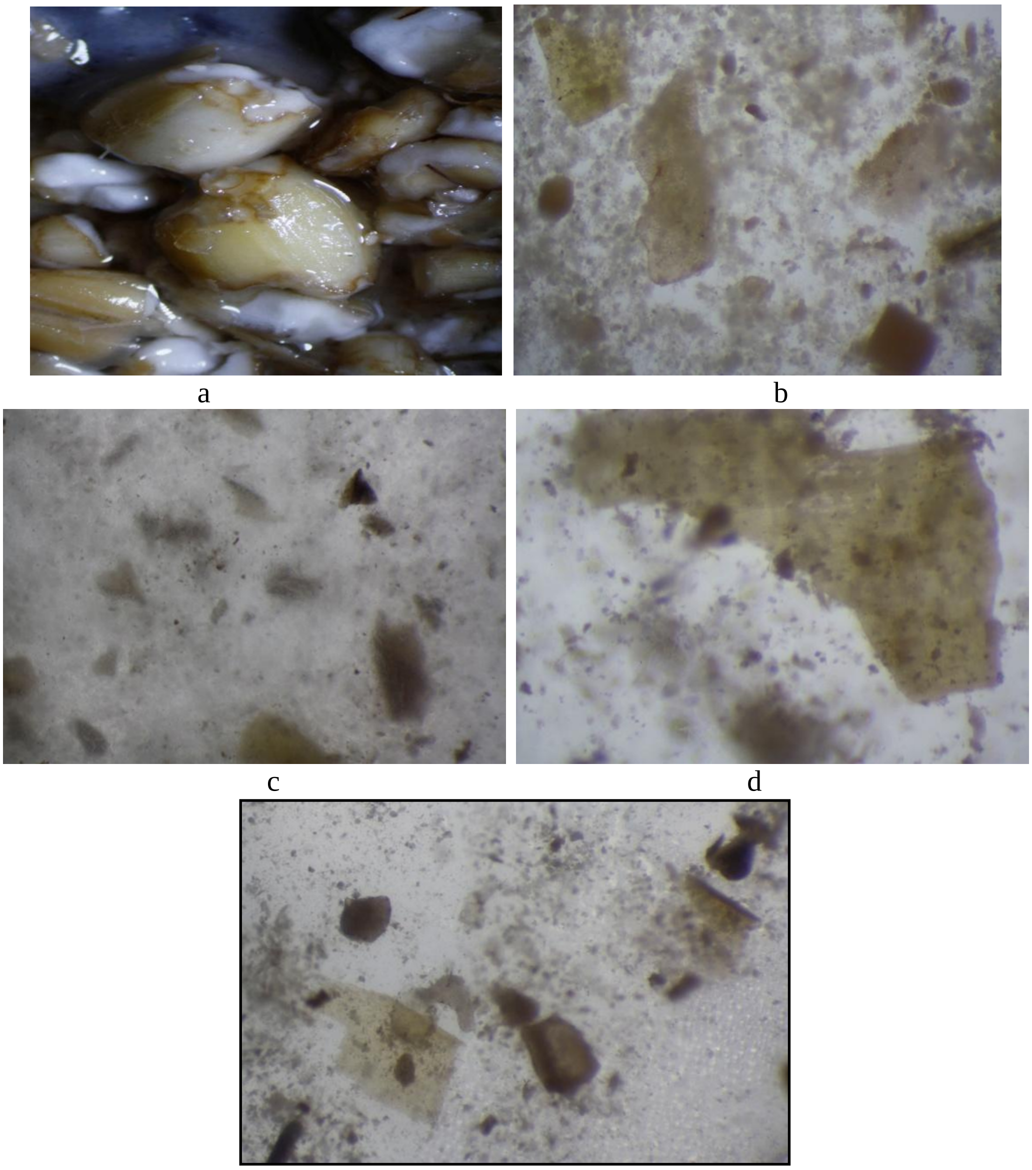


e

Figure 6. Corn cobs, phase 1(enhancement 6X); Corn cobs, phase 2 (enhancement 30X); Corn cobs, phase 3 (enhancement 10X); Corn cobs, phase 4 (enhancement 20X); Corn cobs, phase 5 (enhancement 50X).



a b

c d

e

Figure 7. Degraded barley, phase 1 (enhancement 6X); Degraded barley, phase 2 (enhancement 30X); Degraded barley, phase 3 (enhancement 10X); Degraded barley, phase 4 (enhancement 40X); Degraded barley, phase 5 (enhancement 15X)

In Figs. 6a and 7a are presented the materials in the initial phase, without any degradation process occurring. Figs. 6b and 7b are made after 10 days, time in which the pH is relatively low and the material is starting to deteriorate. In the photos it can be observed that the general structure of the material is still the same. Figs 6c and 7c underline the degradation process after another 10 days, time in which the material starts to deteriorate; as it can be seen the density starts to decrease and the material loses its color partially. After another 10 days of fermentation (Figs 6d and 7d) there can be observed traces of the particles contained in the pH correction liquid together with bacteria formations on the entire surface of the material. The color has almost disappeared and the general density of material is decreasing.

The last phase of the study, after 10 days (Figs 6e and 7e) is connected with almost total lack of color on the batch material and there are parts of material almost entirely degraded together with material in course of degradation. This fact suggests that there is a preferential behavior of the involved bacteria for the general structure of material.

In many practical cases, the connection between two or more parameters which are describing a certain process is sufficiently restraint so the variation of one parameter can be controlled and expressed based on the variation of the other parameters. The functional connections of this type are called probabilistic connections. The study related with this type of connections was linked with the development of the multiple correlation theory.

For an accurate description for the pH variation with temperature and time it was proposed a polynomial equation of second degree expressed by equation 1 (Todinca et. al, 1999), (Borse, 1997).

$$y = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2 + a_3 \cdot x_1 \cdot x_2 + a_4 \cdot x_1^2 + a_5 \cdot x_2^2 \qquad (1)$$

where: ai – equation coefficients;
y – pH;
x1 – temperature [ºC] ;
x2 – time, [days].

The coefficients values in the case of second degree polynomial regression are corresponding to the minimum of the function (Eq. 2):

$$S = \sum_{j=1}^{m} (\hat{y}_j - (a_0 + a_1 \cdot x_{1j} + a_2 \cdot x_{2j} + a_3 \cdot x_{1j}^2 + a_4 \cdot x_{1j} \cdot x_{2j} + a_5 \cdot x_{2j}^2))^2 \qquad (2)$$

Through annulment of the partial derivates of S function in connection with ai coefficients, resulted a linear equations system. The coefficient matrix for the system A and the free coefficients vector, B (Eq. 3):

$$A = \begin{bmatrix}
\sum_{j=1}^{m} 1 & \sum_{j=1}^{m} x_{1j} & \sum_{j=1}^{m} x_{2j} & \sum_{j=1}^{m} x_{1j}^2 & \sum_{j=1}^{m} x_{1j} \cdot x_{2j} & \sum_{j=1}^{m} x_{2j}^2 \\
\sum_{j=1}^{m} x_{1j} & \sum_{j=1}^{m} x_{1j}^2 & \sum_{j=1}^{m} x_{1j} \cdot x_{2j} & \sum_{j=1}^{m} x_{1j}^3 & \sum_{j=1}^{m} x_{1j}^2 \cdot x_{2j} & \sum_{j=1}^{m} x_{1j} \cdot x_{2j}^2 \\
\sum_{j=1}^{m} x_{2j} & \sum_{j=1}^{m} x_{1j} \cdot x_{2j} & \sum_{j=1}^{m} x_{2j}^2 & \sum_{j=1}^{m} x_{1j}^2 \cdot x_{2j} & \sum_{j=1}^{m} x_{1j} \cdot x_{2j}^2 & \sum_{j=1}^{m} x_{2j}^3 \\
\sum_{j=1}^{m} x_{1j}^2 & \sum_{j=1}^{m} x_{1j}^3 & \sum_{j=1}^{m} x_{1j}^2 \cdot x_{2j} & \sum_{j=1}^{m} x_{1j}^4 & \sum_{j=1}^{m} x_{1j}^3 \cdot x_{2j} & \sum_{j=1}^{m} x_{1j}^2 \cdot x_{2j}^2 \\
\sum_{j=1}^{m} x_{1j} \cdot x_{2j} & \sum_{j=1}^{m} x_{1j}^2 \cdot x_{2j} & \sum_{j=1}^{m} x_{1j} \cdot x_{2j}^2 & \sum_{j=1}^{m} x_{1j}^3 \cdot x_{2j} & \sum_{j=1}^{m} x_{1j}^2 \cdot x_{2j}^2 & \sum_{j=1}^{m} x_{1j} \cdot x_{2j}^3 \\
\sum_{j=1}^{m} x_{2j}^2 & \sum_{j=1}^{m} x_{1j} \cdot x_{2j}^2 & \sum_{j=1}^{m} x_{2j}^3 & \sum_{j=1}^{m} x_{1j}^2 \cdot x_{2j}^2 & \sum_{j=1}^{m} x_{1j} \cdot x_{2j}^3 & \sum_{j=1}^{m} x_{2j}^4
\end{bmatrix}
\qquad
B = \begin{bmatrix}
\sum_{j=1}^{m} \hat{y}_j \\
\sum_{j=1}^{m} x_{1j} \cdot \hat{y}_j \\
\sum_{j=1}^{m} x_{2j} \cdot \hat{y}_j \\
\sum_{j=1}^{m} x_{1j}^2 \cdot \hat{y}_j \\
\sum_{j=1}^{m} x_{1j} \cdot x_{2j} \cdot \hat{y}_j \\
\sum_{j=1}^{m} x_{2j}^2 \cdot \hat{y}_j
\end{bmatrix} \qquad (3)$$

Using MATLAB, a mathematical high-level programming language and interactive environment, the equation system was solved and there were analyzed the experimental data.

The obtained data together with the generated surfaces from the statistical mathematical models are presented in Fig. 8.

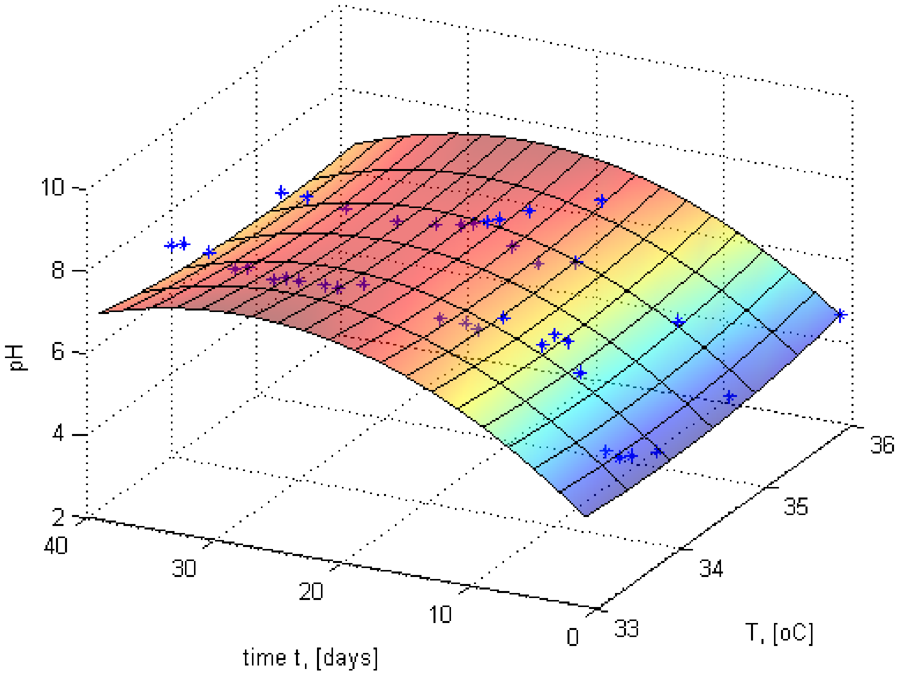


Figure 8. pH evolution in connection with temperature T and time t for the batch containing corn cobs and degraded barley

From the graphics it can be observed that the pH variation has an evolution form acid to neutral or basic levels in time. This process can be explained by the characteristic pH values connected with the phases from which the material starts to degrade (acid phase) until the biogas production where the degradation process is much more intense and the pH tends for a neutral / slight basic value. Also, in order to assure a corresponding value, during the process was used correction liquid (lime based suspension).

The equations for the obtained mathematical statistical models after the linear multiple regressions are presented in Table 2. They are valid on the studied field of values.

Table 2: Equations of the obtained statistical models

Batch	*Equation for the statistical mathematical model*
Corn cobs – degraded barley	$y = 153{,}26 - 8{,}81 \cdot x_1 + 0{,}49 \cdot x_2 - 0{,}007 \cdot x_1 \cdot x_2 + 0{,}13 \cdot x_1^2 - 0{,}005 \cdot x_2^2$

After the computation of the model coefficients it is necessary to make a comparison between model predictions and experimental data. For adequacy indicators there were used the dispersion and R correlation coefficient (Table 3).

- dispersion (Eq. 4) :

$$\sigma^2 = \frac{\sum_{i=1}^{n}(y_{i\,exp} - y_{icalc})^2}{n-1} \qquad (4)$$

- R correlation coefficient (Eq. 5):

$$R = \sqrt{1 - \frac{\sum_{i=1}^{n} (y_i - y_{icalc})^2}{\sum_{i=1}^{n} (y_i - \bar{y})^2}} \qquad (5)$$

Table 3: Adequacy indicators for determined statistical model.

Batch	*Dispersion,* σ^2	*Correlation coefficient, R*
Corn cobs – degraded barley	0,5728	0,7580

The values for the presented adequacy coefficients in Table 3 are indicating a satisfactory correlation between the determined statistical model and experimental data. This confirms the fact that obtained mathematical equations describe with sufficient accuracy the pH evolution in time as a function of temperature.

CONCLUSIONS

Main parameters of influence on the anaerobic fermentation process are the temperature at which the process is done, the pH of slurry, the chemical composition of the materials used and the biomass nature.

The degradation process involved together with the anaerobic fermentation is one of the most important factors that are to be kept in mind related with quantities and qualities for the obtained biogas.

For each batch of material the behavior both in terms of pH and degradation is different, connected with the general structure which can be affected and process duration.

REFERENCES

Borse G. J., Numerical Methods with MATLAB, PWS Publishing Company, Boston, United States of America, 1997.

Chen Y., Cheng J.J., Creamer K. S., (2008), Inhibition of anaerobic digestion process: a review, Bioresource Technology, 99, 4044 – 4064, United States of America.

Deublein D., Steinhauser A., (2008), Biogas from waste and renewable resources, an introduction, Deublein D., Steinhauser A. (Eds), Wiley - VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

Eder B., Schulz H., Biogas praxis. Basics, planning, examples of plants, economy (translation from German language), Ökobuch Verlag, Freiburg, Germany, 2007

Holm-Nielsen J.B., Seadi T., Oleskowicz P., (2009), The future of anaerobic digestion and biogas utilization, 100, 5478, Denmark.

Karellas S., Boukis I., Kontopoulos G., (2010), Development of an investment decision tool for biogas production from agricultural waste, Renewable and Sustainable Energy Reviews, 14, 1273 – 1282, Athens, Greece.

Rasi S., Veijanen A., Rintala J., (2007), Trace compounds of biogas from different biogas production plants, Energy, 32, 1375, Finland.

Todincă T., Geanta M., Chemical processes modeling and simulation (translation form Romanian language), “Politehnica” University Publishing House, Timisoara, Romania, 1999.

Ward A. J., Hobbs P. J., Holliman P. J., Jones D.L, (2008), Optimization of the anaerobic digestion of agricultural residues, Bioresource Technology, 99, 7928 – 7940, United Kingdom.

Weiland P., (2009), Biogas production: current state and perspectives, Applied Microbiology and Biotechnology, 85, 849-860, Germany.

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POSSIBILITIES IN PREVENTING N-NITROSAMINES FORMATION IN RUBBER PROCESSING

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ABSTRACT

During the vulcanization process secondary amines mixture is formed. The secondary amines in the presence of nitrogen oxides form N-nitrosamines. The tire industry is trying to reduce the content of N-nitrosamines in rubber products. This paper presents compounds that can be an alternative to hazardous substances.

Key words: *N-nitrosamines, secondary amines, replacement.*

INTRODUCTION

The secondary amines in the rubber industry are present and there is a need to eliminate them. N-nitrosamines, in the rubber industry, are generated (Speigelhalder et al., 1983; Rounbehler et al., 1983). They are formed during mixing, milling and blending of natural rubber or synthetic elastomers, or of natural rubber and synthetic polymers combined with chemicals, and in the processes which convert the resultant blends into finished products or parts thereof. The resulting amines influence the speed production, the crosslinking reactions, which, depending on the amine structure can accelerator the technological process. Allowable N-nitrosamines concentration in the workplace is up to 2.5 μgm^{-3} in the air (Dost et al., 2000; De Vocht et al., 2007; Kataoka et al., 1996). Ventilation is a possible solution. N-nitrosamines in rubber depend on the stabilization materials, regulators and substances used in polymerization termination. Rubber can contain different N-nitrosamines amounts and in the range from 2 to 380 ppb. Nitrosamines that are use in the rubber industry are presented in the Table 1.

Table 1: N-nitrosamines commonly detected in workplace air

N-Nitrosamine	Abbreviated Name	Chemical Formula	Molecular Weight	Chemical Structure
N-Nitrosodimethylamine	NDMA	$C_2H_6N_2O$	74	$(CH_3)_2$-N-N=O
N-Nitroso-n-methylethylamine	NMEA	$C_3H_8N_2O$	88	CH_3-$CH_2(CH_3)$-N-N=O
N-Nitrosodiethylamine	NDEA	$C_4H_{10}N_2O$	102	$(CH_3$-$CH_2)_2$-N-N=O
N-Nitrosodi-n-propylamine	NDPA	$C_6H_{14}N_2O$	130	$(CH_3$-CH_2-$CH_2)_2$-N-N=O
N-Nitrosodi-n-butylamine	NDBA	$C_8H_{18}N_2O$	158	$(CH_3$-CH_2-CH_2-$CH_2)_2$-N-N=O
N-Nitrosodiphenylamine	NDPhA	$C_{12}H_{10}N_2O$	198	Ph_2-N-N=O

N-Nitrosomorpholine	NMOR	$C_4H_8N_20_2$	116	O-(CH_2-CH_2)(CH_2-CH_2)-N-N=O
N-Nitrosopiperidine	NPIP	$C_5H_{10}N_2O$	114	CH_2-(CH_2-CH_2)(CH_2-CH_2)-N-N=O
N-Nitrosopyrrolidine	NPYR	$C_4H_8N_2O$	100	(CH_2-CH_2)(CH_2-CH_2)-N-N=O

POSSIBLE SOLUTIONS

The accelarator used in the production of car tires is benzothiazyl-2-sulphenemorpholide which during vulcanization process forms morpholine. Nitrosylation of morpholine generates the N-nitrosomorpholine.

The accelarator, known under the name VPKA 9124, which is benzothiazyl-2-tert. amylsulphenamide is a derivative of the primary amine (Figure 1.).

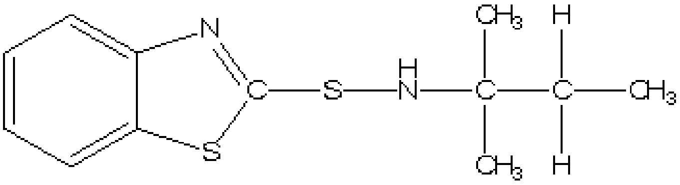

Figure 1. Structure of benzothiazyl-2-tert. amylsulphenamide

Benzothiazyl-2-tert. amylsulphenamide with the natural rubber gives better vulcanization compared to benzothiazyl-2-sulphenmorpholide. Differences in the rate of vulcanization between these two accelarators differ slightly. During vulcanization at 150°C, the vulcanization is slightly shorter when benzothiazyl-2-tert amylsulphenamide is used. Both products provide the same elasticity quality. When mechanical properties are considered there is no significant difference. Elastic properties of benzothiazyl-2-tert. amylsulphenamide is reflected in the dynamic damping determined by Roelig.

REPLACEMENT FOR THIOCARBAMATES

Zinc dithiocarbamates which are used in the solid rubber production and latex are a group of compounds which produce N-nitrosamines. These compounds can be replaced with zinc dibenzyldithiocarbamate and zinc diallyldithiocarbamate (Figure 2.).

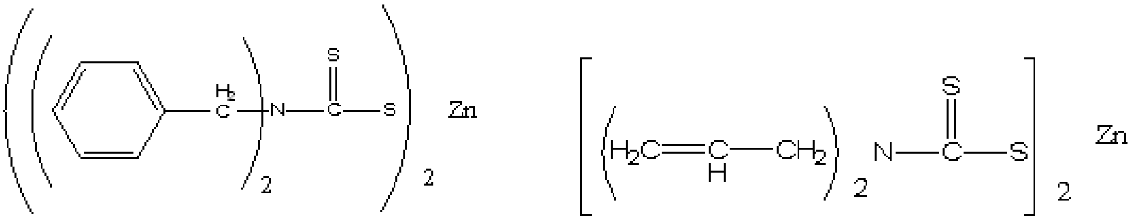

Figure 2. Structure of zinc dibenzyldithiocarbamate(left) and zinc diallyldithiocarbamate (right)

Zinc dibenzyldithiocarbamate is an exception among dithiocarbamates. It creates a secondary amine which is difficult to undergo the reaction of nitrosylation compared to the other dithiocarbamates.

Replacement can also be found among dithiocarbamate derivatives of dithiophosphoric acids: copper and zinc dialkyldithiophosphate.

REPLACEMENT FOR THIURAM

Thiurams are used as accelarators in the vulcanization and as sulfur donors. Possible replacements are shown in Figure 3. For two-thirds of thiurams there is yet no adequate replacement.

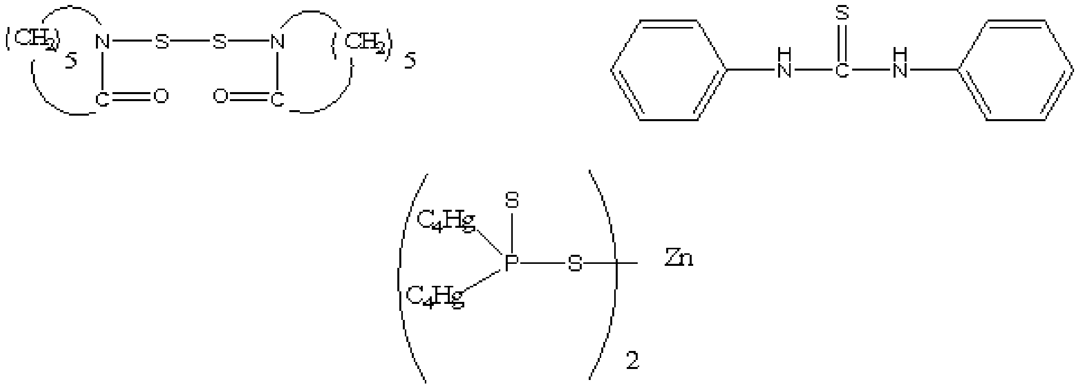

Figure 3. Some of the possible replacements for thiurams as sulfur donors

CONCLUSION

N-nitrosamines, in the rubber industry, have set up an application for finding appropriate technological substitution. Presented compounds are possible solutions for lowering N-nitrosamines quantities. In this paper, the emissions of different rubber compounds that can occur during mixing and vulcanization processes were discussed. In order to reduce or to eliminate the hazardous emissions, several substitutes are recommended as replacement. N-nitrosamines are still an ongoing issue in the rubber industry. In some countries, the latest regulation permits a maximum atmospheric concentration of regulated N-nitrosamines of only 1 mgm^{-3}. For reducing or eliminating the N-nitrosamines, accelerators that can be used and do not produce N-nitrosamines are dithiophosphates or accelerators that generate non-regulated N-nitrosamines like zinc dibutyldithiocarbamate.

REFERENCES

De Vocht, F., Vermeulen, R., Bustyn, I., Sabala, W., Dost, A., Taeger, D., Bergendorf, U., Straif, K., Swuste, P., & Kromhout H. (2007) *Exposure to inhalable dust and it's cyclohexane soluble fraction since 1970s in the rubber manufacturing industry in the European Union.'* Occupational Environmental medicine, online edition.

Dost, A. A, Redman D., & Cox G. (2000) *Exposure to rubber fume and rubber process dust in the general rubber goods, tyre manufacturing and retread industries.* Annals of Occupational Hygiene, vol 44, No. 9.

Kataoka, H.; Shindoh, S. and Makita, M. (1996), Selective determination of volatile N-nitrosamines by derivatization with diethyl chlorothiophosphate and gas chromatography with flame photometric detection. *Journal of chromatography A*, 723, 93-99.

Rounbehler, D. P., & Fajen, J. M. (1983). *N-Nitroso compounds in the factory environment*'. National Institute for Occupational Safety and Health, Cincinnati, Ohio 45226, USA. NIOSH Technical Report (Publication No. 83-114).

Speigelhalder, B., & Preussmann R. (1983). *Occupational nitrosamine exposure. 1. Rubber and tire industry*, Carcinogenesis, *Vol. 4*, No. 9, 1147-1152.

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IMPROVING CARBON MONOXIDE ADSORPTION PROPERTIES OF SUMANENE

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ABSTRACT

In this work we investigated adsorption properties of sumanene towards carbon monoxide (CO) molecule employing density functional theory (DFT) calculations. CO is common atmospheric pollutant which is hardly adsorbed by non-modified carbon based structures, such as carbon nanotubes. However, after certain modifications and fictionalizations, carbon nanotubes are able to detect this pollutant. Sumanene belongs to group of molecular bowls (also known as π-bowls) which can be considered as fragment of fullerenes and carbon nanotubes. Due to its geometry, sumanene has two different surfaces and positive adsorption properties towards CO molecule, even when it is not modified. Thanks to its benzylic positions there are still a lot of possibilities to improve adsorption properties towards CO, and other, molecules.

Key words: *sumanene, carbon monoxide, adsorption, DFT, π-bowls.*

INTRODUCTION

Sumanene belongs to a group of molecules known as buckybowls (or pi-bowls, molecular bowls) which was synthesized in 2003 [1]. Its main structural characteristics include three benzylic locations and two different surfaces with different adsorption properties. The first one is very important for modification possibilities thanks to the three sp3 carbons, while the later one turned out to be crucial for adsorption properties, since more negative charge is located at the concave part of sumanene molecule. Another important fact related to the structure of sumanene is that it can be considered as a model compound of fullerenes and nanotubes [2].

Sumanene also has significant importance for the field of environmental protection. In our recent study [3] we have demonstrated positive adsorption properties of sumanene towards common atmospheric pollutants, such as CO, CO2, NH3. Sumanenes ability, according to our computational study, to adsorb CO molecule without modifications is what makes this molecule special with regard to nanotubes and fullerenes, which cannot detect CO molecules without further functionalization.

We have shown that electrostatic interaction is principally responsible for positive adsorption properties of sumanene towards CO molecule. Sumanene also possesses relatively high dipole moment [4], thanks to which it is possible to induce dipole moment in other molecules and to adsorb them. Such mechanism of adsorption is demonstrated by Scanlon et al [5, 6] and in our recent study as well [4].

Possible modifications of sumanene molecule include substitution of benzylic carbon atoms with nitrogen atoms. This type of modification was investigated in our paper [7]. During these studies it was concluded that dipole moment significantly increase with substitution of benzylic carbon atoms with nitrogen atoms.

As stated earlier in our paper [7] the introduction of nitrogen atom affects the bowl shaped geometry of sumanene. Namely, the bowl depth increases and directly consequences the bowl-to-bowl inversion of sumanene. Beside structural changes the most important change is related to dipole moment, which increases for around 50%. This fact guided us to investigate the adsorption properties of sumanene modified with nitrogen atom towards the CO molecules.

COMPUTATIONAL DETAILS

For all DFT calculations we used three parameter Becke, Lyp and Par exchange functional (B3LYP) [8, 9]. A 6-31G(d,p) basis set was employed. All investigated structures were geometrically optimized at the mentioned level of theory. CO molecules were placed above the central six-membered ring of the sumanene from concave side after which geometrical optimization was performed.

Adsorption energy was calculated according to the following expression:

$$E_{ad} = E_{Sumanene+CO} - E_{Sumanene} - E_{CO} \tag{1}$$

where $E_{Molecule}$ stands for the total energy of CO molecule, while $E_{Sumanene+CO}$ is total energy of a system consisting of Sumanene and CO molecule.

All DFT calculations were carried out using Jaguar, version 8.5 [10] as implemented in Schrödinger Materials Suite, release 2014-3. Since these are initial results concerning the improvement of sumanene adsorption properties, basis set superposition error (BSSE) is not treated.

RESULTS AND DISCUSSION

Geometry of sumanene modified with nitrogen atom (sumanene@N) in this work ia presented in Figure 1. Introduction of nitrogen atom affected the geometry of sumanene, leading to significant changes of bowl depth. These changes of bowl depth are in agreement with the results of Sastry et. al. [11] where they concluded that the bowl depth of heterobuckybowls is affected by the size and location of the substituting atom. Thus, the monosubstitution with larger substituents tends to flatten structure compared with the regular sumanene and vice versa.

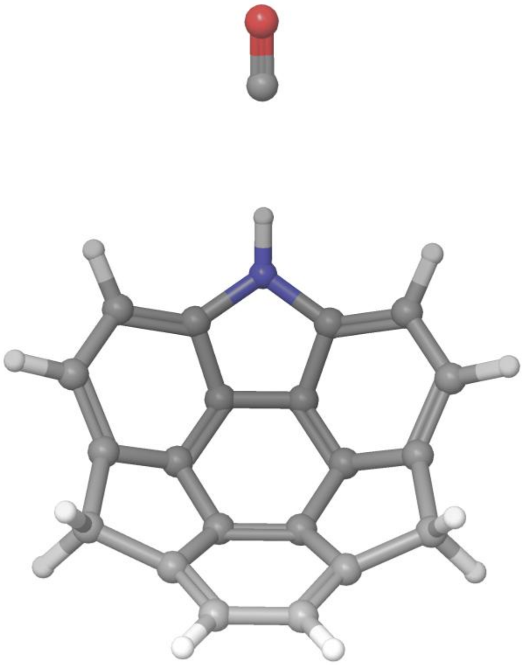

Figure 1. Geometry of system sumanene@N + CO

Introduction nitrogen atom not only affected significantly the structural parameters, but also the charge distribution. This led to the significant increase of dipole moment. Dipole moment is very important for mechanism of physisorption, since the molecule with high dipole moment can induce dipole moment in otherwise non-polarized molecule [5, 6]. Calculated dipole moment of regular sumanene is 1,93 D as shown in our paper [4]. This is relatively high value which is responsible for positive adsorption properties of sumanene towards CO [3]. However, after introduction of nitrogen atom, dipole moment of sumanene significantly increased, as presented in Table 1.

Table 1: Dipole moments and bowl depth of regular and nitrogen modified sumanene

Structure	Dipole moment [D]	Bowl depth [Å]
Sumanene	1,93	1,13
Sumanene@N	2,90	1,20

It can be seen in Table 1 that after modifications of sumanene with nitrogen atom dipole moment increased significantly – to the value of 2,9 D. Thus, the increase in dipole moment is around 50 %.

In order for some structure to be suitable for adsorption, it is essential to have suitable range of adsorption energies. When it comes to the adsorption of CO molecules it is preferred to have as high as possible adsorption energy in order to efficiently eliminate CO from environment. Adsorption energy of regular sumanene towards CO molecule is -0,83 kcal/mol and can be improved after modifications of benzylic positions, due to the increase in dipole moment.

Table 2: Binding energies of sumanene and its derivate with nitrogen atom

Structure	Binding energy [kcal/mol]
Sumanene	-0,83
Sumanene@N	-2,38

It can be seen that the interaction between sumanene and CO molecules is significantly improved after modifications of sumanene nitrogen atom. Namely, for the case when sumanene is modified with one atom of nitrogen adsorption energy is almost three times higher than for regular sumanene!

CONCLUSION

In this work we demonstrated that adsorption properties of sumanene could be improved with the substitution of its benzylic positions with nitrogen atom. Better adsorption properties are result of the increased dipole moment due to the different charge distribution after substitution of sumanene's benzylic positions. Increased dipole moment of sumanene improves the interaction with CO molecules and the adsorption energy is higher, especially for the case when nitrogen atom is introduced at sumanene's benzylic position. The obtained adsorption energies correspond to the mechanism of physisorption so it can be concluded that the electrostatic interaction between sumanene and CO is principally responsible for positive adsorption properties of this organic molecule.

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REFERENCES

Sakurai H, Daiko T, Hirao T (2003) A synthesis of sumanene, a fullerene fragment. Science 301:1878-1878.

Sakurai H, Daiko T, Sakane H, Amaya T, Hirao T (2005) Structural elucidation of sumanene and generation of its benzylic anions. Journal of the American Chemical Society 127:11580-11581.

Armaković S, Armaković SJ, Šetrajčić JP, Jaćimovski SK, Holodkov V (2014) Sumanene and its adsorption properties towards CO, CO2 and NH3 molecules. Journal of molecular modeling 20:1-14.

Armaković S, Armaković SJ, Šetrajčić JP (2013) Hydrogen storage properties of sumanene. International Journal of Hydrogen Energy 38:12190-12198.

Scanlon L, Balbuena P, Zhang Y, Sandi G, Back C, Feld W, Mack J, Rottmayer M, Riepenhoff J (2006) Investigation of corannulene for molecular hydrogen storage via computational chemistry and experimentation. The Journal of Physical Chemistry B 110:7688-7694.

Scanlon L, Feld W, Balbuena P, Sandi G, Duan X, Underwood K, Hunter N, Mack J, Rottmayer M, Tsao M (2009) Hydrogen storage based on physisorption. The Journal of Physical Chemistry B 113:4708-4717.

Armaković S, Armaković SJ, Šetrajčić JP, Šetrajčić IJ (2013) Optical and bowl-to-bowl inversion properties of sumanene substituted on its benzylic positions; a DFT/TD-DFT study. Chemical Physics Letters 578:156-161.

Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. Physical Review A 38:3098.

Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Physical Review B 37:785.

Bochevarov AD, Harder E, Hughes TF, Greenwood JR, Braden DA, Philipp DM, Rinaldo D, Halls MD, Zhang J, Friesner RA (2013) Jaguar: A high-performance quantum chemistry software program with strengths in life and materials sciences. International Journal of Quantum Chemistry 113:2110-2142.

Sastry GN, Rao HSP, Bednarek P, Priyakumar UD (2000) Effect of substitution on the curvature and bowl-to-bowl inversion barrier of bucky-bowls. Study of mono-substituted corannulenes (C19XH10, X= B−, N+, P+ and Si). Chemical Communications 843-844.

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IMPEMENTATION OF EUROPEAN LEGISLATION ON FUEL QUALITY IN REPUBLIC OF SERBIA

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ABSTRACT

In this paper the authors studied the synergy of the legislative and the actual state of protection of fuels quality on the basis of exact parameters due to the territory of the Republic of Serbia, assessing the quality of legal provisions and their applicability, pointing to possible failures in legislation and in implementing these provisions. In the Republic of Serbia, liquid fuels have been produced since 2013, according to EU standard requirements. Besides, the consistent application in practice is needed, improvement of monitoring of fuel quality and ensuring transparency and accessibility of information.

Key words: *legal protection, environmental, fuel quality, Serbian law, EU legislation.*

INTRODUCTION

Nowadays ecological policies take an important place in the activities of European Union. Traffic considerably influences on the environmental because a high percentage of air pollution comes from mobile sources. The main polluters mobile sources are: carbon oxide (II) CO, nitrogen oxides NO_2, hydrocarbons, lead in the form of their organic compounds, as well as photochemical smog special shape, aldehydes, ketones and particles. So, traffic represents a significant pollution source although efficient and flexible system is a base for economy and quality life for every country. Transport is today fuelled to a very large extent by oil. This situation has implications on energy policy, but it is also of great relevance from an environmental perspective, notably in view of climate change.

The authors in this paper present the most important EU regulations in the field of legal protection of fuel quality as one specific issue within environmental protection. Through analysis of European legislation the authors point at normative framework that is being implemented in legislation of Republic of Serbia. Special attention is focused on legislation of Republic of Serbia related to this field by studying the level of harmonization of Serbian regulations of fuel quality fuels with European legislation.

EUROPEAN LEGISLATION ON FUEL QUALITY

With regard to the importance which air quality has, this question is regulated in the legislation of European Union. The Directive on Cleaner Air for Europe (2008/50/EC) (CAFÉ) establishes harmonized health standards for polluting substances in air which arouse greater concern. This Directive requires from governments to define air quality zones which cover the whole country. Boundaries between the zones are determined according to the density of population and criteria of exposure. If the standards are not satisfied, plans for air quality management have to be defined, and by the authorities at the very level which are competent for particular zone, whose object is to reach the quality standard on the territory of the zone in the shortest time possible. Directive 96/61/EEC on Integrated Pollution Prevention and Control (IPPC) is being applied on industrial and other facilities and activities which are classified according to the level of pollution and the risk these activities might have for the health of people and the environment. General framework for regulations in the area of air quality is the directive of the Council 96/62/EC on assessment and management of air quality which has been adopted by Serbian law. By means of this directive a list of polluting substances among which there are SO_2, NO_2, CO, particles, lead, ozone, cadmium, arsenic, nickel, mercury, and benzene is established and maximum allowed concentrations are further defined. Significant are the directives which refer to Air Quality and Daughter Directives (SO_2, NO_x, Pb) – 99/30/EEC**,** Volatile Organic Compounds – 99/13/EC**,** Quality of Fuels – 98/70/EEC**,** Emissions of Non-Road Mobile Machinery – 97/68/EC**,** Carbon Dioxide and Other Greenhouse Gas Emissions – 93/389/EEC**,** Emission from motor vehicles – 70/220/EEC. Council Decision 97/101/EC establishing a reciprocal exchange of information and data from networks and individual stations measuring ambient air pollution within the European Union (Exchange on Information decision (EOI) on Air) held of 27 January 1997. A Community-wide procedure for the exchange of information and data on ambient air quality in the European Community is established by the Council Decision 97/101/EC. The decision introduces a reciprocal exchange of information and data relating to the networks and stations set up in the European Community to measure air pollution and the air quality measurements taken by those stations**.** Reduction of sulfur oxides pollution (SO_2) in the European Union was achieved by implementation of EU legislation on limited pollution from large combustion plants and by implementation of standards of low sulfur content of the fuel for transports.

In the group of regulations for protection from air pollution from mobile sources are also European Union regulated to quality of fuels and discharging cars waste goses from: Council Directive 1999/32/EC relating to a reduction in the sulfur content of certain liquid fuels and amending Directive 93/12/EEC. Amended by: Regulation (EC) No 1882/2003, Directive 2005/33/EC, Regulation (EC) No 219/2009, Directive 2009/30/EC. Directive 1999/32/EC on reduction of sulfur content of certain liquid fuels aims to reduce the emissions of sulfur dioxide resulting from the combustion of certain types of liquid fuels and thereby to reduce the harmful effects of such emissions on man and the environment. These reductions in emissions of sulfur dioxide shall be achieved by imposing limits on the sulfur content resulting from the combustion of certain types of liquid fuels as a condition for their use. Petrol is a complex mixture of volatile organic compounds (VOCs) which readily evaporate into the atmosphere where they contribute to several air pollution problems. These include excessive levels of benzene in ambient air and photochemical formation of ozone which is both an air pollutant and a greenhouse gas. Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/, Directive 2000/71/EC, Directive 2003/17/EC and Directive 1882/2003. Directive 97/68/EC of the European Parliament and of the Council of 16 December 1997 on the approximate on of the laws of the Member States relating to measures against the emission of gaseous and particulate pollutants from internal combustion engines to be installed in non-road mobile machinery amended by: Directive 2001/63/EC, 2002/88/EC and Directive 2004/26/EC. The non-road mobile machinery (NRMM) sector covers a large variety of equipment types which are used in many different economic activities such as construction, agriculture, rail or inland waterway transport. Combustion engines used in this machinery are regulated by Directive 97/68/EC which aims at reducing air pollutant emissions and providing a harmonized basis for placing these engines on the European Union market. Despite the limits set by Directive 97/68/EC and its subsequent amendments, the NRMM sector has become an increasingly important source of air pollution, in particular of NO_2 and particulate matter. The overall objective of the revision is to further contribute to the improvement of the air quality in Europe while at the same time ensuring the correct functioning of the internal market. Non-Road Mobile Machinery (NRMM) covers a large variety of engine installations in machines used for purposes other them for passenger or goods transport. Diesel and spark emission engines installed in these NRMM such as excavators, bulldozers, front loaders, back loaders, compressors contribute greatly to air pollution by emitting carbon oxide (CO), hydrocarbons (HC), nitrogen oxides (NO_2) and particulate matters. In line with the European Union environmental policy it is the objective to progressively reduce the emissions and to phase out polluting equipment. Emissions from these engines are regulated before they are placed on the market by six directives: the "mother" Directive 97/68/EC**,** the amendments Directive 2002/88/EC, Directive 2004/26/EC, Directive 2006/105/EC, Directive 2011/88/EU and the last amendment Directive 2012/46/EU**.** For the various types of NRMM, the Directive stipulates the maximum permitted exhaust emissions as a function of the power of the relevant engine. Moreover the

Directive includes a series of emission limit stages of increasing stringency with corresponding compliance dates. Manufacturers must ensure that new engines comply with these limits in order that they can be placed on the market. Directive 2005/55/EC of the European Parliament and of the Council of 28 September 2005 on the approximation of the laws of the Member States relating to the measures to be taken against the emission of gaseous and particulate pollutants from compression-ignition engines for use in vehicles, and the emission of gaseous pollutants from positive-ignition engines fuelled with natural gas or liquefied petroleum gas for use in vehicles. Commission Directive 2005/78/EC of 14 November 2005 implementing Directive 2005/55/EC of the European Parliament and of the Council on the approximation of the laws of the Member States relating to the measures to be taken against the emission of gaseous and particulate pollutants from compression-ignition engines for use in vehicles, and the emission of gaseous pollutants from positive ignition engines fuelled with natural gas or liquefied petroleum gas for use in vehicles and amending Annexes I, II, III, IV and VI thereto Directive (EC) No 715/2007 of the European Parliament and of the Council of 20 June 2007 on type approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information· This regulation provides that Euro 5 Standards apply for registration and sale of new vehicles since 1 January 2011 and Euro 6 Standards from 1 January 2015.

The main effect of Euro 5 is to reduce the emission of particulate matter from diesel cars from 25mg/km to 5mg/km. Euro 6 will mainly reduce the emissions of NO_2 from diesel cars further, from 180mg/km to 80mg/km. Directive 1999/94/EC of the European Parliament and of the Council of 13 December 1999 relating to the availability of consumer information on fuel economy and CO2 emissions in respect of the marketing of new passenger cars. Amended by: Commission Directive 2003/73/EC of 24 July 2003, Regulation (EC) No 1882/2003 of the European Parliament and of the Council of 29 September 2003, Regulation (EC) No 1137/2008 of the European Parliament and of the Council of 22 October 2008. European Parliament and Council Directive 94/63/EC of 20 December 1994 on the control of organic compound (VOC) emissions resulting from the storage of petrol and its distribution from terminals to service stations Council Directive 72/306/EEC of 2 August 1972 on the approximation of the laws of the Member States relating to the measures to be taken against the emission of pollutants from diesel engines for use in vehicles.

Diesel – fuel is one of the main products of oil refining**.(** Shah, R,, J, and al, 2003**)** It is distilled between 170 and 360°C, and serves for diesel motor drive.(Willey, N, 2007) Quality of fuel is determined by cetane number (quality of lighting). It mustn’t be too big because it causes incomplete combustion and appearance of smoke in combustion gases. Its minimum is between 25 and 45 depending on the type of diesel fuel. In Japan, cars with diesel engines are forbidden.(Wellington, B.F, and al, 1995). High levels of sulfur in diesel are harmful for the environment because they prevent the use of catalytic diesel particulate filters to control diesel particulate emissions, as well as more advanced technologies, such as nitrogen oxide (NO_x) adsorbers (still under development), to reduce emissions.(U.S. Energy Information)

Table 1: The level of sulphur in diesel

Emission standard	**at latest**	**Sulphur content**	**Cetane number**
Euro 1	1. January 1993	max. 2000 ppm	min. 49
Euro 2	1. January 1996	max. 500 ppm	min. 49
Euro 3	1. January 2001	max. 350 ppm	min. 51
Euro 4	1. January 2006	max. 50 ppm	min. 51
Euro 5	1. January 2009	max. 10 ppm	min. 51

In the past, diesel fuel contained higher quantities of sulfur. European emission standards and preferential taxation have forced oil refineries to dramatically reduce the level of sulfur in diesel fuels. In th European Union the sulphur content has dramatically reduced during the last 20 years. Automotive diesel fuel is covered in the European Union by standard EN 590 In the 90's specifications allowed a content of 2000ppm max of sulphur, reduced to a limit of 350pmm by the beginning of the 21st century with the introduction of Euro3 specifications. The limit was lowered with the introduction of Euro 4 by 2006 to 50ppm (ULSD, Ultra Low Sulphur Diesel). The standard currently in force in European Europe for Diesel Fuel is the Euro 5, with a maximum content of 10 ppm. (Tab.1).

Led by Serbia, 15 countries rose in Hart Energy Research & Consulting’s 2013 ranking of countries based on commitment to lower sulfur content in diesel fuel. Serbia’s national specifications required all diesel distributed in the country to be “free” of sulfur (defined as less than 10 parts per million) as of August 2013. The country joins 47 other countries that have adopted sulfur-free diesel as a national policy. (International Fuel Quality Center (IFQC), 2013)

IMPLEMENTATION OF EUROPEAN LEGISLATION ON FUEL QUALITY IN REPUBLIC OF SERBIA

In the Republic of Serbia, there is an ongoing process of harmonization with the European Union regulations. Laws like that regulate quality standards such as of fuel quality as well. In Republic of Serbia the quality of liquid fuels of oil origin is regulated by Rules on Technical and Other Requirements for Liquid Fuels of Oil Origin (hereinafter: Rules). Based on of the Law on Technical Requirements for Products and Conformity Assessment (Art.6 (1)) Minister of Energy, Development and Environmental Protection Republic of Serbia (MEDEP) passed the Rules which was not harmonized with the Directive 1882/2003 and Directives 2005/35EU, 2003/17EU. By Rules technical and other requirements are regulated related to liquid fuels of oil origin which are used as fuels for internal combustion engines and as energy fuels on the market of Republic of Serbia (hereinafter: liquid fuels), as well as the way of evaluation of liquid fuels conformity assessment. (Art.1.) Liquid fuels according to these Rules are: unleaded petrol, aviation petrol, jet fuel, gas oil and fuel oil. (Art. 2.) Unleaded petrol, according to the Rules, are all evaporative fuels of oil origin made for internal combustion engines with force ignition which are used for motor vehicles and they are: EURO BMB 98; EURO PREMIUM BMB 95 and PREMIUM BMB 95. (Art. 3) By the Law on Ratification of the Treaty of establishing the Energy Community EU and Albania, Bulgaria, Bosnia and Herzegovina, Croatia, FYR of Macedonia, Montenegro, Romania, Serbia and Temporary Mission of UN at Kosovo in accordance to Resolution 1244 of Security Council of UN it is prescribed obligation of Republic of Serbia to implement Directive of the Council 1999/32 /EC from 26th April 1999 which is related to reduction of sulfur content in some liquid fuels.

Considering technical and other requirements unleaded petrol EURO BMB 98 must satisfy all requirements of the standard SRPS EN 228, except for research octane number Ron which must be at least 98.0 and motor octane number MON which must be at least 88.0.

Unleaded motor petrol EURO PREMIUM BMB 95 must satisfy all requirements of the standard SRPS EN 228. Unleaded motor petrol PREMIUM BMB 95 is not coloured and must satisfy all requirements of the standard SRPS EN 228, except for density, lead content, sulphur, benzene, flavor, olefin and motor number. Limit values for density, lead content, sulphur, flavor and olefin for unleaded motor petrol 95 are:

Table 2: Limit values for density, lead, sulphur, benzene, aromates and olefin content for unleaded motor petrol EURO PREMIUM BMB 95

Characteristic	**Unit**	**Limit**	**Deadline**
Density (15□ C), highest	kg/m^3	780	Until 31.july 2013
Pb content	mg/l	13	Until 31July 2013
S content	mg/kg	650	Until 31July 2013
Benzene content	% (V/V)	5,0	Until 31 July 2013
Aromates content	% (V/V)	55	Until 31 July 2013
Olefines content	% (V/V)	22,0	Until 31 July 2013
Octane number,		83,0	Until 31 July 2013

In European countries an ammount of sulphur is reduced in diesel fuels according to European norms EN 590. Therefore, the level of sulphur has been 10mg/kg since 2009. Reduction of sulphur in liquid fuels is the simpliest way for reducing emmission of pollutants from mobile ones although it is not enough. When agricultural machines are in question pollution control is mainly performed by reduction of sulphur quantity in fuels. European Directives, among the others, direct EU members to secure certain quantity of fuel with lower sulphur content for agricultural machines on their territories in definite time. Based on the analysis of directives and norms of EU, norms in Serbian legislation, regulations, laws and other legal regulations on liquid fuels and also manuals of agricultural machines producers criteria for selection of necessary fuel quality on the market for definite fuel type are set. It is significant to include these regulations in our legislation correctly especially in the sector of agriculture and its influence on the enviroment taking into consideration negotiations of Serbia related to entering EU.

By the Rules it is stipulated that beside derivates of European quality it is possible to put on the market of Republic of Serbia, until 31st July 2013, liquid fuels whose characteristics are not fully harmonized with European standards. They are: unleaded motor premium bmb 95; diesel fuel d2; diesel fuel d2s; diesel fuel d1e and gas oil extra light el. Taking into account that participants on liquid fuels market have these derivates in their storage capacities they are allowed to spend energy stocks un till the mentioned term. According to the Rules, oil derivates which are not harmonized with European quality should be retreated from the market in July 2013. According to data from MEDEP of Republic of Serbia consumption in 2012 shows that total consumption of motor petrol in Serbia was about 422.000 tons, out of which about 83% (351.000 tons) was consumption of PREMIUM BMB 95P, and 17% (71.000 tons) of EURO PREMIUM BMB 95. Estimation of diesel fuel consumption is about 1.393.000 tons out of which about 31% (433.000 tons) is consumption of diesel fuel D2 and 69% (960.000 tons) consumption of Euro diesel.

Gas oil, according to the Rules, are all liquid fuels of oil origin in which less than 65% of volume (including loss) is distilled at 250o C and at least 85% of volume (including loss) is distilled at 350^{o}C according to SRPS EN ISO 3405. They are: EURO DIESEL, diesel fuel GAS OIL 0,1, diesel fuel D2, diesel fuel D2S, diesel fuel D1E, GAS OIL EXTRA LIGHT EURO EL and GAS OIL EXTRA LIGHT EL.(Art.6(1)(2) Ruels. It is also stipulated by the Rules that until 31st December 2015 it is possible to put on the market fuel oil medium s and fuel oil heavy t whose characteristics are not in accordance to requirements of Directive 1999/32, taking into account that for reduction of sulfur content in these derivates is necessary additional investment in refinery plants. Legislator predicted this because it was considered that if Oil industry „NIS” ad was prevented from placing these heating oils on the market it could cause full stoppage of production of all other derivates necessary for supplying consumers in Serbia. Beside obligation to implement Directive 1999/32 in Serbian law it is also recognized a need to enable military vehicles, tractors and work machines to be supplied with liquid fuel other than Euro diesel. For this reason it is stipulated by the Rules that GAS OIL 0,1 should be used for tractors, work machines, military vehicles (in accordance to the regulation for traffic safety on roads) and trains and boats with diesel drive from 1st August 2013 on the territory of Serbia. (Art.6(4)) Maximum ammount of sulfur of 1000 mg/kg in this derivate of oil is ten times smaller in comparison to diesel fuel D2, D2S and D1E and it is complitely in harmony with requirements of EU Directive which this field is regulated by. By the Rule is also recognized the need for placing supplemented fuels and sales people are given a chance to label these products clearly by commercial names. Since diesel fuel D2 is mostly used in agriculture, economy and for military purposes, the Rules stippulates introduction of new derivate – diesel GAS OIL 0.1 which has lower quotation price. By introduction of this derivate a lower, cheaper price of diesel is kept. All in all, the market will determine the need and price for this product.

In the Serbian market, for domestic products, manufacturer issues Declaration of product conformity with the requirements. (Art.21). Declaration is issued on the basis of the report on investigation which is carried out by the body for conformity evaluation named by Minister for Energy according to the law which determines technical requirements for products and evaluation of conformity as well as according to specific regulations issued on this law which determines the way of appointing the body for conformity evaluation. A producer has an accredited body for investigation and, in this case, the report can be made by accredited body instead of the appointed body.

The procedure of evaluation is carried out by the appoined body and a Confirmation is issued on the basis of the report which is conformed with the Rules.

According to the Rules and in order to be appointed the body for investigation conformity should fulfill the following conditions:

1. Conformity assessment body, its executive or the members of executive board as well as other employed or engaged entities (hereinafter: entities) responsible for performance of conformity assessment according to the Rules cannot be representatives of producers or those dealing with liquid fuels trading which does not exclude exchange of technical information;
2. Conformity assessment body as well as its entities are obliged to perform evaluation of conformity with the highest degree of professional integrity and technical ability and they must not be exposed to any kind of pressure or be in conflict of interest, especially financial that could influence their evaluation or the results of investigation primarily by entities or a group of entities interested in the results of conformity evaluation;
3. Conformity assessment body must have at disposal entities with technical knowledge as well as with appropriate experience for performing evaluation;
4. Conformity assessment body must possess appropriate equipment for evaluation depending on the requirements prescribed by Serbian standards from the Articles 8-19 of the Rules;
5. Entities performing conformity evaluation of liquid fuels must be objective and their fee cannot depend on the number of investigations performed or on their results;
6. Conformity assessment body must have an appropriate general document prescribing the procedure for performing conformity evaluation including decision on complaints related to the work of the body and its decisions;
7. Conformity assessment body must sign a contract of insurance against liability for damage;
8. Entities of conformity assessment body are obliged to keep as business secret all information obtained at performing evaluation conformity according to their general act on business secret, the Rules and other regulations.

Taking samples of liquid fuel is performed according to requirements of the standards SRPS EN ISO 3170 and SRPS EN ISO 3171. (Art..24) Taking samples of liquid fuel for the needs of making a report on investigation and issuing a Declaration or Confirmation is performed from the reservoir of oil and oil derivate warehouse.(Art.25)

Declaration or Confirmation includes:

1. Business name or the name and address of a producer or importer;
2. Name of the product;
3. Amount, number and date of individual delivery note or Customs declaration for liquid fuels, imported and put on the market of Republic of Serbia;

4. The name of the country in which a product is produced;
5. Number and date of the report on investigation and information about accredited body which issued it;
6. Name of technical regulation by which a confirmation assessment of the product is evaluated, including the number of Official Gazette of Republic of Serbia in which the regulation is published;
7. Information on the applied standards which the Rules refers to and related to the statement on conformity assessment;
8. Identification and signature of an entity in charge responsible for issuing a Declaration or a Confirmation in the name of a producer or the named body for conformity evaluation;
9. Place and date of issuing a Declaration or a Confirmation.

Obligatory supplement to Declaration or a Confirmation from the Rules is a Report on investigation. A producer or a named body for confirmation assessment evaluation are obliged to keep this Declaration or Confirmation as well as the Report at least for two years from the day of issuing. (Art.26)

Liquid fuels must be accompanied by the following when putting into traffic on Serbian market: Delivery note; Declaration or Confirmation; Report on investigation; Statement of energy entity who trades with motor or other fuels at stations for vehicles supply (only for additive fuels), other acts according to specific regulations. (Art.27)

Liquid fuels of Euro 5 quality has been produced in Serbia since 2013. NIS in Pančevo has completely converted its production of liquid fuels that meet the Euro 5 Standard requirements. After the commissioning of the new complex, annual fuel production volume by Euro 5 Standard will be increased to 638,000 tones and diesel to 1,000,538 tones. Significant increase of quality and environmental characteristics of produced liquid fuel will affect the environment. Further conciliation of regulations of the Republic of Serbia, in this area, with EU regulations implies, according to the National Programme for Integration with the European Union (NPI): The adoption of technical regulation which would transfer the Directive 1999/32 on restriction of sulphur in certain liquid fuels and amendment to the Directive 93/12/EEU and Directive 2003/17/EU – amendment to the Directive relating to the quality of the gasoline and diesel fuel. (Todic, D, 2010)

CONCLUSION

European Directive on the quality of liquid fuels provides for certain restrictions in order to protect the environment. In the Republic of Serbia, there is an ongoing process of harmonization with the European Union regulations. In Republic of Serbia, liquid fuels Euro 5 quality has been produced since 2013. By the Rules it is stipulated that beside derivates of European quality it is possible to put on the market of Republic of Serbia, until 31st July 2013, liquid fuels whose characteristics are not fully harmonized with European standards. According to the Rules, oil derivates which are not harmonized with European quality should be retreated from the market in July 2013. It is also stipulated by the Rules that until 31st December 2015 it is possible to put on the market fuel oil medium and fuel oil heavy whose characteristics are not in accordance to requirements of Directive 1999/32, taking into account that for reduction of sulfur content in these derivates is necessary additional investment in refinery plants. Beside obligation to implement Directive 1999/32 in Serbian law it is also recognized a need to enable military vehicles, tractors and work machines to be supplied with liquid fuel other than Euro diesel. For this reason it is stipulated by the Rules that GAS OIL 0,1 should be used for tractors, work machines, military vehicles and trains and boats with diesel drive from 1st August 2013 on the territory of Serbia. Significantly increase the quality and characteristics produced liquid fuel will influence the environment.

REFERENCES

Council Directive 1999/32/EC of 26 April 1999 relating to a reduction in the sulphur content of certain liquid fuels and amending Directive 93/12/EEC (OJ L 121, 11.5.1999, p. 13.) Amended by: Regulation (EC) No 1882/2003 (Official Journal 2003L 284 1 31.10.2003), Directive 2005/33/EC (Journal L 191 59 22.7.2005), Regulation (EC) No 219/2009 (Official Journal, 2009L 87 109 31.3.2009), Directive 2009/30/EC.

Commission Directive 2005/78/EC of 14 November 2005 implementing Directive 2005/55/EC of the European Parliament and of the Council on the approximation of the laws of the Member States relating to the measures to be taken against the emission of gaseous and particulate pollutants from compression-ignition engines for use in vehicles, and the emission of gaseous pollutants from positive ignition engines fuelled with natural gas or liquefied petroleum gas for use in vehicles and amending Annexes I, II, III, IV and VI thereto, (OJ L 313, 29.11.2005, pp. 1-93)

Council Directive 72/306/EEC of 2 August 1972 on the approximation of the laws of the Member States relating to the measures to be taken against the emission of pollutants from diesel engines for use in vehicles (OJ L 190, 20.8.1972, p. 1–23).

Directive on Cleaner Air for Europe (2008/50/EC) (CAFÉ) (OJ 32008L0050) 21.05.2008.

Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 concerning integrated pollution prevention and control (Codified version).

Directive 96/61/EEC on Integrated Pollution Prevention and Control (IPPC).

Directive 97/101/EC: Council Decision of 27 January 1997 establishing a reciprocal exchange of information and data from networks and individual stations measuring ambient air pollution, *Official Journal L 035, 05/02/1997 P. 0014 – 0022.*

Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EEC (OJ L 350, 28.12.1998, p. 58–68) .

Directive 97/68/EC of the European Parliament and of the Council of 16 December 1997 on the approximate on of the laws of the Member States relating to measures against the emission of gaseous and particulate pollutants from internal combustion engines to be installed in non-road mobile machinery (OJ L 59, 27.2.1998, p. 1–86).

Directive 2005/55/EC of the European Parliament and of the Council of 28 September 2005 on the approximation of the laws of the Member States relating to the measures to be taken against the emission of gaseous and particulate pollutants from compression-ignition engines for use in vehicles, and the emission of gaseous pollutants from positive-ignition engines fuelled with natural gas or liquefied petroleum gas for use in vehicles (OJ L 275, 20.10.2005, pp. 1–163).

Directive 1999/94/EC of the European Parliament and of the Council of 13 December 1999 relating to the availability of consumer information on fuel economy and CO2 emissions in respect of the marketing of new passenger cars (OJ L 12, 18.1.2000, p. 16–23) Amended by: Official Journal, Directive 2003/73/EC of 24 July 2003 L 186, Regulation (EC) No 1882/2003 of the European Parliament and of the Council of 29 September 2003L 284, Regulation (EC) No 1137/2008 of the European Parliament and of the Council of 22 October 2008.

European Parliament and Council Directive 94/63/EC of 20 December 1994 (OJ L 365, 31.12.1994, p. 24–33).

Law on Technical Requirements for Products and Evaluation of Harmonization ("Official Journal R. of Serbia", No. 36/09).

Law on Ratification of Treaty Establishing the Energy Community between EU and Albania, Bulgaria, Bosnia and Herzegovina, Croatia, FYR of Macedonia, Montenegro, Romania, Serbia and Temporary mission of UN at Kosovo in accordance to Resolution 1244 of Security Council of UN („Official Journal R. of Serbia ", No 62/06).

Regulation (EC) No 715/2007 of the European Parliament and of the Council of 20 June 2007 on type approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information. (OJ L 171 of 29.6.2007, p.1-16).

Rules on Technical and Other Requirements for Liquid Fuels of Oil Origin ("Official Journal R. of Serbia", No. 123, 28th December 2012).

Shah, J, R, Totten,G.O,, Westbrook, S.R. (2003). *Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing*. West Conshohocken, Penn: ASTM International .

Todic, D, (2010). *Guidebook Through EU policy - Environment, European Movement of Serbia,* Belgrade, p. 185.National Programme for Integration with the European Union, p.577-580.

Willey, N, (2007). *Phytoremediation: Methods and Reviews (Methods in Biotechnology*), Totowa, NJ: Humana Press.

Wellington, B.F, Asmus, A, F (1995). *Diesel Engines and Fuel Systems*, Longman Australia.

International Fuel Quality Center (IFQC) http://www.ifqc.org/NM_Top5.aspx, accessed November 2013.

NIS Gazprom Neft http://www.nis.eu/, accessed November 2013.

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EVALUATION OF ROAD VEHICLES EMISSION BY APPLYING THE ADMS ROAD SOFTWARE – THE CASE OF AN INTERSECTION IN THE URBAN AREA OF THE CITY OF BELGRADE

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ABSTRACT

Key trends in sustainable transport show us that the energy consumption in transport per BDP unit at EU-27 in 2011 declined for 8.3%, compared to 2000. Generally, in the observed period, the energy spent in transport was increased for 6.7%, while the economic growth was faster with 16.5%. This trend was slightly increased at the beginning of the economic crisis, as well as the ecological components which followed the transport development, which indicates that there weren't any significant changes of transport and mobility which may exist among countries because of the methodological reasons. Although the objectives of the EU move towards reducing the existing emissions for 20% up to 2020 and 95% up to 2050, at the demand of Germany, the EU postponed the adoption of regulations in October 2013, which doesn't diminish the importance of need for pollutants' emission reduction in public transport. In this paper, the emission evaluation at the wider range of the intersection with four traffic flows flowing into it was performed, by using the EMEP/EEA methodology and the latest ADMS ROAD software. The aim is to point out the emission quantity by pollutants, their spreading and the locations of their greatest concentration.

Key words: *road transport, emissions and emission factors, ADMS Road.*

INTRODUCTION

Emissions in public transport are created by combustion of fuels such as petrol, diesel, liquid petrol gas (LPG) and natural gas in internal combustion engines. According to [6], the suggested emission methodology from road transport (NFR sector 1.A.3.b) is used in most European countries in which the vehicles are coded and classified:
- 1.A.3.b.i Road transport : cars (PA on LPG, diesel and petrol);
- 1.A.3.b.ii Road transport: light goods vehicles (lorries) (LGV on diesel and petrol);

1.A.3.b.iii Road transport: heavy goods vehicles and buses (BUS, diesel);
- 1.A.3.b.iv Road transport: motor driven cycles and motors (MOT, petrol).

The emission distribution differentiates road activities by types of streets: highways, rural and urban roads. For the mission assesment an urban area , through which heavy goods vehicles, except buses, do not transit,was chosen. The analysis includes cars from the M1 subcategory (petrol and diesel, 1.4-2.0 cm^3), LGV N1(< 3,5 t), BUS from M2 (City conventional) and motorcycles from L3 category (50-250 cm^3). With all the vehicles, the EURO III engines (2000-2005) were analyzed, according to the 98/69/EC Directive (Step 1, 2000). According to the detail level of the available data ,the pollutants from group 1 (CO, NO_x i N_2O, PM 2,5-10-TSM (common powdery substances), NH_3, ammonia, NMVOC nonmethanic vaporable organic compounds – given as an equivalent to $THC-CH_4$ and their standard emission factors were chosen. Correction factors (traffic physical and exploatational, engine operation factors and others) were not taken into account.

Data input , according to ADMS ROAD requests, consisted of a several steps. The emission for each street was estimated by the TIER 2 method, with the street net characteristics being used, also the traffic intensity and the standard emission factors of each source of pollution. By space mapping of emissions, their spread at the observed locations was shown.

FLOW ANALYSIS AND THE ELEMENTS NEEDED FOR MISSION EVALUATION

For this analysis, an intersection with four approaches flowing into it was chosen, with a very significant traffic intensity, and of following characteristics: Kneza Višeslava 437 m, Pilota Mihaila Petrovica 1 - 270 m and the other part of Pilota Mihaila Petrovica 2 - 327 m, Patrijarha Joakima 217 m, figure 1. Kneza Višeslava Street starts from Požeška Street, goes across Košutnjak to a busy intersection where it ends, linking Vidikovac to Košutnjak, Banovo Brdo, and across Banovo Brdo, with central city zones. It is a two-way street, with one lane in each direction, except in the intersection zone, where there are two merging lanes, one for left turns, one for straight and right directions, and one for diverging. The city transit vehicles use this street – bus lines 23, 53 and E5 and partially 37, 50, 89 and E5 lines, while movement is forbidden for goods vehicles weighing over 3,5t.

Figure 1. Street position in macro and meso environment

Pilota Mihaila Petrovica Street links The Ibar Highway to Rakovica settlement, spreading from West to East. It is a two-way street with one lane in each direction, except in the intersection zone, where there are two merging lanes, one of which is combined, ie intended for movement of vehicles which keep going straight or turn right , and one for diverging. From the intersection in question, viewed eastward, the city transit vehicles for passengers' transport use this street (bus lanes 37, 50, 59 and E5).

Patrijarha Joanikija Street starts from the actual intersection and goes on to Petlovo Brdo. It is a two-way street, too, with one lane in each direction, except in the intersection zone, where there are two merging and one diverging lane. The city transit vehicles use this street (bus lines 23, 53 and E5) while movement is forbidden for goods vehicles weighing over 3,5t. All the streets creating this intersection are the II order streets.

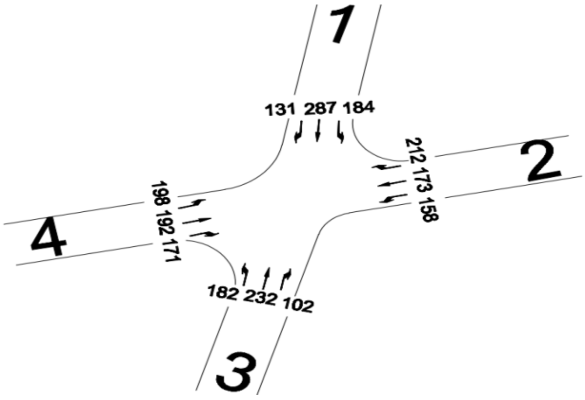


Figure 2. Traffic figure at micro level by accesses

At the intersection, the crossing of streets is in the level and the streets create an inclined, direct, four-way intersection, figure 2. This intersection has a non-restricted (all directions are allowed), but a reduced software, because all the directions don't have their own lane.

According to the way of regulating and managing the traffic, the intersection contains the regular state measures. At this intersection, traffic is regulated by traffic signals followed by appropriate elements of horizontal and vertical signalization. In the immediate surroundings of the intersection, there are also city transit bus stops. The flows were studied by directions and by vehicle categories, table 1. The study period during a working day included the sixty-minute drives which were realized at the peak hours of traffic load and the complete vehicle distribution was based on that, table 1. The research was narrowed to data collecting for the streets with no longitudinal grade and maximum speed limit of 50 km/h and an uninterrupted traffic flow with minimal obstructions. Measuring was performed in the conditions of moderate drive without sudden speeding or slowing down, which is very often a case in traffic.

Table 1: Traffic flows structure by moving directions

Street name	Direction	PA	LTV	BUS	MOT
Pilota Mihaila Petrovica 2	12+21	246	51	28	12
	23+32	293	46	17	6
	24+42	362	55	0	10
∑	1126	901	152	45	28
Pilota Mihaila Petrovica 1	14+41	214	37	0	7
	24+42	352	55	0	10
	34+43	153	34	1	4
∑	867	719	126	1	21
Patrijarha Joakima	34+43	153	34	1	4
	23+32	293	46	17	6
	13+31	348	48	47	10
∑	1007	794	128	65	20
Kneza Viseslava	14+41	214	37	0	7
	13+31	348	48	47	10
	12+21	246	51	28	12
∑	1048	808	136	75	29

Collecting complete sets of data for emission evaluation from every source is a serious methodological problem since some sources aren't determined and it's hard to measure the emissions in continuity and with high precision. Besides, it is not simple to connect the emission values with corresponding conditions in the traffic flow. In some researches, the emission evaluation for one pollutant was used for getting the pondered evaluation of some other pollutant emission. For example, the PM10 emissions from certain processes can be estimated on the basis of the allocational VOC emission processes. In some cases, the known relations of PM10/PM2.5 can be used for the evaluation of PM10 and PM2.5 emissions for similar processes in other areas. In the complete emission, road transport about 16% PM, 42% NOx, 29% CO, HC 16%, etc. in Europe (EEA 2012).

Table 2: Basic vehicle distribution by streets and types of drives

Vehicle distribution		**MOT petrol**	**PA**		**LTV**		**BUS diesel**
Street	Total of veh.		diesel	petrol	diesel	petrol	
Mihajla P. 2.	1126	23	338	563	34	113	56
Mihajla P. 1.	867	17	260	434	26	87	43
Patrijarha J.	1007	20	302	504	30	101	50
Kneza V.	1048	21	314	524	31	105	52
TOTAL	4048	81	1214	2025	121	406	171

According to [9], there are methods for emission evaluation based on the level of details. The „Tier 1“method is the first level which only uses the appropriate emission factors. The „Tier 2“ method is more complex than the previous one , it uses more specific emission factors developed on knowing the kinds of processes and specific process conditions. It also reduces the uncertainty level of the evaluation and is considered as adequate for the emission evaluation. The „Tier 3“ method is considered to be the method which uses the latest scientific findings with more sofisticated approaches and models. By applying „Tier 2“, the emissions' results by streets were evaluated just on the basis of emissions during the active drive (engine running), assuming that the exhaustion gases emissions during the cold engine start or the idling are independent of the driver's conduct, tables 3 to 6. When we evaluate a mission, variability is also important, ie, the uncertainties of the evaluation. When we compare the model values to the real values of emissions used for validation, the model accuracy should be taken into account. It is also important to consider the required emission evaluation quality.

Table 3: Emission in Pilota Mihajla Petrovića Street, approach 2

Street Pollutant	**Pilota Mihajla Petrovića, approach 2.**						**Σ g/h**	**Σ g/s**
	MOT	PA		LTV		BUS		
	Petrol	Petrol	Diesel	Petrol	Diesel	Diesel		
CO	22,78863	335,0638	9,836814	186,60255	5,258814	48,89304	608,444	0.169012
NO_x	1,459074	17,8578	85,10502	4,766679	11,45154	171,58344	292,224	0.081173
N_2O	0,015042	0,368202	1,10526	1,034628	0,100062	0,018312	2,64151	0.073375
PM2,5-10-TSM	0,0263235	0,202511	4,3215666	0,0406461	0,8705394	3,790584	9,25217	0.257005
NH_3	0,0142899	6,296254	4,3215666	1,1159202	0,0133416	0,0531048	11,8145	0.032818
NMVOC	3,497265	21,90802	2,21052	6,983739	1,045092	7,489608	43,1342	0.119817

Table 4: Emission in Pilota Mihajla Petrovića Street, approach 1

Street Pollutant	**Pilota Mihajla Petrovića, approach 1.**						*Σ* **g/h**	**Σ g/s**
	MOT	PA		LTV		BUS		
	Petrol	Petrol	Diesel	Petrol	Diesel	Diesel		
CO	13,9077	213,2676	6,2478	118,6245	3,32046	30,9987	386,367	0.107324
NO_x	0,89046	11,36646	54,054	3,03021	7,2306	108,7857	185,357	0.051488
N_2O	0,00918	0,23436	0,702	0,65772	0,06318	0,01161	1,67805	0.046613
PM2,5-10-TSM	0,016065	0,128898	2,74482	0,025839	0,549666	2,40327	5,86856	0.163016
NH_3	0,008721	4,007556	2,74482	0,709398	0,008424	0,033669	7,51259	0.208683
NMVOC	2,13435	13,94442	1,404	4,43961	0,65988	4,74849	27,3308	0.075919

Table 5: Emission in Patrijarha Joakima Street

Street Pollutant	**Patrijarha Joakima**						**Σ g/h**	**Σ g/s**
	MOT	PA		LTV		BUS		
	Petrol	Petrol	Diesel	Petrol	Diesel	Diesel		
CO	13,1502	199,0498	5,832526	110,68085	3,07923	28,9695	360,762	0.100212
NO_x	0,84196	10,6087	50,46118	2,827293	6,7053	101,6645	173,109	0.048086
N_2O	0,00868	0,218736	0,65534	0,613676	0,05859	0,01085	1,56587	0.043496
PM2,5-10-TSM	0,01519	0,120305	2,5623794	0,0241087	0,509733	2,24595	5,47767	0.152158
NH_3	0,008246	3,740386	2,5623794	0,6618934	0,007812	0,031465	7,01218	0.194783
NMVOC	2,0181	13,01479	1,31068	4,142313	0,61194	4,43765	25,5355	0.070932

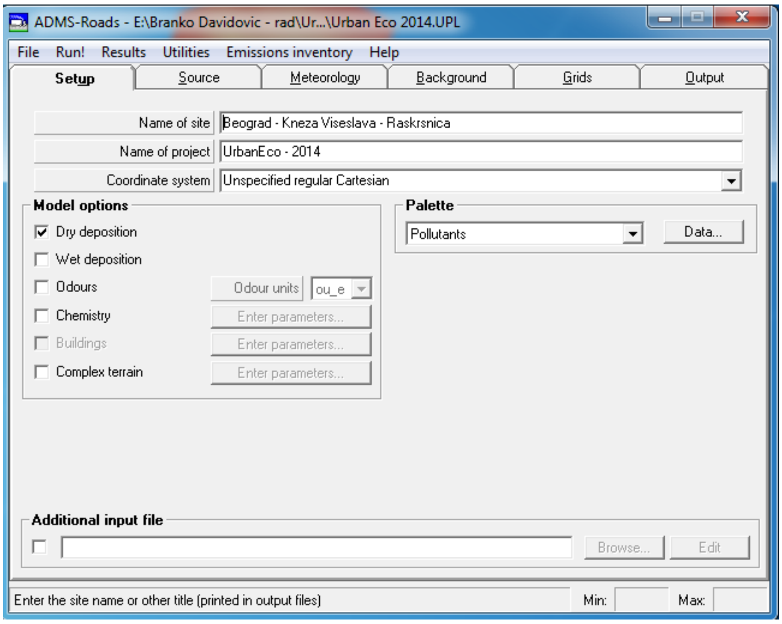
Table 6: Emission in Kneza Višeslava Street

Street Pollutant	**Kneza Višeslava**						**Σ g/h**	**Σ g/s**
	MOT	PA		LTV		BUS		
	Petrol	Petrol	Diesel	Petrol	Diesel	Diesel		
CO	27,80631	416,7582	12,2124	231,71	6,407731	60,67308	755,577	0.209883
NO_x	1,780338	22,2118	105,657	5,919	13,95341	212,9238	362,446	0.100679
N_2O	0,0184	0,4579	1,3721	1,284	0,121923	0,022724	3,27794	0.091054
PM2,5-10-TSM	0,03212	0,2518	5,36522	0,0504	1,0607301	4,70386	11,4643	0.031845
NH_3	0,0174363	7,831	5,36522	1,3857	0,0162564	0,06589	14,6819	0.040783
NMVOC	4,267305	27,249	2,744	8,6722	1,273418	9,2941	53,501	0.014861

Missions obtained point out that diesel engines emit less CO, VOC and NOx, but more particulate matter Maximum NOx emissions are realized with buses because of the greater engine power engagement. High values of CO, especially with diesel drives, indicate that the existing vehicles don'tv have catalyzers which remove CO i N0x from exhaust gases. Pollutants' emissions are greater for buses because they function in the move/stop regime.Even if the moving speed was steady, PA moved a bit faster which caused the greater CO values. Maximum emission appears with sudden and great accelerations.

ADMS ROAD AS TOOLS FOR STREET VEHICLES EMISSION SIMULATION

ADMS ROAD is a software used for numeric modelling of pollution spread from road traffic and industrial sources, with combining these two sources. ADMS ROAD enables the bringing in of many parameters , including over 7 000 roads and industrial sources through three items and 25 different parameters. This software was widely accepted, regarding the managing of the air quality and projecting and evaluating complex situations in cities, on highways and in industrial areas. The data about the project which is actual , ie the title of the research, are entered into the starting window of the software, and we chose the model to be used, figure 3.



ADMS-Roads - E:\Branko Davidovic - rad\Ur...\Urban Eco 2014.UPL

Name of site: Beograd - Kneza Viseslava - Raskrsnica

Name of project: UrbanEco - 2014

Coordinate system: Unspecified regular Cartesian

Model options

☑ Dry deposition

☐ Wet deposition

☐ Odours — Odour units: ou_e

☐ Chemistry

☐ Buildings

☐ Complex terrain

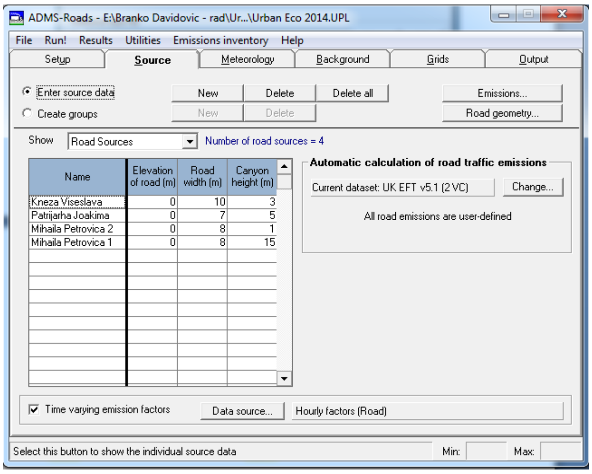
Palette: Pollutants

Additional input file: ☐

Enter the site name or other title (printed in output files)

Figure 3. Setup – start software

In most cases, it is the ``Dry deposition ``option . In the next window we enter the pollution sources, and in this case they are the streets from figure 2, their names and dimensions (street height and width). In this window we can also enter the dot plots, the industrial pollution if we have the data about their pollution emissions. Further on, the data about the streets’ characteristics, figure 4, and emissions, pollutions on the streets, the two- way flows were entered, figure 5.



● Enter source data
○ Create groups

Show: Road Sources — Number of road sources = 4

Name	Elevation of road (m)	Road width (m)	Canyon height (m)
Kneza Viseslava	0	10	3
Patrijarha Joakima	0	7	5
Mihaila Petrovica 2	0	8	1
Mihaila Petrovica 1	0	8	15

Automatic calculation of road traffic emissions

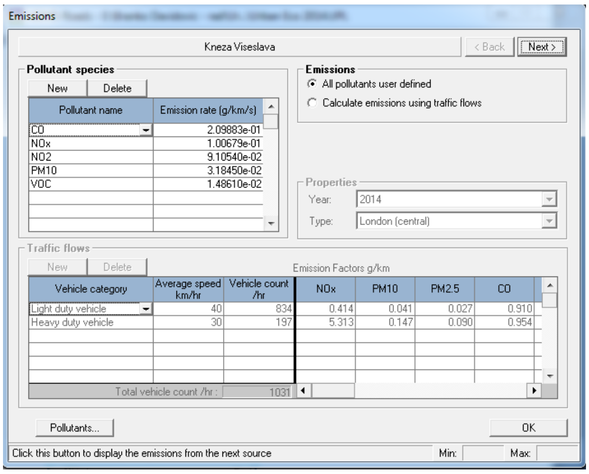
Current dataset: UK EFT v5.1 (2 VC)

All road emissions are user-defined

☑ Time varying emission factors — Hourly factors (Road)

Select this button to show the individual source data — Min: — Max:

Figure 4. Pollution sources – streets and their dimensions



Kneza Viseslava

Pollutant species

Pollutant name	Emission rate (g/km/s)
CO	2.09883e-01
NOx	1.00679e-01
NO2	9.10540e-02
PM10	3.18450e-02
VOC	1.48610e-02

Emissions

● All pollutants user defined
○ Calculate emissions using traffic flows

Properties — Year: 2014 — Type: London (central)

Traffic flows — Emission Factors g/km

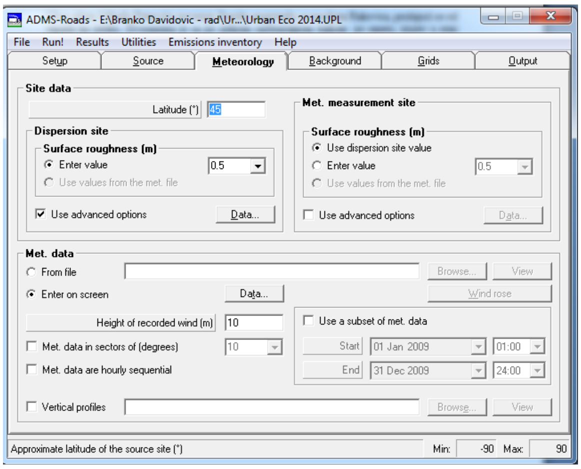
Vehicle category	Average speed km/hr	Vehicle count /hr	NOx	PM10	PM2.5	CO
Light duty vehicle	40	834	0.414	0.041	0.027	0.910
Heavy duty vehicle	30	197	5.313	0.147	0.090	0.954

Total vehicle count /hr : 1031

Click this button to display the emissions from the next source — Min: — Max:

Figure 5. Values of pollutants

The ADMS ROAD software has the possibility of automatically generating the emissions' value, depending on the type of vehicles (light or heavy), number of vehicles in the streets during an hour's period as well as on the average vehicle speed in the street. Here we meet a restriction regarding the division of vehicles only by size and type, to light and heavy ones , which is different from the valid classification. The possibility of entering the emissions' values and individual pollutants the values of which are calculated and shown in tables 3,4,5 and 6 was used.



Site data

Latitude (°): 45

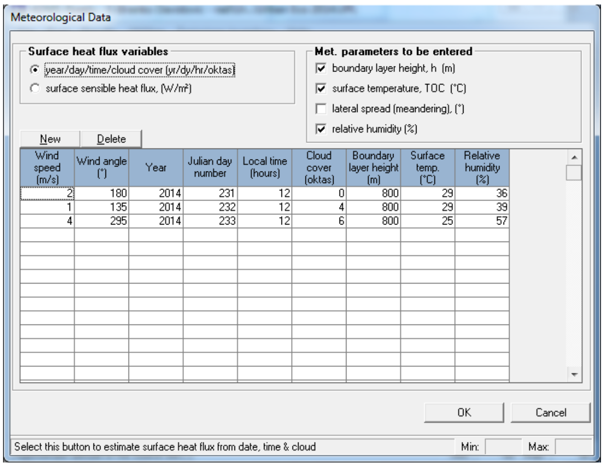
Dispersion site — Surface roughness (m):
● Enter value: 0.5
○ Use values from the met. file
☑ Use advanced options

Met. measurement site — Surface roughness (m):
● Use dispersion site value
○ Enter value: 0.5
○ Use values from the met. file
☐ Use advanced options

Met. data

○ From file
● Enter on screen
Height of recorded wind (m): 10
☐ Met. data in sectors of (degrees): 10
☐ Met. data are hourly sequential
☐ Use a subset of met. data — Start: 01 Jan 2009 01:00 — End: 31 Dec 2009 24:00
☐ Vertical profiles

Approximate latitude of the source site (°) — Min: -90 — Max: 90



Surface heat flux variables

● year/day/time/cloud cover (yr/dy/hr/oktas)
○ surface sensible heat flux, (W/m²)

Met. parameters to be entered

☑ boundary layer height, h (m)
☑ surface temperature, TOC (°C)
☐ lateral spread (meandering), (°)
☑ relative humidity (%)

Wind speed (m/s)	Wind angle (°)	Year	Julian day number	Local time (hours)	Cloud cover (oktas)	Boundary layer height (m)	Surface temp. (°C)	Relative humidity (%)
2	180	2014	231	12	0	800	29	36
1	135	2014	232	12	4	800	29	39
4	295	2014	233	12	6	800	25	57

Select this button to estimate surface heat flux from date, time & cloud — Min: — Max:

Figure 6. The window–meteorological data

Figure 7. The display of meteorological data

The next window is used for entering meteorological data, figure 6, and then the window in figure 7. In this paper, meteorological data for August 19, 20 and 21, 2014, were taken into account. The data were received from the Hydrometeorological Institute site, from its station at Košutnjak, very close to the streets which are the subject of research, table 7.

Table 7: Meteorological data in the research period

Date	Wind speed	Wind direction	Day of the year	Cloudiness	Temperature	Relative humidity
19.08.2014	2	180	231	0	29	36
20.08.2014	1	135	232	4	29	38
21.08.2014	4	295	233	6	25	57

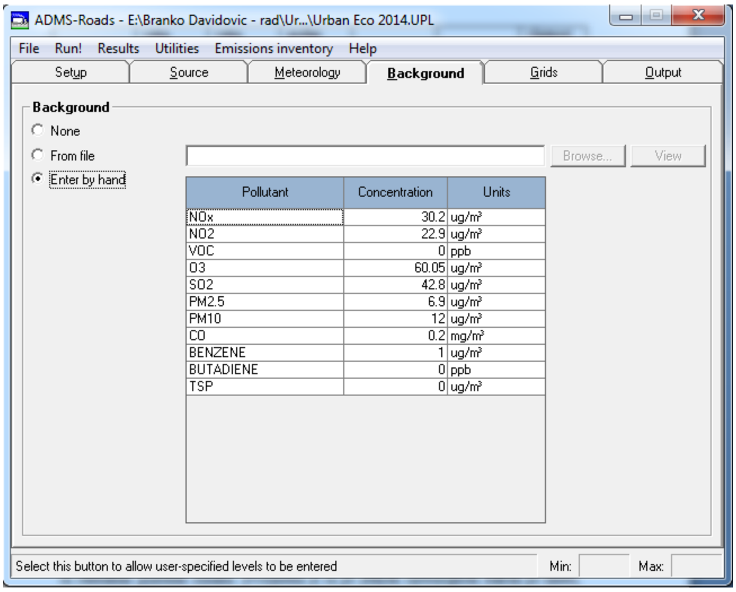
It is interesting that in the software we do not enter the full date, as in 21.08.2014, but the ordinal day of the year. In this case, August 19 is the 231st day of the year.

In the software there is a possibility of entering the initial state, the environment pollution. It is a very important element of research because it is logical that there already is a certain pollution in the environment and, if we have those data, we will also have the more credible and more accurate simulations. In some cases, these data are very hard to get, considering that there are parts of Serbia which are not covered by automatic stations for monitoring the air ambient quality. In the case when we don’t have the initial data, it is recommended that these data should be measured on the spot, if the laboratories performing the researches and creating the simulations have the appropriate equipment. In our case, considering that the urban part of Belgrade is being analyzed, the data from the automatic station of a state Agency for Environment Protection SEPA were used. The automatic station is located in Novi Beograd . the data about the air quality are given in Table 8.

Table 8. Values of air quality for August 18, 2014 – Automatic station - Novi Beograd

CO	NOx	NO2	O3	PM10	PM 2,5	Benzen
0.2 mg/m3	30,02 µg/m^3	22.9 µg/m3	60.05 µg/m^3	12 µg/m^3	6.9 µg/m^3	1 µg/m^3

The medium daily values of polluting components for the previous day, August 18,2014, are shown. Entering the data about the air quality was performed as shown in the window in figure 8.



Background

○ None

○ From file

● Enter by hand

Pollutant	Concentration	Units
NOx	30.2	ug/m³
NO2	22.9	ug/m³
VOC	0	ppb
O3	60.05	ug/m³
SO2	42.8	ug/m³
PM2.5	6.9	ug/m³
PM10	12	ug/m³
CO	0.2	mg/m³
BENZENE	1	ug/m³
BUTADIENE	0	ppb
TSP	0	ug/m³

Select this button to allow user-specified levels to be entered

Figure 8. Environment air quality data

SIMULATION AND ANALYSIS OF THE RESULTS OBTAINED

After the emissions' distribution evaluation, they were shown in several different spatial forms, including various dimensions (polygons, lines and dotted sources) and each of them was determined by the space characteristics of the original data. The aim of emissions' modelling is the development of emission maps and models which enable us to characterize the particular space emissions.

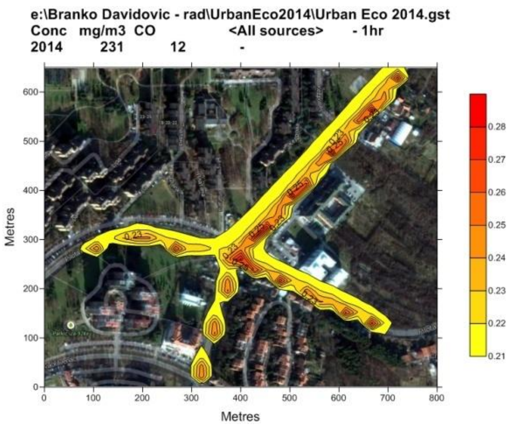


Figure 9. Value of CO for August 19, 2014

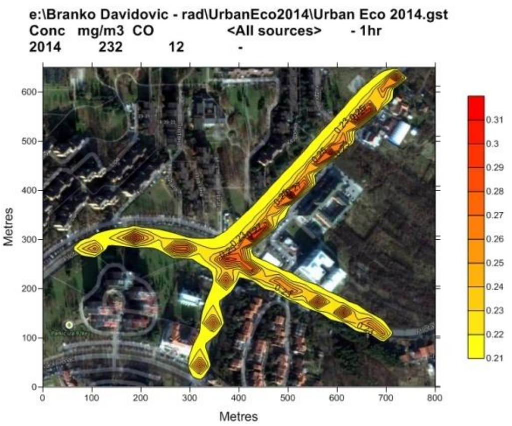


Figure 10. Value of CO for August 20, 2014

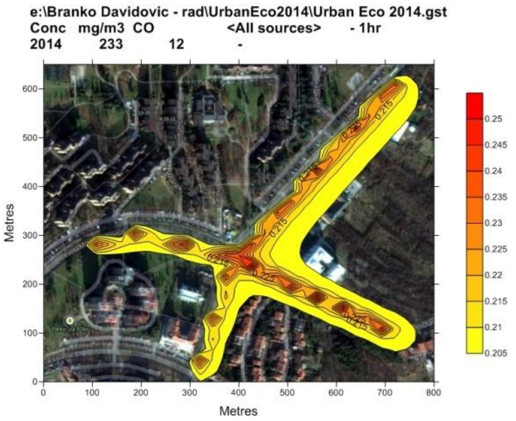


Figure 11. Value of CO for August 21, 2014

As you can see in figures 9, 10 and 11, the CO concentration for the area analyzed was from 0,2 mg/ m^3 - 0,31 mg/ m^3 . For the first day analyzed, August 19, the greatest concentration was recorded at the intersection itself and it was 0,28 mg/m^3 .On that day, the most burdened was the Kneza Višeslava Street, and that was conditioned by the terrain configuration and meteorological conditions (on that day the south wind was dominant, speed 2 m/s.). In the other streets, the concentration was from 0.20 - 0.23 mg/m^3. It's interesting to notice that the CO concentration , conditioned by a strong north-west wind, caused the smaller concentration of carbon-monoxide in the area analyzed, but that pollution spread to a wider area of residential units in Kneza Višeslava and Pilota Mihajla Petrovića streets.

The greatest CO concentration was predicted for August 20, when the wind speed was the - it was 1m/s and , for that day, the CO concentration was maximal 0.31 mg /m^3 at three spots in Kneza Višeslava Street, which can be seen in figure 10.

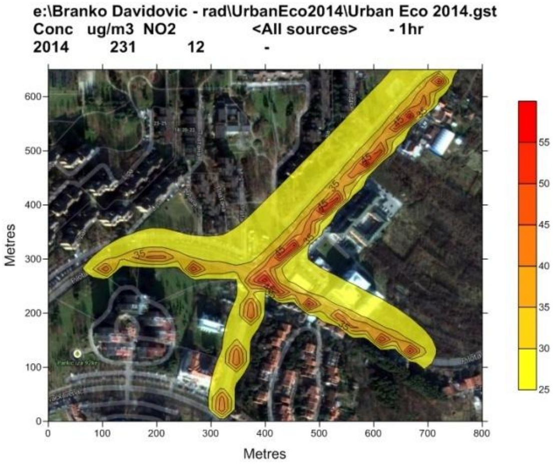


Figure 12. Value of NO_2 for August 19, 2014

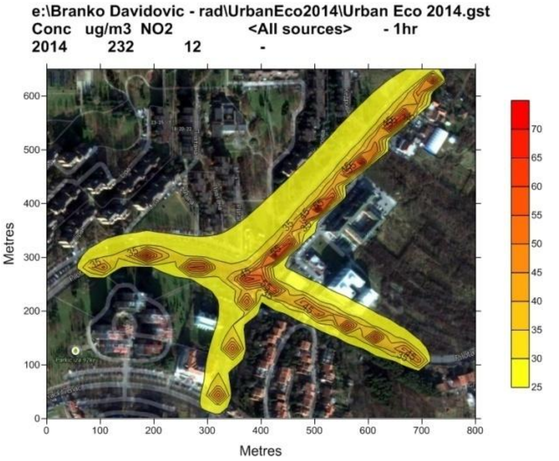


Figure 13. Value of NO_2 for August 20, 2014

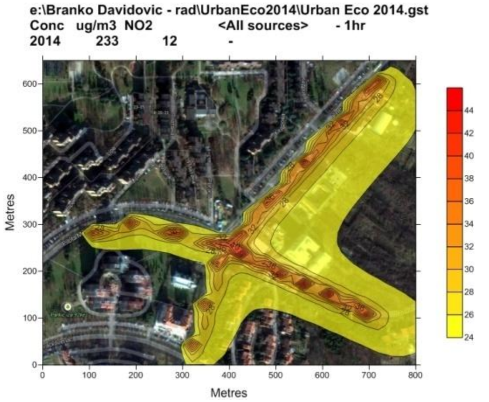


Figure 14. Value of NO_2 for August 21, 2014

The NO_2 concentrations for the analyzed streets were from 24 – 70 μg/m^3 . The greatest concentration of 70μg/m^3 was predicted for August 20, 2014, when meteorological conditions were such that the wind speed was 1m/s and the pollution stayed on the streets. As in the previous analyses, the most polluted was Kneza Višeslava Street, and the concentration in this street was from 55-65μg/m^3 , and in the middle of the analyzed street, the concentration reached its maximum of 70 μg/m^3.

In Pilota Mihajla Petrovica 2 and Patrijarha Joakinia streets , the NO_2 concentration was from 25-45 μg/m^3. The pollutant specificity caused broader pollution and pollution spread in Kneza Višeslava and Pilota Mihajla Petrovica streets, which can be seen in figures 12, 13 and 14. The greatest pollutant spread of NO_2 is shown in figure 14, when meteorological parameters were such that the wind speed was the highest for the analyzed period , 4m/s. For this day it is normal that the concentration of pollutants is somewhat smaller in all the streets, but the greatest concentration was recorded at the intersection.

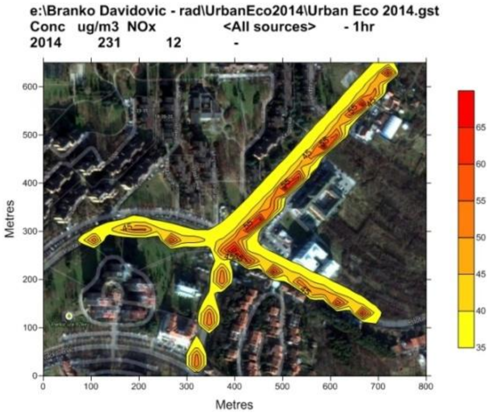


Figure 15. Value of NO_x for August 19, 2014

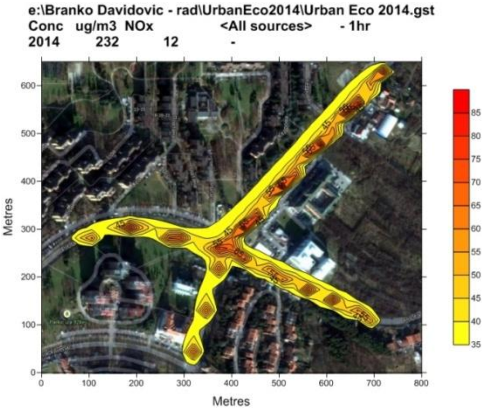


Figure 16. Value of NOx for August 20, 2014

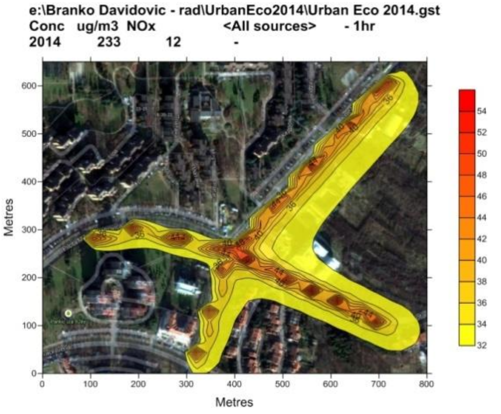


Figure 17. Value of NO_x for August 21, 2014

The concentration of NOx in the analyzed area was from 32-85 µg/m^3, depending on the day and the meteorological conditions predicted for that day. The highest concentration was predicted for August 20, when the wind speed is the lowest and the pollution level predicted for the streets' intersection and in Kneza Višeslava Street 85 µg/m^3 . In other streets, the NOx concentration was form 40-55µg/m^3.

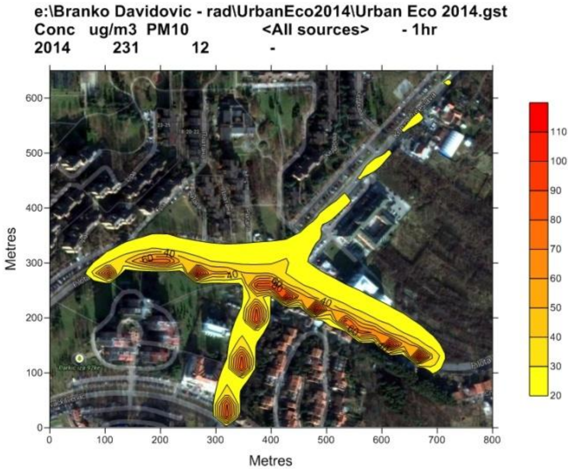


Figure 18. Value of PM10 for August 19, 2014

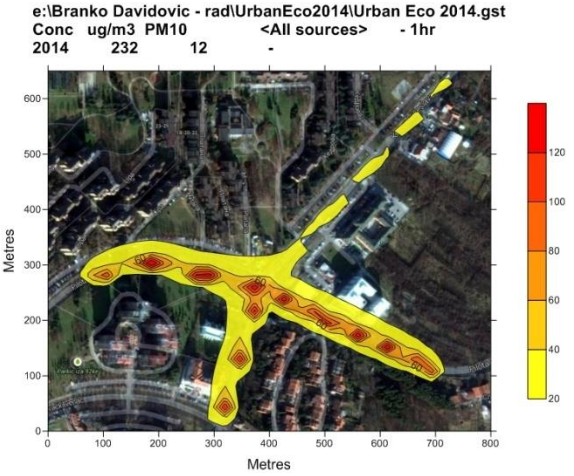


Figure 19. Value of PM10 for August 20, 2014

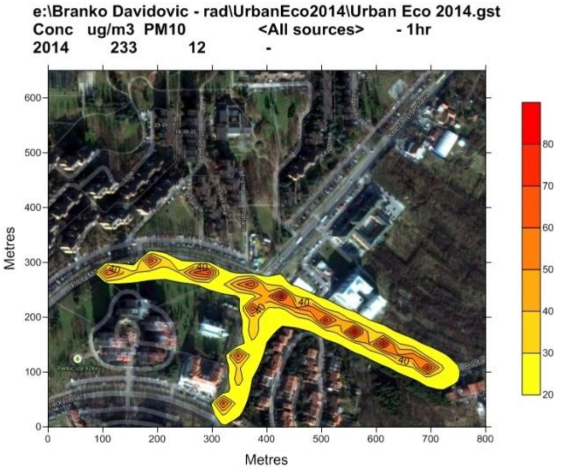


Figure 20. Value of t PM10 for August 21, 2014

PM10 represents an important factor of the environment quality, and traffic is one of the greatest generators of this pollutant. The PM10 concentration for the analyzed streets was from 20-135 µg/m^3. The terrain configuration and meteorological conditions caused the concentration of this pollutant in Kneza Višeslava Street to be under 28 µg/m^3 or so low that it couldn't be registered, as shown in figure 20, and this street was most burdened by pollutants until now.

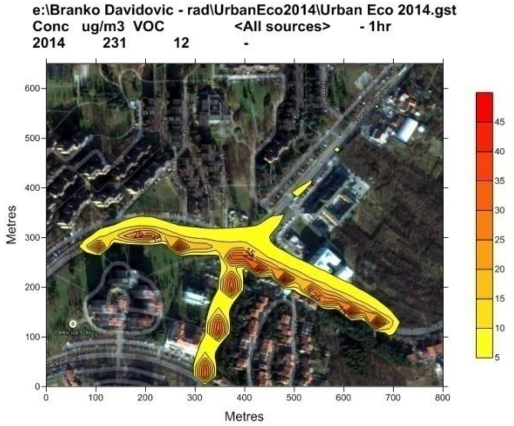


Figure 20. Value of VOC for August 19, 2014

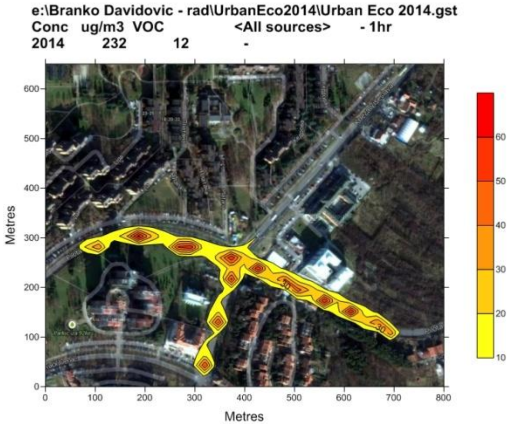


Figure 21. Value of VOC for August 20, 2014

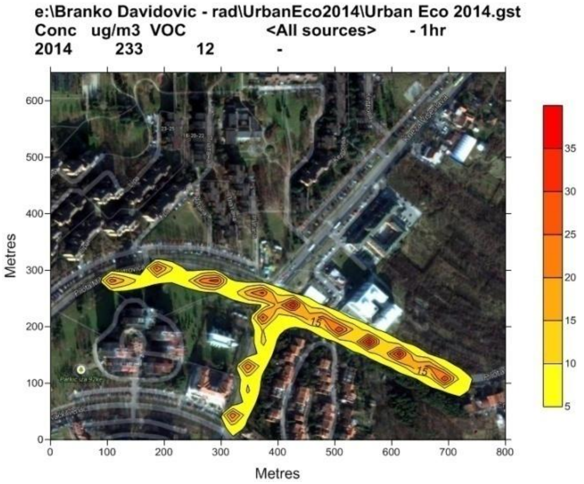


Figure 21. Value of VOC for August 21, 2014

The highest concentrations are predicted for Pilota Mihajla Petrovica Street, for August 20, when the wind speed is the lowest, and other meteorological conditions, temperature and humidity, of similar values as in the other days analyzed. The highest concentration of 135 μg/m^3 is predicted at the streets’ intersection.

The VOC concentration was from 5-60 μg/m^3. The highest concentration is predicted for August 20, 2014, at the intersection itself, and it is 60 μg/m^3. As in the case of PM10, the concentration of this pollutant in Kneza Višeslava Street is very low, almost immeasurable(except for the first day, August 19, 2014, when the concentration was 5 μg/m^3 is predicted).

The simulation showed that Pilota Mihajla Petrovića Street 1 and 2 is most burdened by this pollutant and that concentrations are gathered in concentric circles at certain places, both in that street and in Patrijarha Joakima Street. The EMEP (European Monitoring and Evaluation Software) network can be used jointly, and it covers an area in the resolution of 0,1^o · 0,1^o geographical latitude-longitude of the VGS84 coordinate system. The domain covers a geographical area between 30 ° N-82 ° of northern geographical latitude and 30 ° E-90 ° of eastern geographical longitude. Other networks, based on the national coordinates, can also be used. There is a special methodology for converting different types of emissions into a common network. The data bases (INSPIRE, CORINE, ESA Glob Cover, ESRI, UROPEAID etc.) can also be used.

Beside ADMS ROAD software, a number of other models and software for emission evaluation in road transport have recently been developed (COPERT, CAL Roads View**,** MOBILE**,** EMFAC, PHEM etc**)** which basically contain models for evaluation by some of previously listed three levels of complexity. The huge importance of emissions’ measuring in driving should be combined with emissions of other sources on the location chosen, uniting them into a unique format , which would help forming the complete emission maps for the complete pollution evaluation.

CONCLUSION

Requests for the environment preservation, improvement and stimulation of all kinds of «pure technologies» in traffic represent the basis of the state policy. The guidelines for such development were established on the EU transport system level (ECMT Council, Prague , 2000). They are based on reduction of effects harmful for the environment. With road vehicles, the zero emission vehicle has appeared for years as the final goal, although it is known that there is no human product which has no influence on its environment since the man himself produces about 4 t CO$_2$/year. The new target emissions for vehicles *NZEV* – Near *ZEV,* ie close to the minimum and *EZEV*- equivalent to a minimum emission have been introduced recently.

High level of transport emission can be reduced in different ways, from: improving the technical characteristics of vehicles by types, developing sustainable fuels with carbon content reduction, development of propulsion systems, reducing the speed of vehicles, minimizing the empty drives etc. Different ways of managing the light signals in the intersections also have an important influence on the traffic flow emissions. Coordinated work of light signals in the street corridors influence the reduction of aero-pollutants' emissions. By introducing the work coordination of light signals of the «green wave» type, we get the reduction of CO_2 and NO_x emissions for 10%. Average emissions of CO and Nox in speeding regimes, the increase of r.m.p (o/min) and engine breaking are increasing.The greatest average emission at small speeds (to 30 km/h) appears when we slow down. At speeds over 30km/h, the average emissions when speeding are higher then the ones when slowing down.

In the next period we should work on forming a universal data base of good quality about the emissions which should develop into a set of emission models , as precise as possible, which would be used for describing the emission characteristics of vehicles and space. These would later be used for ecological evaluation in the process of planning traffic solutions and for decision making from an ecological aspect about the impact on the environment.

LITERATURE

Andersson, J.D., Jemma, C.A., Bosteels, D., Searles, R.A. 2002. Particle emissions from a EU 3 heavy-duty diesel engine with catalyst-based diesel particle filter and selective catalytic reduction system: Size, number, mass and chemistry. 11. Aachener Kolloquium Fahrzeug- und Motorentechnik 2002, 7-9 October 2002, Aachen, Germany.

Cheung, K. L. , Ntziachristos, L. , Tzamkiozis, T. , Schauer, J. J. , Samaras, Z. , Moore, K. F. and Sioutas, C.(2010) 'Emissions of Particulate Trace Elements, Metals and Organic Species from Gasoline, Diesel, and Biodiesel Passenger Vehicles and Their Relation to Oxidative Potential, Aerosol Science and Technology, 44: 7, 500—513.

Comparative Analysis of Energy Consumption and CO Emissions of Road Transport and Combined Transport Road/Rail. IFEU-SGKV, Scientific study, IRU Energy & CO2 Emissions, Heidelberg, 2002.

Davidović B., Standardi i kvalitet vazduha. Banat air Quality 2011.Sustainable development for Banat region by means of academic education and scientific research & development in transboundary air quality monitoring issues. Universitatea „Politehnica” din Timişoara. Savetovanje o kvalitetu vazduha. Tehnički fakultet M.Pupin. Zrenjanin. 2011.

Guidelines for Measuring and Managing CO_2 Emission from Freight Transport Operations. European Communities Trade Mark Association, Issue 1. Brussels. 2011.

EMEP/EEA air pollutant emission inventory guidebook. Technical guidance to prepare national emission inventories. EEA technical report No.12/2013. Kopenhagen. 2013.

Jourquin B. et al.,Towards better Performing Transport Network. Routledge Studies in Business Organizacion and Networks. New Yourk. 2006.

McKinnon A., Piecyk M., Measuring and Managing CO_2 Emissions of European Chemical Transport. Logistics Research Centre Heriot-Watt University EDINBURGH, UK. 2010.

Procene količina emitovanih gasovitih zagađujućih materija poreklom od drumskog saobraćaja primenom Copert IV modela Evropske agencije za životnu sredinu. Institut saobraćajnog fakulteta, Beograd, 2010.

Özsalih H., A methodology for transport buying companies to estimate CO_2 emissions in transport: Application in Unilever European Logistics, Industrial Engineering - Bilkent University, Ankara, 2009.

Pravilnik o tehničkim merama i zahtevima koji se odnose na dozvoljene emissione faktore za ispraljiva organska jedinjenja koji potiču iz procesa skladištenja i transporta, “Službeni glasnik RS”, broj 36/09.

Pravilnik o podeli motornih i priključnih vozila i tehničkim uslovima za vozila u saobraćaju na putevima, ”Službeni glasnik RS", br. 40/2012.

Uredba o uslovima za monitoring i zahtevima kvaliteta vazduha, ”Službeni glasnik RS“, broj 11/2010.

Zakon o zaštiti vazduha, ”Službeni glasnik RS“, broj 36/2009.

Linkovi:

http://www.havakalitesi.cevreorman.gov.tr/english/training
http://www.lml.rivm.nl/data/kaart/actueel.html
http://www.kvvm.hu/olm/info.php?id=6
http://inspire.jrc.ec.europa.eu/
http://due.esrin.esa.int/globcover/

http://epp.eurostat.ec.europa.eu/portal/page/portal/eurostat/home
http://www.ceip.at/
http://www.eea.europa.eu/data-and-maps/data/corine-land-cover-2006-raster-2
http://due.esrin.esa.int/globcover/
http://www.eea.europa.eu/emep-eea-guidebook
http://www.emisia.com/copert
http://www.sepa.gov.rs/ams/xajax_data/eas_kvalitet_vazduha_1.php# -data about the ambient quality

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THE ANALYSIS OF METEOROLOGICAL DATA INFLUENCE ON THE DISPERSION OF AIR POLLUTANTS, SIMULATION OF THE SINGLE SOURCE EMISSION USING THE SOFTWARE ADMS 5

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ABSTRACT

One of the major concerns in urban areas is the environmental quality in terms of air quality. Due to the trafic and industrial growth the environmental quality in cities has been decreasing rapidly. In order to predict air quality are widely used. The paper desribes and demonstrates the influence of meteorological condition changes on air pollutants dissipation based on the calculations conducted using software ADMS 5. Applications are run for one point emitter in the City of Zrenjanin for various meteorological data. The paper focuses on the description and demonstration of how meteorological data change air pollutant's dispersion plum with the same emission factors. The dispersions of NOx and PM10 have been observed. The numerical simulations applied on the air pollution dispersion problem have become a standard tool for creating strategies and perspectives of environmental quality in Urban Areas. The case study was conducted for the single point emission source from »TeTo Zrenjanin« from the city of Zrenjanin for two days with different meteorological conditions. Beside that the software/model itself was introduced as well as meteorological conditions.

Key words: *meteorology ,air pollutants, dispersion.*

INTRODUCTION

Air pollution dispersion modeling is one of the methods for the ambient air quality assessment. Mathematical models are widely used tools for predicting air pollution and accurately assessing the spatial distribution of air pollutants in the city (Dėdelė, A., Miškinytė, A., 2014). For any model, an important feature of its use is access to reliable input data (Arciszewska, C., and McClatchey, J., 2001) regarding the emission and meteorological data. However, the degree of sophistication within the model will determine the extent of the input requirements. This paper treats problem of the dispersion of air pollutants using the software ADMS5 with respect of the meteorological and emission data from the single point emission source from »TeTo Zrenjanin« from the city of Zrenjanin. The study aim is to determine the dispersion of nitrogen oxides (NOx) and particulate matter (PM10) under various meteorological conditions at ground level with constant emission factors.

The important meteorological parameters that influence air pollution can are classified into primary and secondary parameters (Rao, M., 2007). Primary parameters are: wind direction and speed, temperature, atmospheric stability, mixing height. While, secondary parameters are: precipitation, humidity, solar radiation, visibility. These parameters vary widely as a function of latitude. Season and topography (Rao, M., 2007).

RELEVANT METEOROLOGICAL PARAMETERS

The minimum data requirements to run ADMS 5 model are: wind speed, wind direction, and one of either Julian day number, time of the day and cloud cover or sensible surface heat flux, or reciprocal Monin-Obukhov length. Because of that we will focus further on their influence on dispersion (CERC, 2012).

The direction and speed of surface winds define the drift and diffusion of air pollutants discharged near the ground level. The higher the wind speed at or near the point of discharge of pollution, the more rapidly air pollutants are carried away from the source. It causes dilution of air pollutants with greater and greater volumes of air. Opposite of that is when wind speeds are low, pollutants tend to be concentrated near the area of discharge and the longer the periods of such light winds, the greater will be the concentration of pollutants. Other things being equal, the concentration downwind from a source will be inversely proportional to wind speed. In rough terrain, it cannot be assumed that the wind direction and speed near the source govern the subsequent motion of the contaminants. Hills may deflect the air flow either horizontally, vertically, or both, the amount of deflection depending on the vertical stability of the atmosphere. Yet in the area of Banat hills are scarce. In valleys, the winds carrying a pollutant tend to flow either up or down the valley, following its meanderings. The deeper the valley, the more pronounced is this channeling effect (Rao, M., 2007).

It is important to provide a dependable scaling factor in the surface layer of the atmosphere which is dominated by turbulent forces and is characterized by large gradients in meteorological parameters. The stability index provided by Reynolds is essentially a ratio between viscous and kinetic forces and is not taking into consideration thermal forces. Richardson’s number is the ratio of thermal and kinematic forces which over comes the defect of Reynolds’s number, but is not still a know function with height and not dependable with weak gradients also when either thermal or kinematic forces are dominant. The Monin and Obukhov developed the similarity theory and developed the stability parameter (Murty, V) now recognized by boundary layer meteorologists as appropriate for the surface layer which is the Monin-Obukhov length scale (Murty, V., 1998).

ADMS5 Dispersion Software

When creating a dispersion model three types of data are needed: emission data, meteorological data and desired output data. There is a minimum of data amounts that are needed to run the software ADMS 5 (Atmospheric Dispersion Modeling System). These data have to define: general site details and desired modeling options; information about source of pollutant’s emission; meteorological conditions in the modeling area; background pollution data; grid and required output. The later data are introduced through six menus of the software, namely Setup, Source, Meteorology, Background, Grids and Output (CERC, 2012).

CALCULATION MODEL

The simulation has been conducted over the area of the City of Zrenjanin, with one emission point source from the „TETO Zrenjanin“ for two days of June 2014.

METEOROLOGICAL DATA IN THE SIMULATION AREA

The observed simulation area is the City of Zrenjanin, where the dispersion of pollutants from „TETO Zrenjanin“ has been analyzed. In order to observe the influence of meteorological conditions on the dispersion of air pollutants two simulations are implemented with the same emission factors. The first simulation is conducted for the clear day with no percipation, which is the 22nd of June 2014, while the second simulation is conducted for the cloudy rainy day. Wind roses for the later days are shown in Figure 1a) and 1b) respectively which have been generated using software ADMS 5.

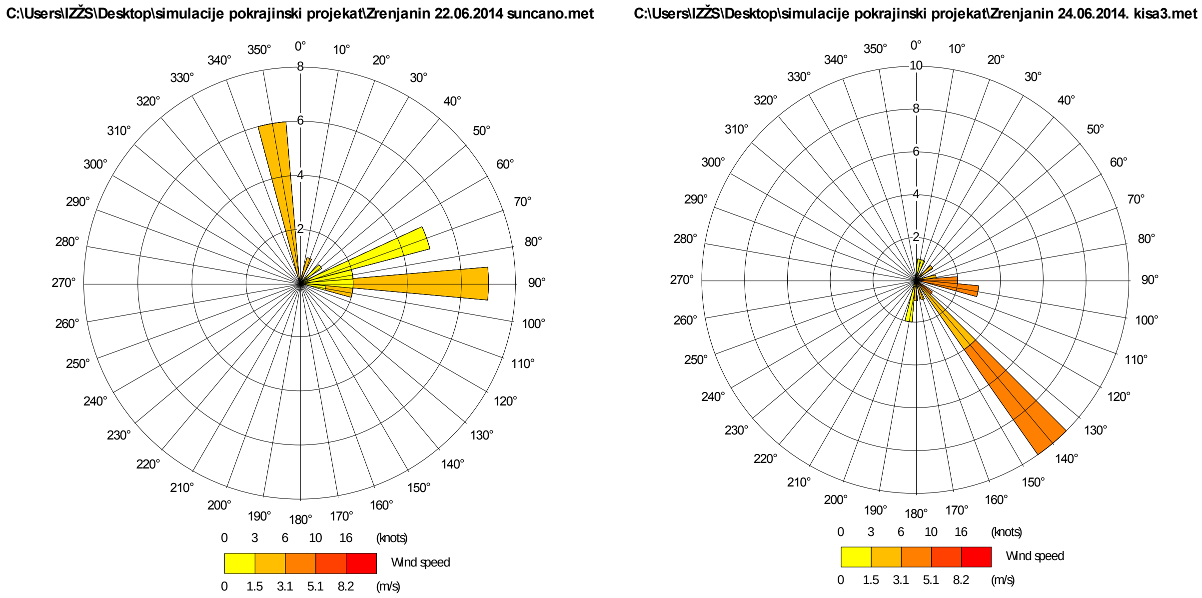

Figure 1. a) wind rose for 22.06.2014; b) wind rose for 24.06.2014.

Table 1 contains meteorological data for the 22nd of June 2014. (***) where can be observed that:

- Wind speed varies from 0.8 m/s to 2.7 m/s;
- Predominant wind directions are E and N (Figure 2a);
- Cloudiness is 0 octa;
- Temperature varies from 12 °C to 27 °C;
- Percipation is zero;
- Relative humidity varies from 33 % to 79 %.

Table 1: Meteorological data for the 22nd of June 2014. (***)

Hour	Wind speed, m/s	Wind dir., °	Cloudiness, octa	Temperature, °C	Precipation, mm	Rel. hum., %
1	1.7	101.3	0	14	0	68
2	1.5	99	0	13	0	70
3	1.4	90	0	13	0	73
4	1.3	90	0	12	0	76
5	1.1	81	0	14	0	79
6	0.8	78.5	0	16	0	67
7	0.8	67.5	0	19	0	57
8	1	67.5	0	22	0	51
9	1.5	71	0	23	0	42
10	1.6	90	0	24	0	38
11	1.6	90	0	25	0	36
12	1.6	90	0	26	0	35
13	1.8	90	0	27	0	34
14	1.7	88	0	27	0	33
15	1.4	71	0	27	0	33
16	1.4	67.5	0	27	0	33
17	1.4	45.5	0	27	0	34
18	1.7	22	0	26	0	39
19	2	350	0	23	0	58

20	2.4	350	0	22	0	55
21	2.5	350	0	20	0	58
22	2.6	350	0	19	0	62
23	2.7	350	0	18	0	65
24	2.6	350	0	18	0	68

Table 2 contains meteorological data for the 24th of June 2014. (***) where can be observed that:

- Wind speed varies from 0.8 m/s to 3.8 m/s;
- Predominant wind direction is SE (Figure 2b);
- Cloudiness varies from 0 to 8 octa;
- Temperature varies from 18 °C to 28 °C;
- Percipation varies from 0 mm/h to 1.03 mm/h;
- Relative humidity varies from 37 % to 91 %.

Table 2: Meteorological data for the 24th of June 2014. (***)

Hour	Wind speed, m/s	Wind dir., °	Cloudiness, octa	Temperature, °C	Precipation, mm	Rel. hum., %
1	0.8	192	8	22	0.89	91
2	0.8	192	8	21	1.03	91
3	0.9	11	8	21	0.83	90
4	1.3	22.5	8	21	0.88	89
5	1.6	45	8	21	0.94	89
6	2.3	81	8	22	1.01	85
7	3.2	100	8	22	1.01	84
8	3.5	100	8	21	1.03	85
9	3.4	95	8	21	0.64	84
10	3.6	90	8	22	0.18	80
11	3.7	93	6	24	0.06	72
12	3.6	130	6	26	0.06	58
13	3.7	135	6	27	0.13	48
14	3.7	140	6	28	0.11	41
15	3.8	140	4	28	0.1	37
16	4	140	0	28	0	34
17	4	140	0	28	0	34
18	3.5	140	0	26	0	41
19	2.9	140	0	23	0	59
20	2.7	140	0	21	0	58
21	2.6	140	0	20	0	61
22	2.5	140	4	19	0	63
23	2.5	160	6	19	0	65
24	2.5	176	6	18	0	65

SIMULATION SETUP

This paper covers two simulations that are implemented over the City of Zrenjanin for various meteorological conditions, shown in Table 1 and Table 2.

The first simulation is conducted for the dispersion of air pollutants from the „TETO Zrenjanin“ over the area of the City of Zrenjanin with special respect to Bega river. Model setup is done according the next data:

1. Model options / dry deposition, because the simulation period is without precipitation;
2. Emission source data are given in Table 3;

Table 3: Emission source data

Type	Height, m	Diameter, m	Velocity, m/s	Volume flux, m^3/s	Temp., °C	Position x, m	Position y, m
Point	160	5,5	1.89	44,903	117,7	0	0

*data acquired from „TETO Zrenjanin“

3. Emission factors are given in Table 4;

Table 4: Emission factors

NOx, g/s	39,7820
PM10, g/s	0,0130

*data acquired from „TETO Zrenjanin“

4. Meteorological data:
   - Latitude: 45°;
   - Surface roughness: 1 m, according the ADMS 5 for urban areas;
   - Meteorological data imported as .met file based on the Table 1;
5. Background: no data;
6. Grid, 40000x40000x200m, number of points 80x80x5;
7. Output NOx and PM10 short term calculations.

The second simulation is conducted for the dispersion of air pollutants from the „TETO Zrenjanin“ over the area of the City of Zrenjanin with special respect to Bega river for diferent meteorological conditions (precipitation and cloudiness included, as well as diferent wind direction). Model setup is done according the next data:

1. Model options / dry deposition, because the simulation period is without precipitation;
2. Emission source data are given in Table 3;
3. Emission factors are given in Table 4;
4. Meteorological data:
   - Latitude: 45°;
   - Surface roughness: 1 m, according the ADMS 5 for urban areas;
   - Meteorological data imported as .met file based on the Table 2;
5. Background: no data;
6. Grid, 40000x40000x200m, number of points 80x80x5;
7. Output NOx and PM10 short term calculations.

SIMULATION RESULTS

Simulations are implemented on the hardware equipment Lenovo Lenovo Think Station E32 and installed ADMS 5 software, where the hourly values of NO_x and PM10 are calculated. Figures 2, 3, 4 and 5 present characteristic simulation results.

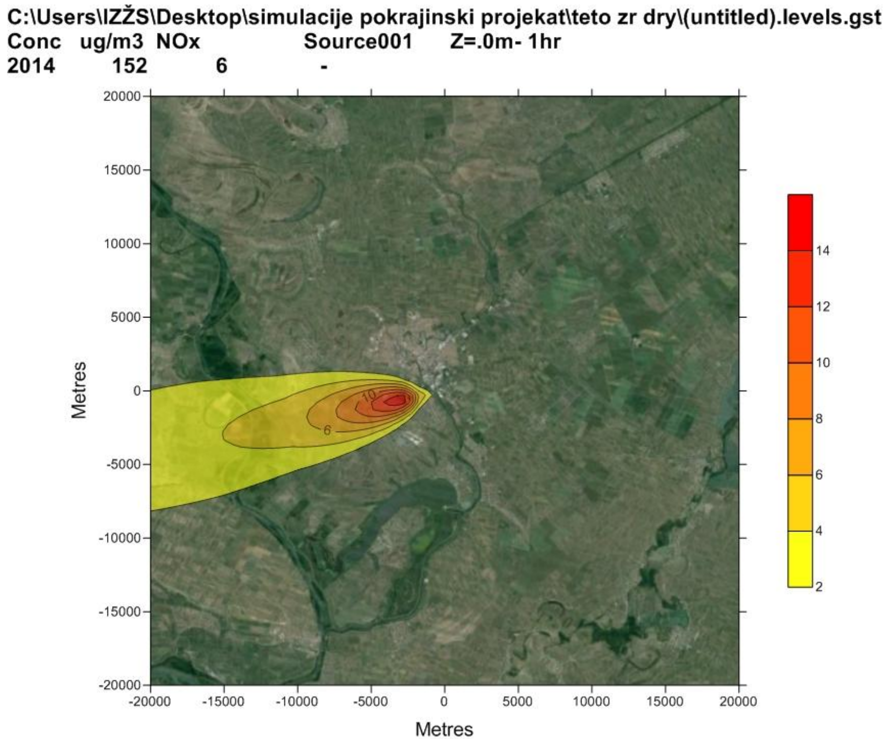

Figure 2. NOx ground level dispersion in the 6th hour of the 22nd June 2014

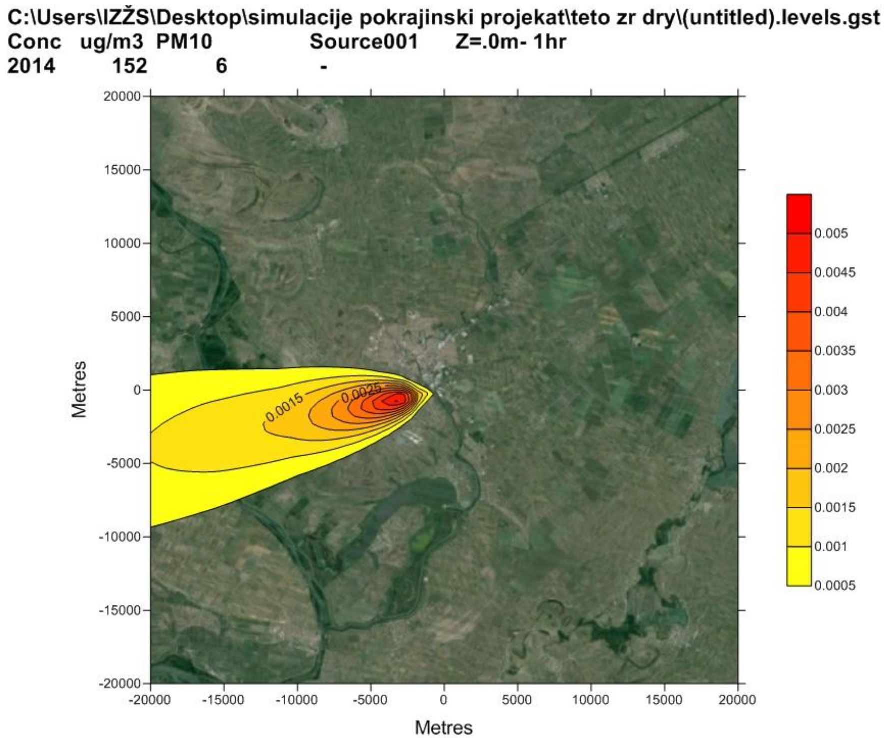

Figure 3. PM10 ground level dispersion in the 6th hour of the 22nd June 2014

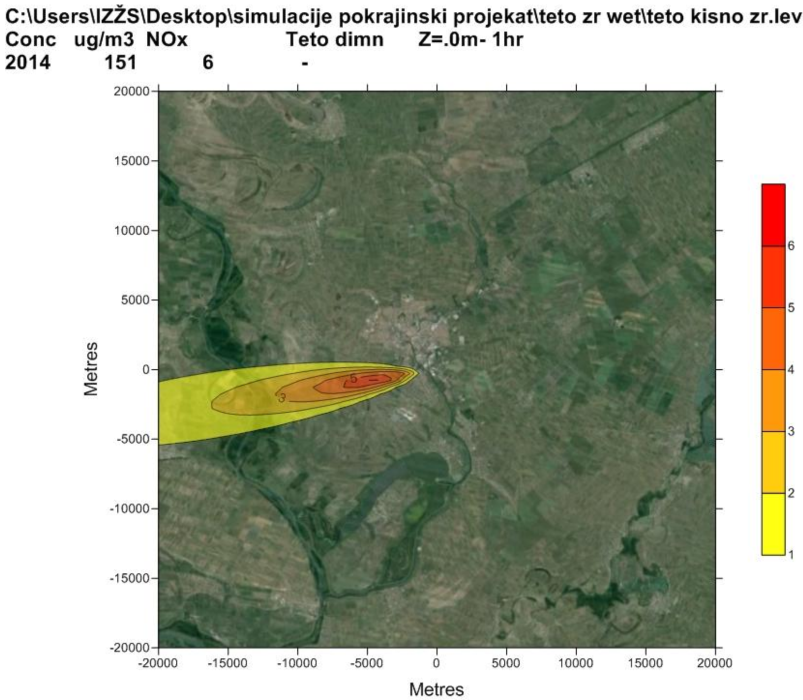

Figure 4. NOx ground level dispersion in the 6th hour of the 24th June 2014

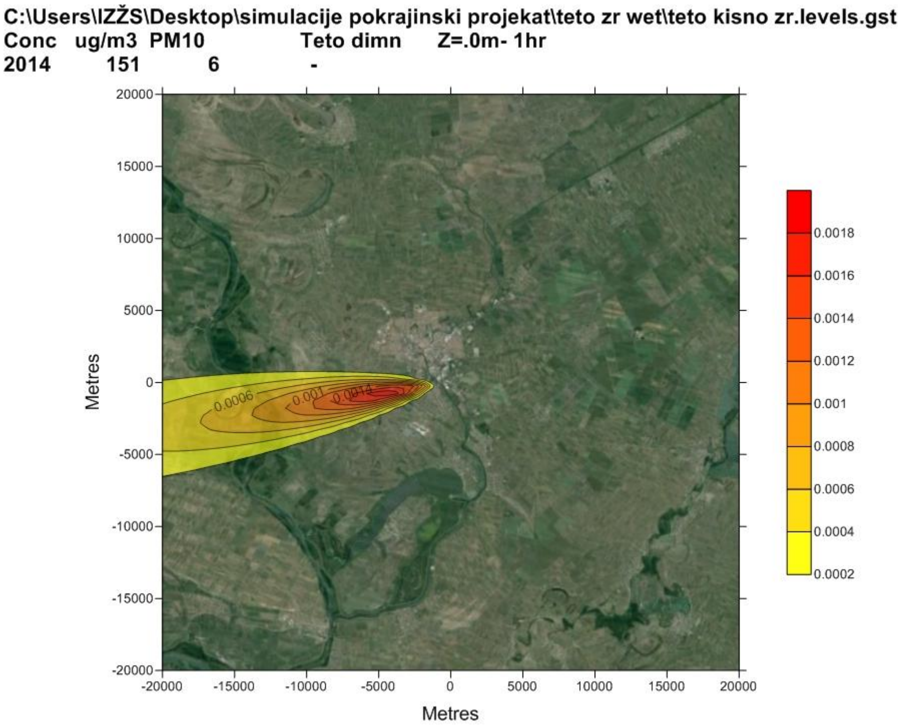

Figure 5. PM10 ground level dispersion in the 6th hour of the 24th June 2014

Based on the simulation results we have created the table of average hourly values of NOx and PM10 pollutants above Bega river in the city of Zrenjanin that originate from „TETO Zrenjanin“ emission. These data are shown in Table 5.

Table 5: Average hourly values of pollutants on 22nd and 24th of June 2014 above Bega river

Hour 22.06.	NO_x µg/m^3	PM10 µg/m^3	Hour 24.06.	NO_x µg/m^3	PM10 µg/m^3
1	0.02	0.000006	1	0	0
2	0.015	0.000006	2	0	0
3	0.01	0.000004	3	0.004	0.000002
4	0.01	0.000003	4	0.4	0.00012
5	0.006	0.0000015	5	1.8	0.00053
6	4	0.001	6	2	0.0006
7	4	0.001	7	1.5	0.0005
8	2	0.0015	8	1	0.0006
9	2	0.001	9	1	0.0004
10	2	0.0005	10	1.5	0.0005
11	2	0.0005	11	1	0.0004
12	2	0.0005	12	0.5	0
13	2	0.0005	13	0	0.0001
14	2	0.0005	14	0	0
15	2	0.0005	15	0	0
16	2	0.0005	16	0	0
17	2	0.0005	17	0	0
18	1	0.0004	18	0	0
19	0	0	19	0	0
20	0	0	20	0	0
21	0	0	21	0	0
22	0	0	22	0	0
23	0	0	23	0	0
24	0	0	24	0	0

After the data comparison from Table 5 it is obvious that changes in meteorological conditions are connected with air pollution dispersion in the next manner: the better meteorological conditions are, the pollutant’s dispersion is higher. This can be observed in all hours except in the 5th hour, which can be explained with specific meteorological data observed in Table 1 and Table 2.

CONCLUSION

Results of the simulations presented in the paper show that it is possible to make easy comparison of the simulation results when changing only meteorological data using software ADMS 5. Figures 2, 3, 4 and 5 show the simulation results and dispersion of air pollutants over the City of Zrenjanin from a single emission source. Based on the analysis of average hourly simulation results data form Table 5 are obtained where comparison of concentrations under diferent weather conditions is possible. The conducted simulation under difference meteorological conditions shows that calm weather increases the intensity of dispersion in comparison to the cloudy and rainy weather conditions, which is in accordance to the expected results and literature recommendations.

ACKNOWLEDGEMENT

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REFERENCES

Dėdelė, A., Miškinytė, A., (2014) Estimation of inter-seasonal differences in NO2 concentrations using a dispersion ADMS-Urban model and measurements, Air Qual Atmos Health, DOI 10.1007/s11869-014-0272-9

Arciszewska C, Mcclatchey J (2001) The importance of meteorological data for modelling air pollution using ADMS-Urban. Meteorol Appl 8:345–350

Rao, M., Rao H., (2007) Air Pollution, Tata McGraw-Hill, ISBN 0-07-451871-8

MURTY, V., et. al., (1998) THE STABILITY OF THE SURFACE LAYER AS INDICATED BY MONIN-OBUKHOV LENGTH SCALE, Congressos Brasilieros de Meteorologia

CERC, (2012) ADMS 5 User Guide, Cambridge Environmental Experts Consultants, Cambridge, UK

***, http://www.weather2umbrella.com/

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NON-STATIONARY SOURCES OF AIR POLLUTION

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ABSTRACT

Mobile sources of pollution are motor vehicles, whose number increases on a daily basis, which causes them to become the ever-growing air pollutants inside and outside of urban areas, throughout the year. According to data from the IPCC (Intergovernmental Panel on Climate Change), the share of traffic in emissions of greenhouse gases compared to other potential pollutants is 13%. By combustion of petrol and other petroleum products in motor vehicles, the air at low altitudes receives numerous dangerous components of air pollution (soot, nitrogen oxides, sulfur oxides, carbon monoxide, organic peroxides, lead, cadmium, etc.). It is believed that the exhaust gases from motor vehicles are the main contributor to air pollution, especially in larger cities. In Serbia, due to poor quality of fuel, there is a high concentration of sulfur and lead in the air, which is an especially serious health problem. The illustrated example shows an estimated concentration of pollution in urban areas for various types of vehicles and fuels used.

Key words: *mobile sources, air pollution, traffic.*

INTRODUCTION

During the last decade, owing to the development of road transport and aviation, air pollution that comes from mobile sources has increased sharply. It is estimated that in urban areas (depending on the economic development and the number of mobile sources) the share of air pollution originating from mobile sources ranges from 30% to 70%. In the United States, the share of air pollution originating from mobile sources is 40% of the total air pollution.

Car transport is the most frequent form of road transport. The number of cars in the world is constantly growing. Thus, for example, the number of cars in the world in 1900 was 11 thousand, in 1950 - 54 million, in 1970 - 181 million, in 1982 - 330 million. Today, it is estimated that there are about a billion cars worldwide.

Unfortunately, car transport is one of the main sources of air pollution (especially in big cities) and has a negative impact on the health of the population. Virtually all modern cars have internal combustion engines. Each of them (if functional) emits into the atmosphere around 3 kg of hazardous substances daily. It was observed that the exhaust gases of motor vehicles contain around 200 different substances. The most common are: lead, nitrogen oxides, sulfur, carbon, carbon monoxide, hydrocarbons, soot, benzo[a]pyrene, etc. (Zhdanov, 2012).

The degree of the combustion and the composition of the exhaust gases emitted depend on the type and features of the engine. The majority of cars have engines running on petrol, although in recent years there are more and more cars with diesel engines. Petrol is a mixture of liquid hydrocarbons-pentanes, hexanes, heptanes, octanes, nonanes, decanes. During the combustion of such fuel, many harmful substances are emitted, as a result of varying combustion conditions and the presence of various impurities which remain after the processing of fuel and additives (tetra methyl and tetraethyl lead), which are added as an anti-knock agents and substances which increase the octane rating of fuel.

There is a lot of soot and dust in the exhaust fumes from diesel engines, but there are no lead compounds and toxic carbon oxides, since diesel fuel practically burns completely. The amount of hydrocarbons (which do not burn or do not burn completely) increases significantly in the exhaust gases when the engine is running at low rpm, or at times when speed is increased when starting the vehicle (e.g. at traffic lights). In these situations, the number of unburned particles increases tenfold compared to the normal mode of engine operation. Ecological circumstances in our country are negatively affected owing to a large number of cars whose lifetime in most cases is over 10 years. (Statistical Yearbook, 2012)

METHODS FOR ASSESSING AIR POLLUTION BY MOBILE SOURCES

Assessment of the distribution of air pollution from mobile sources is a very complicated task. The process of fuel combustion, pollutant emissions and their diffusion in the atmosphere around the source is an extremely complex task and to this day has not been sufficiently studied. Vehicles in traffic are viewed as linear mobile sources or surface sources when a line of vehicles is observed. These sources are non-stationary and non-homogeneous operating in complex urban conditions. Application of accurate methods for the calculation of air pollution emissions based on differential equations of ***hydro-thermodynamics*** is quite problematic. For this reason, there are a relatively small number of methods and models that can deal with this problem (Berlyand, 1975).

In the environmental calculations of air pollution from mobile sources, simplified models based on experimental data and empirical relationships are frequently applied. It is clear that these methods do not have a universal character and that they have a limited scope of application. As a rule, the authors of the various proposed models, regardless of the great potential of information technology in terms of possibility of applications of numerical methods, create simple methods, which often disregard the essence of the analysed process.

One of the first models proposed for assessing the amount of air pollution requires information on the amount of pollutants emitted per unit of distance travelled by each vehicle in the monitored area. Knowing the total traffic of the monitored area the mass of pollutants emitted into the atmosphere can be calculated. The amount of emitted substances is adjusted depending on the technical validity and time of the vehicle exploitation. This model is important because it allows one to move from a qualitative assessment of air pollution to the quantitative assessment of pollutants emitted for an arbitrary period of time (month, quarter, year). A drawback of the model is that the distance covered by a vehicle is estimated by using statistical data obtained from companies in transport business. As there is no information about the distance covered by vehicles for personal use, it is estimated based on the amount of fuel purchased at petrol stations. Apart from these shortcomings, these methods do not take into account the hydro-meteorological conditions, the terrain of the region, the mode of vehicle movement, etc.

Subsequent methods fixed shortcomings of the original model in terms of the analysis of air pollution emission by vehicles according to individual groups of vehicles (passenger cars, freight vehicles and buses). For some groups, their specific features were included. For passenger cars engine capacity was included, for freight vehicles their carrying capacity and for buses their size. Also, the mode of movement was included as a factor that contributes to the emission of harmful substances into the atmosphere. Subsequent models calculated the mass of emitted air pollution as the sum of the masses emitted during constant motion and masses emitted while vehicle is at a standstill. The mass of the emitted air pollution is calculated based on the distance travelled in constant motion and based on the time of the operation of vehicle at a standstill. In addition, the newer models calculated the mass of air pollution emitted according to the mode of transport in urban conditions (acceleration, braking, idling, delay at intersections). Improvement of this method is also the fact that the parameters required for the calculation of air pollution can be obtained directly and not from statistical estimates. The latest models allow you to individually assess the emissions of a wide range of harmful substances: carbon oxides, nitrogen, sulfur, hydrocarbons, soot, lead compounds, formaldehyde, benzo[a]pyrene.

AIR POLLUTION ASSESSMENT METHODICS

A consequence of the increase in road traffic is the increase of anthropogenic effects on the surrounding environment, especially the atmosphere. Vehicle exhaust fumes are particularly dangerous because they are in the ground layer of the atmosphere where the wind speed is low and where such gases do not disperse easily. Apart from the pollution of the atmosphere as a result of vehicle traffic, there are high levels of noise, as well as land and waterways pollution. In the paper we are only interested in air pollution that comes from cars in road traffic (since it is the highest), not including air pollution originating from aircraft and vessels.

Assessment of air pollution will be done by computation on an illustrative example.

We will observe a city street without any slopes or rises, 2 km long, with an intersection where traffic is regulated by traffic lights. Vehicles involved in traffic are divided into eight classes:

I Domestic cars
II Foreign cars
III Vans and minibuses
IV Buses with engines running on petrol
V Buses with engines running on diesel
VI Freight vehicles with engines running on petrol
VII Freight vehicles with engines running on diesel up to 12 tons
VIII Freight vehicles with engines running on diesel over 12 tons

The calculation of the assessment of emissions is carried out for the following materials: carbon monoxide, nitrogen oxides, hydrocarbons, particulate matter, sulfur dioxide, formaldehyde and benzo[a]pyrene.
Emissions of the *i*-th substance in g/s during the transport of road vehicles along the road with the length *L* (km) is determined by the formula (Molodtcov, 2014)

$$M_{Li} = \frac{L}{3600} \sum_{i}^{k} M_{k,i}^{P} G_k k_{v_{k,i}} \tag{1}$$

where:

$M_{k,i}^{P}$ (g/km) is the emitted mass of the *i*-th substance of the vehicle of the *k*-th group of vehicles, which is determined from the Table 1.
k-number of the vehicle classes
G_k (1/hour)-number of cars of the *k*-th class which go through which pass through an imaginary cross-sectional times per unit of time in both directions
$k_{v_{k,i}}$ - correction coefficient which includes an average speed of vehicle v_k (km/hour) and which is determined from the Table 2.

Table 1:

Class	Emission (g/km)						
	CO	NO_x	CH	PM	SO_2	Formaldeh.	Benzo[a]py.
I	5,0	1,3	1,1	0,03	0,03	0,005	$0,4\ 10^{-6}$
II	2,0	0,7	0,4	0,02	0,03	0,002	$0,2\ 10^{-6}$
III	12,0	2,0	2,5	0,08	0,06	0,011	$0,8\ 10^{-6}$
IV	35,0	5,2	8,5	-	0,04	0,04	$1,2\ 10^{-6}$
V	7,0	6,0	5,0	0,3	0,07	0,025	$2,0\ 10^{-6}$
VI	60,0	5,2	10,0	-	0,05	0,05	$4,0\ 10^{-6}$
VII	9,0	7,0	5,5	0,4	0,10	0,025	$2,0\ 10^{-6}$
VIII	12,0	8,0	6,5	0,5	0,12	0,03	$2,4\ 10^{-6}$

Table 2:

	Speed v_k (km/hour)												
	10	15	20	25	30	35	40	45	50	60	75	80	100
$k_{v_{k,i}}$	1,35	1,28	1,2	1,1	1,0	0,88	0,75	0,63	0,5	0,3	0,45	0,5	0,65

The intensity of traffic is determined from Table 3.

Table 3:

Street	The number of cars according to the class								Speed km/hour		
	I	II	III	IV	V	VI	VII	VIII	I,II,III	IV,V	VI,VII,VIII
	171	88	67	12	-	-	1	-	60	40	40

Emission of harmful substances in the area of intersection regulated by traffic lights is determined by the formula (Molodtcov, 2014)

$$M_{Ri} = \frac{R}{40}\sum_{n=1}^{N_c}\sum_{k=1}^{N_{kl}} M_{R_{i,k}} G_{k,n} \tag{2}$$

where:
R (min)- duration of the red and yellow light at the traffic lights
N_c - number of cycles at the traffic lights of the red and yellow lights during 20 minutes
N_{kl} - number of vehicle classes
$M_{R_{i,k}}$ (g/min)- emitted quantity of the *i*-th harmful substance from the *k*-th class of vehicles which are at a standstill at the traffic lights
$G_{k,n}$ -number of vehicles of the *k*-th class which are at a standstill at the end of the *n*-th cycle at the traffic lights
Values $M_{R_{i,k}}$ are determined from the Table 4

Table 4:

Class	Emission (g/min)						
	CO	NO_x	CH	PM	SO_2	Formaldeh.	Benzo[a]py.
I	0,8	0,02	0,12	0,02	0,006	0,0005	$0{,}4\ 10^{-6}$
II	0,3	0,01	0,05	0,01	0,006	0,0003	$0{,}2\ 10^{-6}$
III	2,0	0,04	0,25	0,04	0,012	0,0011	$0{,}8\ 10^{-6}$
IV	4,0	0,08	0,9	-	0,009	0,4	$1{,}2\ 10^{-6}$
V	1,1	0,11	0,6	0,2	0,015	0,0025	$1{,}6\ 10^{-6}$
VI	10,0	0,12	1,2	-	0,009	0,005	$4{,}0\ 10^{-6}$
VII	1,5	0,12	0,6	0,23	0,02	0,0025	$2{,}0\ 10^{-6}$
VIII	12,0	8,0	6,5	0,5	0,12	0,03	$2{,}5\ 10^{-6}$

Number of vehicles at a standstill at an intersection for a period of time of 20 minutes is given in Table 5

Table 5:

intersection	Time of standstill in min	The number of vehicles according to the class							
		I	II	III	IV	V	VI	VII	VIII
	0,77	237	120	74	9	-	12	3	-

By using formulae (1) and (2) and data from the Tables (1)-(6) we find the emitted quantity of harmful substances for our example. The results are given in the Table 7.

Table 6:

	Emission (g/s)						
	CO	NO_x	CH	PM	SO_2	Formaldeh.	Benzo[a]py.
Street	1,268	0,23753	0,2761	0,00617	0,0057	0,00126	$0{,}082\ 10^{-6}$
Intersection	0,1739	0,00371	0,0025102	0,00312	0,00106	0,001254	$1\ \ 10^{-6}$

To determine the level of concentration of harmful substances from the vehicle at low altitudes at different distances from the road the Gaussian model of distribution of impurities in the atmosphere is applied (Lazaridis, 2011)

$$C_L = \frac{2M_{Li}/L}{1000\sigma \sin\varphi u\sqrt{2\pi}}; \quad C_R = \frac{2M_{Ri}/L}{1000\sigma \sin\varphi u\sqrt{2\pi}} \qquad (3)$$

where the φ-angle formed by an axis of the road with the observed point, u-wind speed in the observed moment and the standard deviation of the Gaussian distribution in the vertical direction (Table 7) (Sportisse, 2008)

Table 7:

	Emission (μg/m^3)						
	CO	NO_x	CH	PM	SO_2	Formaldeh.	Benzo[a]py.
Street	337,28	99,83	73,44	1,64	1,52	0,34	$2{,}18\ 10^{-5}$
Intersection	46,26	0,98	0,67	0,83	0,28	0,33	$2{,}66\ 10^{-4}$

For the chosen example, all values of the concentration of hazardous substances at a distance of 10 m next to the road are below the limit values.

Table 8:

Day and night		Distance from the road (m)					
		10	20	40	60	80	100
Day	Clear	2	4	6	8	12	16
	Overcast	1	2	4	6	8	10
Night	Clear	0,1	0,2	0,4	0,8	1	1,4
	Overcast	0,3	0,6	1	1,8	2,5	3,1

In the case when it is day and it is overcast at a distance of 10 meters from the road in the direction perpendicular to the road, the concentration of harmful substances are given in Table 8.

TOOLS FOR ASSESSMENT OF AIR POLLUTION BY MOBILE SOURCES

To describe the interaction of vehicle-receptor (object at a distance from the source) in the conditions of urban transport a series of semi-empirical models based on a priori parameterization of transmission conditions and dispersion of impurities scattering has been developed. Such a widely exploited model is the California Line Source Dispersion Model (CALINE) and the Danish Operational Pollution Model (OSPM). CALINE model is based on a Gaussian model of the smoke column and enables estimation of the concentration of impurities in a radius of not more than 500 m from the road, on which the source is moving. The classes of stability of the ground layer of the atmosphere are determined by the modified Pasquill-*Gifford* curves (Spotrisse, 2008). Ease of implementation of the given model and a small amount of input data have made this model very popular. However, the results of modelling are often seen only as a qualitative assessment, as the model does not take into account many factors that affect the dispersion of impurities: the characteristics of urban traffic, the relief of the terrain, components of the turbulent diffusion tensor, meteorological characteristics such as humidity, different speeds of wind, etc. (Lazaridis, 2011).

OSPM model includes urban aerography and weather conditions. It also allows the inclusion of different configurations of city streets, width and height of buildings, mechanical turbulence caused by the movement of the vehicle. A drawback of the OSPM model is the inability to include deformations of wind flow depending on the terrain and assessment of air pollution in points distant from the road on which the vehicle is moving.

A software solution that we will use to analyse the assessment of air pollution is MOVES. MOVES has the tools that allow uploading and editing of local data in order to adjust the parameters and elements to be considered in the selected cases. Calculations result in tables in MySQL environment. It is possible to define the areas that are of interest and which carry a certain number of parameters, connecting via ID of each zone. After the completion of the calculations according to the given parameters, visualization of the results can be obtained in a sophisticated software environment for working with spatial data, such as GIS tools (Jackson, 2010).

For a certain geographic location and time period, MOVES provides an overview of emissions and emission rates of the following pollutants (Wigonyk, 2011):

- HC (THC, NMHC, NMOG, TOG, VOC)
- CO
- NOx (NO, NO_2)
- NH_3
- SO_2
- PM10, 2.5 (organic carbon, elemental carbon, sulfate, brake wear, tire wear)
- Greenhouse Gases (CO_2, CH_4, N_2O)
- Toxics: Benzene, Ethanol, MTBE, Naphthalene, 1,3-Butadiene, Formaldehyde, Acetaldehyde, Acrolein

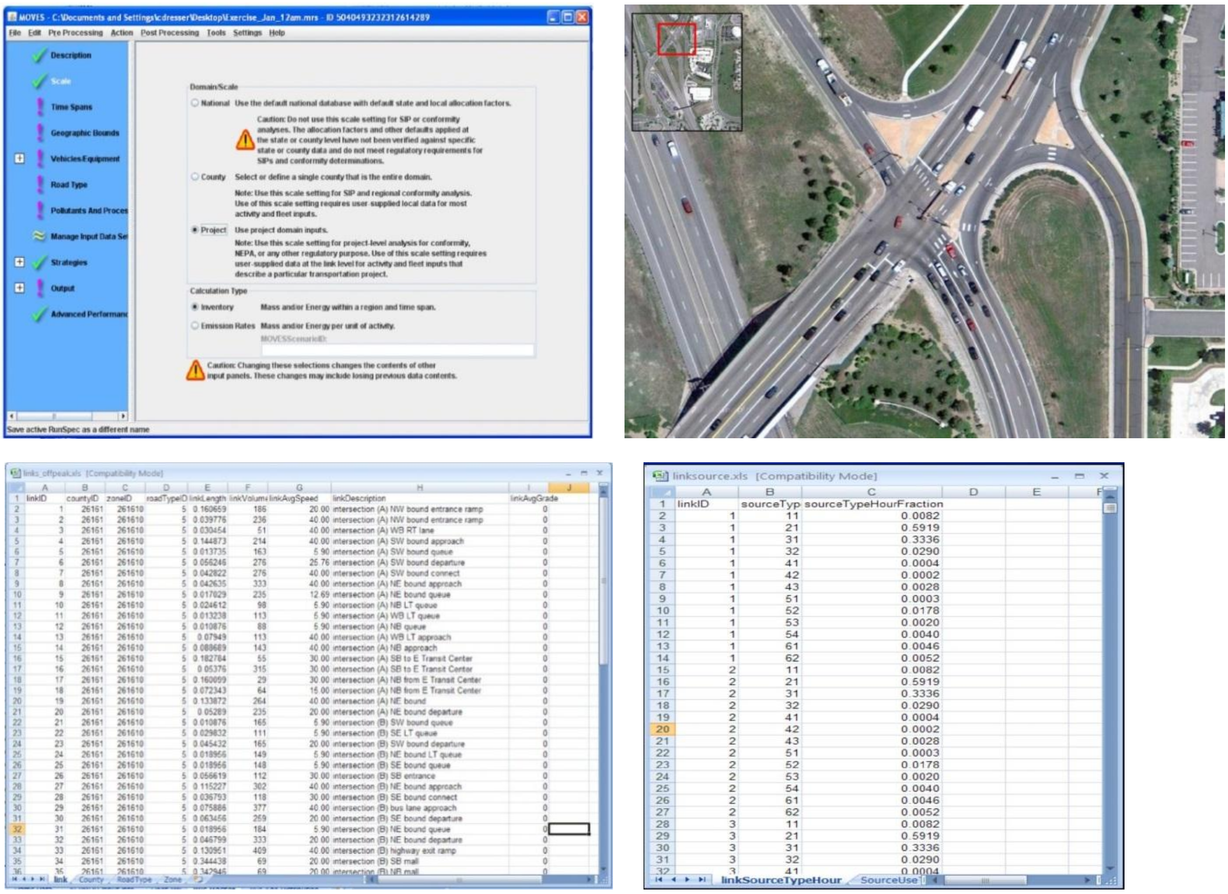
It is possible to determine different levels of results in relation to the desired output result, in accordance with the following selected categories:

- Vehicles - with the possibility of setting or the inclusion of one or more types of vehicles with their general features into calculations and estimates of the total emissions of pollutants.
- Types of fuels - which are used and the corresponding types of vehicles, such as petrol, diesel, gas, etc.
- The road – possibility of choice of the road category enabled primarily on the urban and rural territories, and then by category of road and speed limits. Parameters can be adjusted and changed.

Adaptation and change of parameters are enabled through the interface of the software package MOVES, but also directly by entering data in forms and templates that are generated and contain data in text format or excel format.

Emission processes are also defined categories related to moving and stationary vehicles at certain locations.

Example of application MOVES package (Dresser, 2012) for the evaluation of the effects of mobile sources of emissions of pollutants of the environment based on the initial preparation of data processing, i.e. after the choice of location.



Domain/Scale

○ National Use the default national database with default state and local allocation factors.

Caution: Do not use this scale setting for SIP or conformity analyses. The allocation factors and other defaults applied at the state or county level have not been verified against specific state or county data and do not meet regulatory requirements for SIPs and conformity determinations.

○ County Select or define a single county that is the entire domain.

Note: Use this scale setting for SIP and regional conformity analysis. Use of this scale setting requires user-supplied local data for most activity and fleet inputs.

● Project Use project domain inputs.

Note: Use this scale setting for project-level analysis for conformity, NEPA, or any other regulatory purpose. Use of this scale setting requires user-supplied data at the link level for activity and fleet inputs that describe a particular transportation project.

Calculation Type

● Inventory Mass and/or Energy within a region and time span.

○ Emission Rates Mass and/or Energy per unit of activity.

MOVESScenarioID:

Caution: Changing these selections changes the contents of other input panels. These changes may include losing previous data contents.

links_offpeak.xls [Compatibility Mode]

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3	2	26161	261610	5	0.039776	236	40.00	intersection (A) NW bound entrance ramp	0	
4	3	26161	261610	5	0.030454	51	40.00	intersection (A) WB RT lane	0	
5	4	26161	261610	5	0.144873	214	40.00	intersection (A) SW bound approach	0	
6	5	26161	261610	5	0.013735	163	5.90	intersection (A) SW bound queue	0	
7	6	26161	261610	5	0.056246	276	25.76	intersection (A) SW bound departure	0	
8	7	26161	261610	5	0.042822	276	40.00	intersection (A) SW bound connect	0	
9	8	26161	261610	5	0.042635	333	40.00	intersection (A) NE bound approach	0	
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26	25	26161	261610	5	0.018966	148	5.90	intersection (B) SE bound queue	0	
27	26	26161	261610	5	0.056619	112	30.00	intersection (B) SB entrance	0	
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32	31	26161	261610	5	0.018966	184	5.90	intersection (B) NE bound queue	0	
33	32	26161	261610	5	0.046799	333	20.00	intersection (B) NE bound departure	0	
34	33	26161	261610	5	0.130951	409	40.00	intersection (B) highway exit ramp	0	
35	34	26161	261610	5	0.344438	69	20.00	intersection (B) SB mall	0	
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7	1	42	0.0002		
8	1	43	0.0028		
9	1	51	0.0003		
10	1	52	0.0178		
11	1	53	0.0020		
12	1	54	0.0040		
13	1	61	0.0046		
14	1	62	0.0052		
15	2	11	0.0082		
16	2	21	0.5919		
17	2	31	0.3336		
18	2	32	0.0290		
19	2	41	0.0004		
20	2	42	0.0002		
21	2	43	0.0028		
22	2	51	0.0003		
23	2	52	0.0178		
24	2	53	0.0020		
25	2	54	0.0040		
26	2	61	0.0046		
27	2	62	0.0052		
28	3	11	0.0082		
29	3	21	0.5919		
30	3	31	0.3336		
31	3	32	0.0290		
32	3	41	0.0004		

Figure 1. Selection of the location and input of the types of vehicles and types of fuels used

In order to demonstrate the possibilities of application of the MOVES tools, Despot Stefan street in Belgrade was selected, and the initial analysis was performed of the area for which it is necessary to prepare the appropriate parameters relevant in terms of the preparation of the input parameters for the selected project area. For this purpose, an overview of the segments of streets with intersections was made, the zone defined around the block and around the intersections with special emphasis on the beginning and the end of the street. From the point of analysis, different time periods are of interest, such as morning or afternoon rush hour, the level of day or month or year. One possibility is to calculate the emission and emission rates per unit of distance for moving vehicles and starting the engine of the vehicle, which are in operating mode, but are not moving and the vehicles that are at a standstill.

Taking into account the possibility of the MOVES package for parameter calculation, the parameter can be determined, based on an analysis of the expert team, which would carry out the calculations of emission of air pollutants for the set parameters, as well as create the visualization and display using GIS tools (3SAQS, 2013).

The data obtained on the basis of the calculations can be used for evaluation of the conditions in the past, the present, and to make predictions in the upcoming period. Furthermore, since estimates are based on actual data monitored over a given period, the results and predictions can significantly contribute to the further planning, both in terms of environmental protection, but also in terms of improvement and development in the field of traffic safety (Ozbay, 2013).

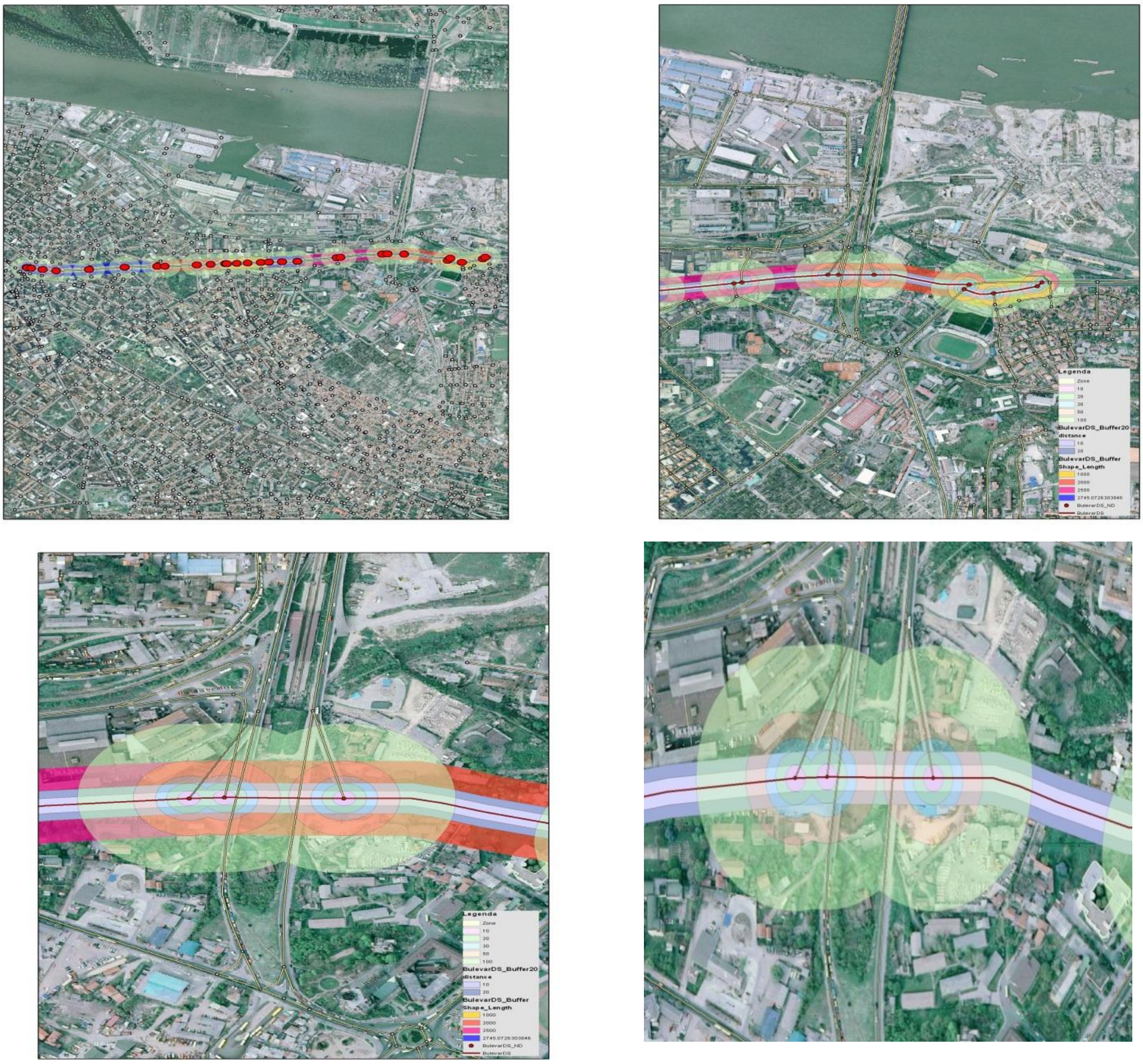

Figure 2. Representation of air pollution in Despot Stefan street in Belgrade

CONCLUSION

The paper analyses the case of air pollution originating from mobile sources. This primarily refers to air pollution originating from vehicles in road traffic. Air pollution originating from aircraft and vessels is not taken into account. This type of air pollution is not seasonal but daily and very pronounced in larger towns during the so-called rush hours when traffic particularly intensifies. The exhaust gases of motor vehicles were observed to contain around 200 different substances, some of which are very dangerous to human health. Vehicle exhaust gases are particularly dangerous because they are in the ground layer of the atmosphere where the wind speed is low and where these gases do not disperse easily. In addition to the pollution of the atmosphere as a result of vehicle traffic, there are also high levels of noise and pollution of land and waterways, but these effects were not analysed in the paper. In Belgrade, the pollution levels are often above the limits: CO has a threshold limit value

(TLV) concentration of 3 mg/m^3, the lowest value was measured in the period of 2006-2010 is 4.4 mg/m^3. For NO_2, TLV is 40 μg/m^3 and the lowest value observed in the same period was 85 μg/m^3, while for lead TLV has a value of 0.5 μg/m^3, and the measured values in this period range from 0.6 μg/m^3 - 1.7 μg/m^3 (source is the Institute of Public Health of Serbia "Dr Milan Jovanovic Batut"). It is obvious that this is a major problem in the surrounding environment and the health of people not only in Belgrade but also in other cities of our country. Ecological circumstances in our country are negatively affected owing to a large number of cars whose lifetime in most cases is over 10 years. Therefore, it is of the utmost importance to establish a permanent measurement of the level of air pollution in these areas. In addition, it is necessary to create appropriate models and tools that would simulate a realistic situation in road transport and predicted what the concentration of air pollution would be. It is necessary to connect these models and tools with the GIS tools for visualization and prediction of the existence and spread of air pollution. Furthermore, owing to such a complex approach, we can predict and suggest an optimization in regulating the traffic flow of vehicles and minimization of the emitted air pollution (Figliozzi, 2010), which would, on the other hand, affect the problems related to traffic safety.

Assessment of distribution of air pollution from mobile sources is quite a complicated task. The paper highlights a simple approach how an assessment of concentrations of some harmful substances emitted in the case of road traffic in a street with an intersection where traffic is regulated by traffic lights can be calculated at different distances and in different weather conditions. Moreover, some software tools that are used in these applications nowadays are given. MOVES tool was specifically analysed, which was applied in the case of Belgrade and Despot Stefan street.

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REFERENCES

Wygonik E., Goodchild A. (2011), Evaluating CO2 emissions, cost, and service quality trade-offs in an urban delivery system case study, *IATSS Research, IATSS Research 35 pp. 7–15.*

Figliozzi M. (2010), Vehicle Routing Problem for Emission Minimization, *Department of Civil and Environmental Engineering*, Portland State University, http://web.cecs.pdx.edu/~maf/Journals/Emissions%20Minimization%20Vehicle%20Routing%20Problem.pdf

Ozbay K., Bartin B., Mudigonda S., Iyer S. (2013), ASSIST-ME: a post-processing tool for transportation planning model output, *Journal of Transportation Research*, Washington, USA

Three-State Air Quality Modeling Study (3SAQS) (2013), Final Modeling Protocol, *Emissions & Air Quality Modeling Platform*, University of North Carolina.

Jackson E., Aultman L.(2010), Analysis of Real-World Lead Vehicle Operation for the Integration 1 of Modal Emissions and Traffic Simulation Models, *Journal of Transportation Research*, Washington, USA.

Lazaridis M. (2011), *First principles of Meteorology and Air Pollutant*, Springer, New York, pp.201-232

Жданов В.Л.(2012), *Экологические проблемы автомобильного транспорта в городах*, КГТУ, Кемерово, ст. 46-54

Молодцов В.А., Гусыков А.А. (2014), *Определение выбросов загрязнающих вещуств от автотранспорта*, ТГТУ, Тамбов, ст. 6-20

М.Е.Берлянд (1975), *Современние проблемы атмосфеной диффузии и загрязнения атмосферы*, Гидрометеоиздат, ст. 11-78, Ленинград

B.Sportisse (2008), *Fundamentals in Air Pollution*, Springer, pp. 239-241,New York

Statistički godišnjak (2012), Republički zavod za statistiku, Beograd, str.303-316

Dresser C. (2012), A PM Hot-Spot Analysis for a Hypothetical Transportation Project, US EPA - Office of Transportation and Air Quality

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GENERAL APPROACH TO EXHAUST EMISSION CONTROL OF INTERNAL COMBUSTION ENGINES

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ABSTRACT

One of the most significant technical products are the IC engines as the main part of the motor vehicles. During the many years of increased production and use, the presence of global warming, energy and economical crisis and nowadays the intensive exhaust-emission control, thus leading to set the stronger IC engines quality. That relates to exhaust-emission control as well as efficiency. European economic commision in 1988. based on UN regulations R84 have been determined the first test methodology and conditions of fuel consumption of passengers vehicles. The exhaust-emission limits apply to spark-ignition engines and diesel engines considering the components: carbon monoxide, nitrogen monoxide, hydrocarbons and particulates. In this paper is given a general approach to ECE regulations as well as global approach to actual possibilities in exhaust emission control.

Key words: *IC engines, exhaust emission control, ECE regulations.*

INTRODUCTION

The by-products of complete combustion in internal combustion engines (IC engines) are carbon dioxide and water. The major proportion of the exhaust gas is composed of non-toxic and toxic components. The toxic are: CO, NO_X, HC and PM (particulates). The methods used to alter the composition of the exhaust gases from both spark-ignition engines and diesel engines are divided into two basic categories: engine design measures and exhaust-gas treatment (aftertreatment). The emission standards are defined in a series of European Union directives staging the progressive introduction of increasingly stringent standards. Compliance with this legislation is achieved using emission control systems which incorporates the 3-way catalytic converter. The EU nations, with their markets, have been moving toward implementation of the stringent exhaust emission regulations.

Engine efficiency has been steadily improved with improved engine design, more precise ignition timing and electronic ignition, more precise fuel metering, and computerized engine management.

PROPERTIES OF EXHAUST-GAS COMPONENTS

The major proportion of the exhaust gas is composed of the three components: nitrogen, carbon dioxide and water vapor. The exhaust gas also contains the toxic, dangerous and unpleasant components:

- carbon monoxide CO. It is colorless, odorless and tasteless gas. Inhalation of air with a volumetric concentracion of 0,3% CO can result in performing loss of vital human functions in 30 minutes. The most important fact is that the CO content of the exhaust gas from spark ignition engines is especially high at idle, thus do not run engines in a closed space!

- nitrogen monoxide NO. A colorless, odorless and tasteless gas. In air it is gradually transformed into NO_2. Pure NO_2 is a poisonous gas with a penetrating odor. The concentrations found in exhaust gases and in extremely polluted air can induce irritation in mucous membranes.
- hydrocarbons HC, are present in exhaust gases in a variety of forms. When exposed to sunlight and NO_2 they react to form oxidants, which can be a source of irritation to mucous membranes. Some of HC's are considered to be dangerous to health with severe consequences.
- particulates (particulate matter or PM) are defined as all substances which under normal circumstances are present in exhaust gases in a solid or liquid state.

AIR-FUEL MIXTURE FORMATION

The fuel used in spark ignition engines is more volatile than diesel fuel, while the air-fuel mixing process preceding combustion also extends over a longer period than in diesel engine. The result is that spark ignition engines operate on a more homogenous mixture than diesel engines (Tomić M., 2012). Spark ignition engines run on a stoichiometric mixture or close to it, Figure 1.

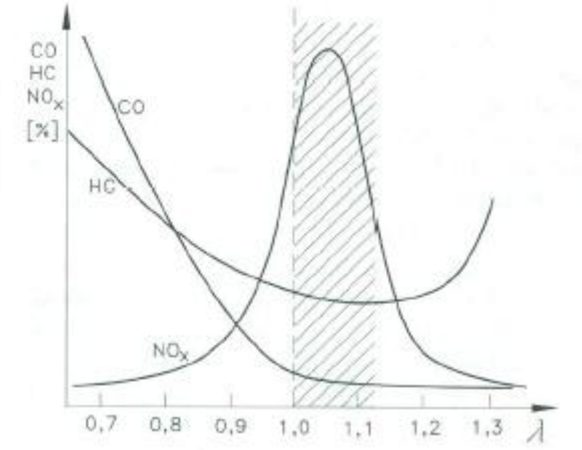

Figure 1. Excess-air factor and toxic components

Figure 1 shows how concentration of the toxic components in exhaust gases of the spark ignition engines depends on mixture formation. It is obvious that is very hard to make kind of mixture formation which would result in low amount of all three analyzed components.

In a domain of the rich mixture content of the nitrogen oxide (NO_X) is very low, but the content of the carbon monoxide (CO) and hydrocarbons (HC) that did not combust is very high. Besides, in this domain, the cost-effectiveness of the engine is very poor.

However, in the past when the cost-effectiveness and exhaust emission have not been given enough attention, the system for mixture formation was mostly regulated to work in this domain, because of the high stability of the rich mixture combustion, and possible malfunction does not make any problems.

Today, we use mostly semi-poor mixture (hatched domain in Figure 1), which gives low content of CO and HC, and, at the same time, good cost-effectiveness, although it has high content of NO_X. High content of NOx, in critical modes of engine work is managed by some other means (for example: lowering the angle of ignition point, by introducing of the recirculation of the exhaust gas and so on). It should be said, that the domain of very poor mixture (right to the hatched area in Figure 1) is very attractive because it gives low content of all toxic components, but in that case the problem of combustion stability process should be solved (to extend the boundaries of lean mixtures). A lot of intensive work of so called extremely poor mixture engines could be expected. So far, acceptable solution has been the work in domain indicated in Figure 1.

In the case of using devices after-neutralization of the toxic components in gases, so called "three-way catalytic converters", stoichiometry compound of mixture is highly demanded ($\lambda=1$), which provides efficient function of catalyst.

The diesel engine operates on fuel with a higher boiling point than that burned in gasoline engines. The diesel also has less time to form the air-fuel mixture, which is less homogenous as a result. Diesel engines always operate with excess air ($\lambda>1$), i.e. they are lean running (Tomić M., Petrović S., 2004). If the excess-air level is not high enough, this results in increased emissions of soot, CO and HC, Figure 2.

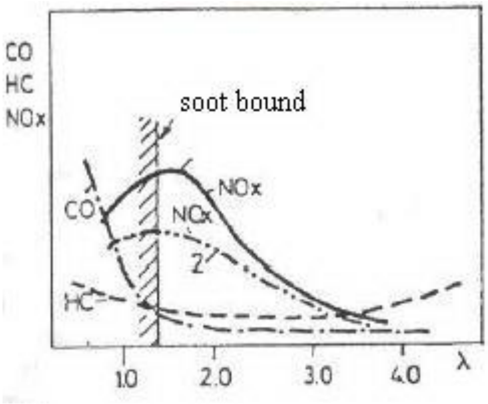

Figure 2. Toxic components in diesel exhaust gases vs. excess-air factor

Combustion in diesel engines is initiated when the injector starts to discharge fuel. The point at which combustion actually starts, as defined relative to TDC has a decisive influence on combustion temperature with consequences on NO_X formation.

Figure 2 shows how the emission of gas toxic components acts in the exhaust gases of diesel engine, in function of average compound of the mixture that engine works with. Basically, with the higher engine load, i.e. decreasing excess-air factor, toxic emission share rises.

Carbon monoxide (CO) is appeared as a result of locally insufficient air (oxygen) during combustion, and it’s emission highly rises during maximum load, when the emission of NO_X also rises because of the increase of combustion temperature, still sufficient amount for oxidation of nitrogen. The emissions of unburned hydrocarbons is less dependent on the composition of the mixture, although it is also the highest during maximum load. In any case, the main problem of exhaust emission from diesel engine are still particles of smoke and NOx which are mainly targeted legislation.

Smoke emission is usually solved by intensifying the flow, and NO_X emission by adopting the later pre-injection, thereby reducing the maximum combustion temperature.

EMISSIONS CONTROL

The methods used to alter the composition of the exhaust gases from spark-ignition engines are divided into two basic categories: engine design measures and exhaust-gas treatment (aftertreatment) (Bosch R., 1993).

Engine design measures is consists of, respectively: fuel metering, mixture formation, uniform distribution of mixture, exhaust-gas recirculation (EGR), valve timing, compression ratio, combustion-chamber design, ignition system and crankcase ventilation.

EGR or exhaust-gas recirculation means that the exhaust-gas can be conducted back to the combustion chamber to reduce peak combustion temperatures. Higher combustion temperatures overproportionally increase in the formation of NO_X. EGR can be implemented in either of two ways: (1) internal exhaust-gas recirculation is achieved with appropriate valve timing (overlap), (2) external exhaust-gas recirculation employing controlled EGR valves.

Exhaust-gas aftertreatment is provided in two ways: thermal afterburning and catalytic afterburning.

Thermal afterburning was initial attempts to reduce emissions employing a specific residence time at high temperatures for burning the exhaust-gas components which failed to combust during normal combustion in cylinders. In the rich range (λ=0,9÷1,0) process occurs with supplementary air injection. In the lean range (λ=1,1÷1,2) the residual oxygen in the exhaust gas is sufficient for afterburning. Thermal afterburning with air injection can be used to achieve compliance with tomorrow's more stringent limits by reducing emissions in the warm-up phase.

Catalytic afterburning needs catalytic converter located in the engine's exhaust system. The catalytic converter is composed of a carrier substrate, which serves as a base for the catalytic material, mounted within a housing using vibration-proof, heat-insulated supports. For automotive catalytic converters, the core is usually a ceramic monolith with a honeycomb structure. The active catalytic layer consists of small quantities of precious metals (platinum, palladium and rhodium). Platinum (Pt) is the most active catalyst and is widely used. Rhodium (Rh) is used as a reduction catalyst, palladium (Pd) is used as an oxidation catalyst, and platinum is used both for reduction and oxidation.

The three-way or selective catalytic converter with lambda closed-loop control has proven to be an effective concept for exhaust-gas aftertreatment. It is capable of providing the required reduction of all three pollutants provided the engine is operated with a stoichiometric mixture and has three simultaneous tasks: 1) reduction of NO_X to nitrogen and oxygen, 2) oxidation of CO to carbon dioxide, 3) oxidation of unburnt HC to carbon dioxide and water.

The composition of the exhaust gases is monitored with an exhaust-gas oxygen sensor (EGOS), the so-called Lambda sensor (Bosch R., 1993). This reflects a stoichiometric mixture (λ=1) by generating a voltage peak, thus indicating whether the mixture is richer or leaner then λ=1.

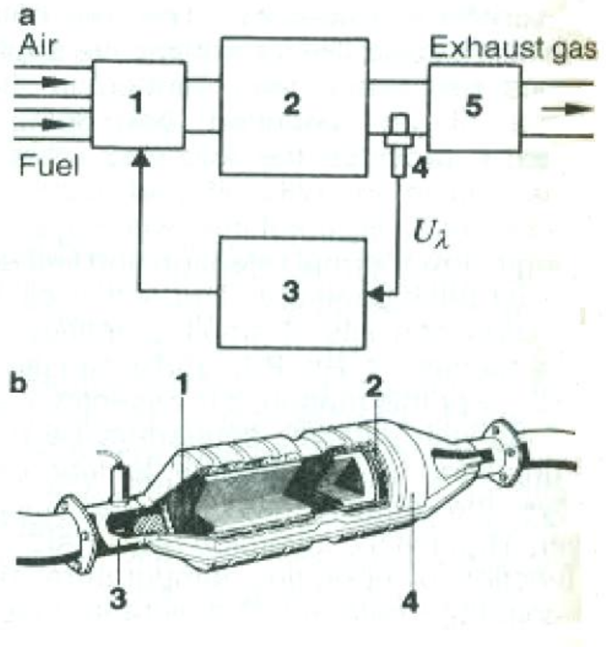

Figure 3. Emission treatment with 3-way catalytic converter and lambda oxygen sensor a) Schematic illustration 1.Fuel-metering device, 2.Engine, 3.ECU, 4.Lambda sensor, 5. 3-way catalytic converter, U_λ sensor voltage b) 3-way catalytic converter, 1.Ceramic monolith, 2.Wire screen, 3.Lambda sensor, 4.Housing

For diesel engines (Petrović, P. et al., 2000, Petrović, P., Marković, Lj., 2002, 2007), the most commonly used catalytic converter is the Diesel Oxidation Catalyst (DOC). This catalyst uses O_2 (oxygen) in the exhaust gas stream to convert: CO to CO_2, and HC to CO_2 and water. These converters often operate at 90% efficiency and helping to reduce visible particulates (soot). These catalyst are not active for NO_X reduction because any reductant present would react first with the high concentration of O_2 in diesel exhaust gas. There are two techniques that have been developed for the catalytic reduction of NO_X emissions under lean exhaust conditions: 1) selective catalytic reduction (SCR) and 2) the lean NO_X trap or NO_X adsorber.

Instead of noble metal most manufacturers use reagent such as ammonia to reduce the NO_X into nitrogen. Ammonia is supplied to the catalyst system by the injection of urea into the exhaust, which then undergoes thermal decomposition and hydrolysis into ammonia. One trademark product of urea solution, also referred to as Diesel Exhaust Fluid (DEF), is well known AdBlue.

Diesel exhaust contains relatively high levels of particulate matter (soot), consisting in large part of elemental carbon, (Petrović, P., Marković, Lj., 2001). Catalytic converters cannot clean up elemental carbon, so particulates are cleaned up by a soot trap or diesel particulate filter (DPF). Contemporary DPFs can be manufactured from a variety of rare metals that provide superior performance at a greater expense. As the amount of soot trapped on the DPF increases, so does the back pressure in the exhaust system. Periodic regenerations (high temperature drivings) are required to initiate combustion of the trapped soot and thereby reducing the exhaust back pressure. During the re-generation cycle, most systems required the engine to consume several litres of fuel in a relatively short amount of time in order to generate the high temperatures necessary for the cycle to complete.

EMISSIONS STANDARDS

European emission standards define the acceptable limits for exhaust emissions of new vehicles sold in EU. The emission standards are defined in a series of European Union directives staging the progressive introduction of increasingly stringent standards. Currently, emissions of nitrogen oxide (NO_X), total hydrocarbon (THC), non-methane hydrocarbons (NMHC), carbon monoxide (CO) and particulate matter (PM) are regulated for most vehicle types. For each vehicle type, different standards apply. Compliance is determined by running the engine at a standardised test cycle. Non-compliant vehicles cannot be sold in the EU, but new standards do not apply to vehicles already in use. No use of specific technologies is mandated to meet the standards, though available technology is considered when setting the standards.

Within the EU, road transport is responsible for about 20% of all CO_2 emissions, with passengers cars contributing about 12%. The target fixed at Kyoto Protocol was an 8% reduction of emissions in all sectors of the economy compared to 1990 levels by 2008÷2012. Relative CO_2 emissions from transport have risen rapidly in recent years, from 21% of the total in 1990 to 28% in 2014., but currently there are no standards for limits on CO_2 emissions from vehicles. EU transport emissions of CO_2 currently account for about 3,5% of total CO_2 emissions.

Emission standards for light duty vehicles are given in Table 1, well known as ECE regulations or stages.

Table 1: Stages of Euro standards for light duty vehicles

STAGES	DATE	EU DIRECTIVES, STANDARDS
Euro 1	1993	for passenger cars - 91/441/EEC
		for passenger cars and light trucks - 93/59/EEC
Euro 2	1996	for passenger cars - 94/12/EC (& 96/69/EC)
		for motorcycle - 2002/51/EC (row A) - 2006/120/EC
Euro 3	2000	for any vehicle - 98/69/EC
		for motorcycle - 2002/51/EC (row B) - 2006/120/EC
Euro 4	2005	for any vehicle - 98/69/EC (& 2002/80/EC)
Euro 5	2008/2009	for passenger cars and commercial vehicles - 715/2007/EC
Euro 6	2014	

EU Regulation No 443/2009 sets an average CO_2 emissions target for new passenger cars of 130 grams per kilometre. The target is gradually being phased in between 2012 and 2015. A target of 95 g/km will apply from 2021. For light commercial vehicle, an emission target of 175 g/km applies from 2017, and 147 g/km from 2020.

Emission standards for passenger cars and light commercial vehicles (category M) are summarised in the Table 2, (www.unece.org).

Table 2: Emission standards for passenger cars and light commercial vehicles

	DATE	CO	THC	NMHC	NO_X	$HC+NO_X$	PM
Diesel							
Euro 1	July 1992	2,72 (3,16)	-	-	-	0,97 (1,13)	0,14 (0,18)
Euro 2	January 1996	1,0	-	-	-	0,7	0,08
Euro 3	January 2000	0,64	-	-	0,50	0,56	0,05
Euro 4	January 2005	0,50	-	-	0,25	0,30	0,025
Euro 5	Sept. 2009	0,50	-	-	0,180	0,230	0,005
Euro 6	Sept. 2014	0,50	-	-	0,080	0,170	0,005
Petrol(gasoline))							
Euro 1	July 1992	2,72 (3,16)	-	-	-	0,97 (1,13)	-
Euro 2	January 1996	2,2	-	-	-	0,5	-

Euro 3	January 2000	2,3	0,20	-	0,15	-	-
Euro 4	January 2005	1,0	0,10	-	0,08	-	-
Euro 5	Sept. 2009	1,0	0,10	0,068	0,060	-	0,005
Euro 6	Sept. 2014	1,0	0,10	0,068	0,060	-	0,005

Whereas for passenger cars, the standards are defined by vehicle driving distance, g/km, for trucks they are defined by engine output energy, g/kWh, and is not comparable.

Emission standards for trucks and buses are given in Table 3. The official category name is heavy-duty diesel engines, which generally includes trucks and buses, (www.unece.org).

Table 3: Emission standards for trucks and buses

	DATE	TEST CYCLE	CO	HC	NO_X	PM	SMOKE
Euro 1	1992, < 85kW	ECE R-49	4,5	1,1	8,0	0,612	-
	1992, > 85kW		4,5	1,1	8,0	0,36	-
Euro 2	October 1996		4,0	1,1	7,0	0,25	-
	October 1998		4,0	1,1	7,0	0,15	-
Euro 3	October 1999, EEVs only*	ESC&ELR	1,0	0,25	2,0	0,02	0,15
	October 2000	ESC&ELR	2,1	0,66	5,0	0,1	0,8
Euro 4	October 2005		1,5	0,46	3,5	0,02	0,5
Euro 5	October 2008		1,5	0,46	2,0	0,02	0,5
Euro 6	31.December 2013		1,5	0,13	0,4	0,01	-
	*Enhanced environmentally Friendly vehicle						

As Europe's requirements for vehicles head toward of 98 g/km of CO_2 by 2020, some experts says the only way the carmakers can achieve it and produces vehicles is with plug-in vehicles. Many EU member states have responded to this problem by exploring the possibility of including electric vehicles related infrastructure into their existing road traffic system. Some of states has begun its "plugged-in-places" in order to create a network of charging points for electric vehicles.

CONCLUSIONS

Combustion in IC engines is followed by exhaust emissions. The exhaust gas contains the toxic, dangerous and unpleasant components: carbon monoxide, nitrogen monoxide, hydrocarbons and particulates. European emission standards define the acceptable limits for exhaust emissions of new vehicles since 1992. in a series of European Union directives staging the progressive introduction of increasingly stringent standards, referring stages from Euro 1 to Euro 6. In addition, in 2009 EU Regulation sets CO_2 emissions target for new cars.

The engine and vehicle manufacturers follows emission standards by improving engine-vehicle design and management, optimal power management and distribution, and developing new generation of vehicles such as hybrid drives, electric drives, fuel cells and so on. Many of them are the vehicles of future.

REFERENCES

Petrović, P., Marković, Lj., Mačvanin, M., (2000). Identification of toxic parameters of unregulated diesel engine emission, ISATA, Dublin, Ireland.

Petrović, P., Marković, Lj., (2001). Toxic parameters of unregulated diesel engine emission control, ATT-Automotive and Transportation Technology Congress and Exhibitions, Barcelona, Spain.

Bosch, R., (1993). Automotive Handbook, 3rd edition.

Tomić, M., Petrović S., (2004). Motori sa unutrašnjim sagorevanjem, Mašinski fakultet u Beogradu.

Tomić, M., (2012). Oprema motora, Mašinski fakultet u Beogradu.

Petrović, P., Marković, Lj., (2007). Interakcija motora i motornih ulja, Savez inženjera i tehničara Srbije.

Petrović, P., Marković, Lj., (2002). Stanje i trend razvoja emisije izduvnih gasova dizel motora traktora i vanputne mehanizacije, naučni časopis Poljoprivredna Tehnika, br.1, 2. Poljoprivredni fakultet, Beograd.

http://www.unece.org

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EMISSIONS OF RELOADING MECHANIZATION IN TERMINALS

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ABSTRACT

The emission in terminals is generated from several sources, depending on the type, location, kind and the number of material handling equipments (means of water transport, terminal tractors, reloading mechanization, locomotives, road vehicles in removal and cartage), as well as of other non road machines used in the terminal (compressors, changers, pumps, fans etc.). The size of the emission depends on the amount of work, kinds of tecnical operations and the degree of means load. According to EPA, through two groups of sources, the influence of several specific pollutants is estimated ((NOx, CO, PM10, PM2.5, SO) and of those which create the so–called «greenhouse effect» - GHG (CO_2,CH_4 i N_2O). When reloading, the emission is expressed by the transport work unit (TEU/per.,t/per), according to the time of exploiting a certain engine in the reloading cycle. Some reloading devices have more engines for certain tecnological operations functioning alternately. The aim of this paper is to indicate the approaches of emission estimate with mostly used reloading conventional means in terminals (stackers and RTG) with diesel drive. The emission factors used as «standard» are in accordance with the IPCC principles from 2006.

Key words: *Terminals, reloading devices, emission factors, emissions.*

INTRODUCTION

The terminals in freight transport are functionally structured, built objects in which the primary, starting and finishing operations in the transporting process are being performed among various vehicles, same or different means of transport, where the conversion of flows is performed, with cargos arriving and leaving the transporting vehicle or the terminal, where the cargo consolidation and distribution are performed, as well as supplying the fuel, vehicle tecnical exploitation and/or other services. They are located either in the end of transport lines(routes)of vehicles, ie on the modal net, or they regularly along the network and very often inside the city itself as collective and distributive centres. Depending on the type, terminals have corresponding infrastructural elements with equipment for special purposes. According to SRPS ISO 5053:2001, the classification and the coding of reloading devices were performed, according to different marks, location, construction of transport facilities, kinds of technological operations performed, types of material (for individual, scattered, liquid and gaseous) etc. In most terminals, stackers (forklifts, ISO code 3.1.3.1.1 and gantry stackers, ISO code 3.1.3.2.3) are used.

If a terminal is declared as a system, its functioning can be described by a few interdependant processes and/or subprocesses through which it performs its functions. The basic subprocess is the reloading (loading, direct reloading and/or unloading), where the reloading devices emit the pollutants. Depending on the type of drive (diesel, electro, LPG), technical characteristics of reloading devices and the tecnological working process, the elements of emission estimate are different. The gantry stackers (cranes) have usually four built-in engines (two for moving the crane on each up right pillar, one for lifting and lowering the load on the spreader or hook and one engine for horizontal movement trolley. All these engines don't work at the same time, which means that the segments of their work should be carefully specified. Classic forklifts have only one one engine , except for some special types which have two.

The aim of the paper is to point to some approaches in the emission estimate at chosen typical devices with diesel drive as the basic means in a certain family and the most used reloading devices in terminals. When collecting certain data, it is necessary to be familiar with the working technology of a terminal, functional characteristics of devices and to establish precisely the engagement of some drive elements of devices which participate in performing certain processes.

Basically, the emission estimate is performed in a few steps: establishing the research aims, the choice of estimate approach and defining the boundaries of research, collecting the necessary data and choosing the emission factors, verification and publishing the results obtained.

ELEMENTS FOR MISSION ESTIMATE

When a mission is estimated in the transport chain, besides the emission in pure transport, there is also the emission at locations of starting and finishing operations, ie in terminals on the transporting road as well as at the sender's and recipient's. There are many different types of transporting chains which depend on the aspects of transport included in the chain realization and hence the number of terminals, figure 1. It is considered that up to 24 reloads can be realized in the international transport.

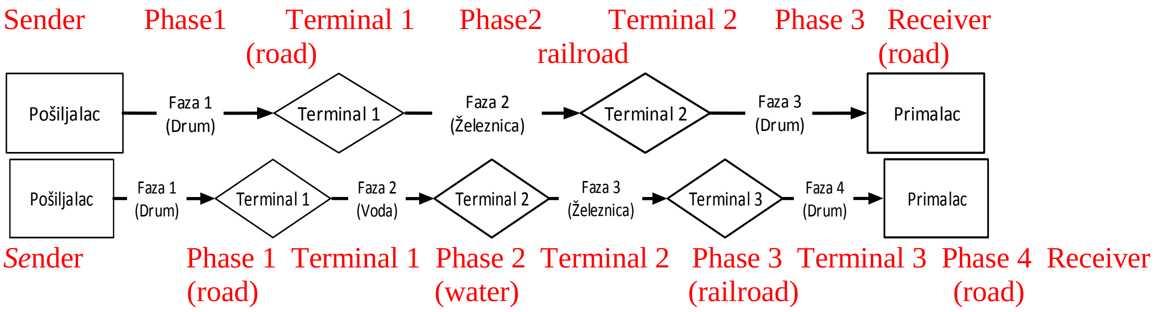

Figure 1.The display of terminal position at bimodal and trimodal transporting chain

In the first approach, it is necessary to define the percentage of load of certain operating elements (F_i) during the cycle of conventional diesel RTG (Rubber Tired Gantry), figure 2.

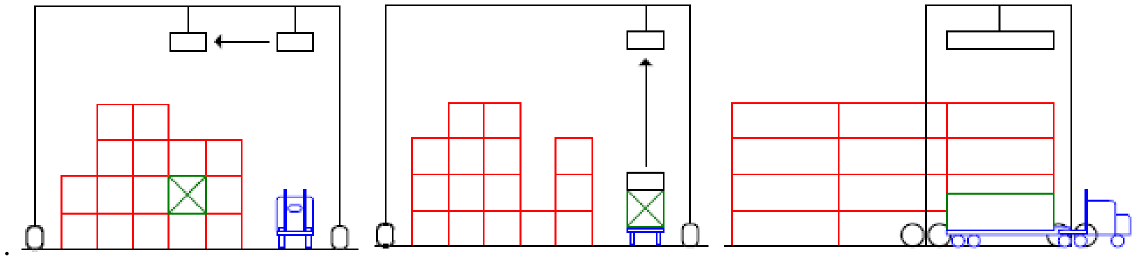

Figure 2. The display of initial and final situation in the reloading cycle

The time of cycle duration in the loading state (t^{tov}) is:

t_{c1} tov $= t_1+t_2+t_3+t_4+t_5+t_6=28+14+20+14+10+16 = 102$ s, where :

t_1 - time of the movement spreader (9 sec) with lower hoist to pick up, 28s,

t_2 – time of lifting the load from the floor to the transmission height, $t_2=H_d/V_d$, 14 s,

t_3 – time of removing the load by crane and cart (wagon) to the place of disposal

$t_3 = L_{pr}/V_{pr}= 20$ s,

t_4 – time of lowering the load, $t_4 = 14$ s,

t_5 – manoeuvring around the place of unloading, 10 s,

t_6 – load disposal, 16 s.

Part of the cycle in an empty state (t^{pr}) for the new operation is:

t_{c1} pr = $t_7+t_8+t_9+t_{10}$=18+15+20+10 = 63s, where:

t_7 – lifting of the empty gripping device, $t_7(H_d/V_d)$=17,6 ⇒ 18s,

t_8 – moving the crane for the new operation, t_8 (L_{pm}/V_{pm}), 15s,

t_9 – time of lowering to the place of gripping, t_9 (H_s/V_s), 20s,

t_{10} – time of manoeuvring for the new operation, 10 s.

The total duration of reloading (loading) with moving the crane to a different manipulative place is 165s , of which 62% and in an empty state 38% during the cycle, table 1.

Table 1: The display of time and power of certain RTG stacker elements

Part of process	Time (s)	Participation	Power needed (kW)	Total power (kW)
Hoist - Lifting and lowering	76	0,46	100-350+empty	113-363
Trolley	38	0.23	15 + empty	28
Crane loaded	36	0,22	45 + empty	58
Idle	15	0,09	13	13

Using the time in the work regime and the volume of power, the theoretical loading factor for nominal crane power 450 kW can be defined from the relation:

F_i (RTG) = [P_i (Hoist)·46.0% + P (trolley) · 23.0% + P (crane) · 22.0% + P (Idle · 9.0%]
The lower power volume:
(113 kW · 0.46) + (28 kW · 0.23) + (58 kW · 0.22) + (13 kW · 0.09) = 68.56 kW/ 450kW = 16%
The higher power volume:
(363 kW · 0.46) + (28 kW · 0.23) + (58 kW · 0.22) + (13 kW · 0.09) = 191.56 kW/450 kW = 41%

Unlike most of the reloading devices, the forklifts use one drive engine (diesel, electro, LPG, CNG, bio-diesel or hybrids as the electro-diesel or diesel-hydraulic) for moving and manipulating the load. Because of the required air quality in closed facilities, the use of diesel is limited and, regardless of the potentials of modern filters, the forklifts with electro drive are mostly used. By analysing the duration of the forklift performance during the loading ((36kW, V_k^{tov}=15km/h, V_k^{pr}=20km/h, h_d=3m, V_d=0,2 m/s (empt–load.); H_s=3m; V_s=4m/s (empt-load.); t''_1=15s; t'_3=3 s; t_4=20s; t_7=18s; τ_{sm}=8h, sa 26 turns/h), the cycle duration when loading and in an empty state ,ie t_c=70+68=138s. The loading factor is approximately 50%. According to experiences from abroad, the loading factor for some mechanization devices is as follows: cranes 0.43, excavators 0.57, container manipulators 0.59, loco tractors 0.55 and the other equipment in average 0.51.

The next element needed for the mission estimate is the emission factor (E_f) which can be used as «standard» in the estimation , according to the IPCC principles from 2006 or via LCA (Life Cycle Assessment, ISO 14040/44:2006) when the whole life cycle of energy carrier in all according to EN 16001:2009 is taken into account. The standard emission factors are based on the obligatory carbon content in every fuel of which CO_2 is the most important, and the CH_4 i N_2O emissions shouldn't be calculated. Anyway, if they are estimated , the following mass relations can be used: 1 t CH_4 - 21 t CO_2-eq and 1 t N_2O – 310 t CO_2-eq (according to IPCC,2007). LCA is a more reliable approach some important documents are based on, eg. Thematic Strategies on Natural Resources and Waste, Ecodesign Directive and Ecolabel Regulations. The standard CO_2 emission factor (acc. to IPPC,2006) and CO_2 equivalent LCA emission factors (from ELCD) for drive fuels are respectively for petrol ((0,249 and 0,299) in tCO_2/MWh and diesel ((0,267 i 0,305) in tCO_2/MWh. The emission factors are available in detail in data base ELCD at:
http://lca.ec.europa/lcainfohub/datasetList.vm?topCategory=End-oflife+treatment&= Landfilling.

The emission factors are usually defined as the quantity of pollutants expressed in mass units divided by a unit mass value, volume, distance or the duration of activity the emitted pollutant derives from.

The emission factors are expressed in different ways: g/kWh$_{r,}$ or g/MWhr, fuel consumption g/kg etc. In most cases , the emission factors demand a statistical analysis of average value gained by measuring larger quantities, volumes, ie greater distances or a longer realization period of the pollution process and not for only one type of pollution source but for more kinds of pollutants which are similar or even the same. Calculations are based on the experiential data base, average values and a good understanding of a certain process, table 2. In any case, the appliance of emission factors is an outstanding method for getting quick or global estimates.

Table 2: Average emission factors of manipulative devices with diesel drive

Pollutant g/kWh$_r$	Power in kW							
	0-20	20-37	37-75	75-130	130-300	300-560	560-1000	>1000
NOx	14,4	14,4	14,4	14,4	14,4	14,4	14,4	14,4
N_2O	0,35	0,35	0,35	0,35	0,35	0,35	0,35	0,35
CH_4	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05
CO	8,38	6,43	5,06	3,76	3,00	3,00	3,00	3,00
NMVOC	3,82	2,91	2,28	1,67	1,30	1,30	1,30	1,30
PM	2,22	1,81	1,51	1,23	1,10	1,10	1,10	1,10
NH_3	0,002	0,002	0,002	0,002	0,002	0,002	0,002	0,002
FC	271	269	265	260	254	254	254	254

Source: [8]

When estimating the complete terminal mission, the emission factor is easily transformed and expressed in kg/kWhr, ie kg-t/period. The size of the emission factor depends on the degree of load and the type of fuel (sulphur content) which the device uses. For machines with LPG fuel, standard emissions factor are noted in table 3.

Table 3:Average emission factors of manipulative devices with LPG drive

Pollutant g/kWh$_r$	Power in kW							
	0-2	2-5	5-10	10-18	18-37	37-75	75-130	130-300
NOx	4,00	4,00	4,02	4,04	4,08	4,15	4,28	4,58
N_2O	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03
CH_4	5,30	2,25	1,40	0,96	0,71	0,54	0,46	0,39
CO	2300	871	567	433	370	336	320	309
NMVOC	106	45,1	28,7	19,1	14,1	10,9	9,10	7,78
NH_3	0,002	0,002	0,002	0,002	0,002	0,002	0,002	0,002
FC	430	409	396	386	376	366	358	348

It is important to notice that the values of some pollutants don't change significantly regardless the available output power of the drive engine. Beside the listed pollutants, heavy metals which are being emitted, such as Cadmium 0.01, Copper 1.7, Chrome 0.05, Nickel 0.07, Selenium 0.01 and Zinc 1 can also be analyzed, all in mg/kg of fuel.

If more families of manipulative devices with different supporting equipment are circulating in a terminal, an estimate of the emission factors for each kind of devices should be performed and their dimensions coordinated in the given period of time. Besides, it is important to know precisely the statistical data about the kind of fuel (mass or volume), kind of drive and the power (locomotives 200 kW to 2000 kW, tractors 25 kW to 75 kW, cranes 100kW to 250 kW, stackers from 20kW to 120 kW, compressors from 10kW to 120 kW, the year of production and the consumption by the types of devices and their total number, structure and the average cycle duration, content of carbon in the basic and in the improved fuel, the age of device , the load dimensions and mass etc.

EMISSIONS IN TERMINALS

The complete emission in reloading is expressed in different measuring units (g/yearly, g-kg-t/km, kg/TEU, g-kg/t fuel, t/ha/monthly etc) and the measuring unit used for expressing capacity in a concrete chain and in a certain period of time (day, month, year) is used. The emission of reloading devices can be estimated by three basic approaches, by:

- measuring the specific device load during the typical work cycle,
- a direct emission measuring using the electronic control module during the work, installed on the exhaust pipe, and
- as a product of the average fuel consumption and pollutant emission by a fuel consumption unit.

The complete yearly emission of manipulative devices can be estimated by the expression:
$E_i = \sum(N_{ri} \cdot P_{kWi} \cdot E_{fi} \cdot F_{ii} \cdot T)$ (t/year), where:
E_i –the mass of pollutants' emission in the given work period,
N_r – number of working devices,
E_f – the emission factor (g/kWhr),
P_{kW} – the average maximum strength of a certain type /family of devices (kW),
F_i –the typical load degree of each device (%), according to ISO DP 8178,
T – the effective working time in the given period (h_r/year)
i – the type of device.

Most often, the emission of CO_2 in a certain period is estimated, table 4. According to [10], the emission can be estimated as a product of CO_2 emission by a net tone of a reload, the mechanization capacity and the average degree of device utilization by capacity. The effective working time implies everyday eight-hour work and 22 working days a month.

Table 4: The CO_2 emission estimate of some typical devices

Kind of device and the drive	Power kW	Emission factor	Degree of load	Emission
Diesel RTG	450	661	50	314,12
Crane	99	145	26	7,88
Diesel stacker	88	129	30	8,10
Petrol stacker	30	44	30	0,84
LPG stacker	30	43	30	0,82
Bulldozer	112	164	40	15,52
Grader	149	219	37	25,50
Tractor in ind.	62	91	30	3,60
Compressor	70	103	60	9,14

Ef for typical diesel engines: 661 g CO_2/kWhr (for specific consumption 209 g/kWhr), of C content 86.3% in GHG: 209 g/kWhr·0.863·(relation mol.mass 44/12) = 661g/kWhr

In the total summary of single emissions, depending on the structure of the load handling device, we come to the emission of pollutants in the terminal. The same procedure can be used for estimating the other emissions. The average number of emissions in the container reload can be estimated by the number of operations performed for cranes 0.002 t/ CO2 /operation and/or the container manipulator (RS) 0.007tCO»/operation (loading, unloading or just reloading).

For the emission estimate, besides [2], there are softwares as the SoFi, offered by PE INTERNATIONAL's COPERT IV, based on MS Windows surroundings, Versit+emission model EnViVer based on VISUM GIS, E coPorts Self-diagnosis Method and others with the world data bases of the highest quality which supply the companies with both the emissions and the financial effects of sustainability, suggestions how to improve the sustainability of operations, supply chains and/or the quality of services.

CONCLUSION

The diversity of loading mechanization and of other additional equipment in terminals situated in urban areas shows the growing importance of emissions' reduction and their influence both onthe air and the water. In traffic, as the final object , the zero emission vehicle has appeared for years (*ZEV – Zero Emission Vehicle*), although it is a fact that there isn't a human product which has no influence on the environment since the humans themselves produce $CO_{2,}$ about 4t/year of it. Recently, the new object emission for vehicles: *NZEV* – Near *ZEV,* ei near the minimum and *EZEV* – equivalent to a minimum emission, have been introduced.

For emissions' reduction, the application of the new «greener» technologies is required. There are different ways to influence the emission reduction in terminals, such as: the improvement of mechanical devices tecnical characteristics by families, broader application of hybrids which are slower but with a significantly reduced emission, development of sustainable fuels with reduction of carbon and sulphur intensity, rational use of devices capacity according to their capacity and time, optimum managing of SCM (maximum accordance of requests) etc. Today, the hybrid RTG reloading devices „E-One2“ of zero emission are produced, with fuel saving of 70% , of significantly smaller mass, reduced maintenance of parts such as the batteries, starters, alternators, smaller replacements of the air and fuel filters , the NO_x reduction 78% to 90%, the PM emission reduction 62 % to 70 % etc. There is a similar situation in forklift production.

In the following period it is necessary to provide the stimulus for the new technologies implementation and inovations in reloading and the systems which will reduce the obstacles in measuring their emissions, especially $CO_{2,}$ enable the further development of e-load till the harmonization and standardizing of data and information exchange are performed, tracking and obligatory expressing of emissions in all kinds of terminals, the acquisition of systems which support the carbon-dioxide estimate (automatic data collecting etc.), data integration by using the advanced ICT technologies (RFID, bar codes, digital tachograph etc.) which will create the conditions for a more reliable pollutants' estimate, the interface improvment and the electronic data exchange in terminals and among the potential users of terminal services,coordination and signing the agreement with major users about the standardized systems usage which can increase the technologies profitability together with pollutants' emission reduction.

LITERATURE

Air emission calculations and methodology, Virginia Offshore Wind Technology Advancement Project (VOWTAP), Tetra Tech, Inc. Glen Allen, 2013.

Cofret, Carbon Footprint of Freight Transport, Existing methods and tools for calculation of carbon footprint of transport and logistics, 7 FP Final V 1.0, VTT Technical Research Centre of Finland. 2011.

Combined Transport – CO_2 Reduction. Pact programme. International Union of Combined Road-Rail Transport Companies (UIRR), Brussels, Belgium, 2001.

Davidović B.,Tehnologije kombinovanog transporta”, Vedes, Beograd, 2012.

Davidović B., Unutrašnji transport – Intralogistika, Intelekt, Beograd, 2012.

Guidelines for Measuring and Managing CO_2 Emission from Freight Transport Operations. European Communities Trade Mark Association, Issue 1. Brussels. 2011

McKinnon A., Piecyk M., Measuring and Managing CO_2 Emissions of European Chemical Transport. Logistics Research Centre Heriot-Watt University EDINBURGH, UK. 2010.

Emission Inventory Guidebook, Part Other mobile sources and machinery, US-EPA 1996.

Procene količina emitovanih gasovitih zagađujućih materija poreklom od drumskog saobraćaja primenom Copert IV modela Evropske agencije za životnu sredinu. Institut saobraćajnog fakulteta, Beograd, 2010.

Ozal M. Ekol logistics intermodal route, Congess of Southeast European Freight forwaders and logistics operators, Istanbul, 2011.

Özsalih H., A methodology for transport buying companies to estimate CO_2 emissions in transport: Application in Unilever European Logistics, Industrial Engineering - Bilkent University, Ankara, 2009.

Piecyk M. et al. Modelling the future impact of road freight transport on the environment. Heriot Watt University. Edinburg. 2007.

Pravilnik o tehničkim merama i zahtevima koji se odnose na dozvoljene emisione faktore za ispraljiva organska jedinjenja koji potiču iz procesa skladištenja i transporta, (“Službeni glasnik RS”, broj 36/09).

Vujičić A., Zrnić N., Jerman B., Ports Sustainability: A life cycle assessment of Zero Emission

Cargo Handling Equipment. Strojniški vestnik - Journal of Mechanical Engineering 59(2013)9, 547-555.Ljubljana.

Uredba o uslovima za monitoring i zahtevima kvaliteta vazduha. „Sl.Glasnik RS“, broj 11/2010.

World Ports Climate Initiative, Environmental Ship Index ESI. 2010.

Zakon o zaštiti vazduha, „Sl.Glasnik RS“, broj 36/2009.

Linkovi

http://www.havakalitesi.cevreorman.gov.tr/english/training

http://www.lml.rivm.nl/data/kaart/actueel.html

http://www.kvvm.hu/olm/info.php?id=6

http://www.cofret-project.eu

MANAGEMENT OF SOLID URBAN WASTE

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APPLICATION OF OXIGEN ENRICHED AIR ON GRATE INCINERATORS

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ABSTRACT

Urban areas are characterized also by a large amount of waste production. Very often, best available technologies are applied to turn it into energy (waste to energy procedures). Environmental protection in urban areas is deeply affected if these options are applied or not. Thus, grate incinerators are widely applied for the use of the energy content of waste (bio-waste or mixed not selected waste) by burning. Form and size of the grate determine the size of the cross-section of the incineration chamber. Combustion takes place above the grate in the incineration chamber, under support of primary and secondary air injection. The detailed design of incineration chamber demands certain flexibility, as the combustion process change unpredictable with the fuel characteristics. For obtaining a higher efficiency for the incineration process, the primary air used for combustion the authors propose to enriched the primary air with oxygen. Rapid and efficient combustion can result in very low and controllable CO concentration in the flue gas (meaning a higher efficiency of combustion, up to 100%) and reduction of other combustion related pollutant emissions (mainly unburned compounds based on C, H and N). On the other side, by using oxygen enriched air, the volume of exhaust gases will be reduced proportionally to the rate 79 by volume percentage of Nitrogen in the air, that implies as consequence a smaller size of the flue gas treatment plant from the final end of the incinerator, not mentioning also the benefit that one has the possibility to increase the mass flow of the incinerated waste. In conclusion, the article focuses in general to the benefits of a modern technology of using O2 enriched air support during combustion of municipal waste. The case study approached will confirm the conclusion that by this means benefits concerning air quality improvements in urban areas are occurring, by reducing the amount of possible pollutant exhaust at such kind of sources.

Key words: *grate incinerator, oxygen enriched air, efficiency.*

INTRODUCTION

Municipal solid waste incineration (MSWI), following a long history, remains today the main suitable solution for waste management. Environmental issue is becoming more and more severe all over the world and result in a strong demand for environmentally friendly waste incineration plants. A large effort directed towards this goal has been devoted in the last few decades. One of significant a breakthrough in waste incineration has been the introduction of oxygen enriched air. In recent years, the topic of oxygen combustion in waste incinerators has experience a strong come back, due to the appearance of new drives. Oxygen enrichment is an effective tool in reducing emissions, and in using low calorific fuels.

This technology has been applied with success on new MSWI plants and it proves to be one of the best solutions to significant reduction of emissions in the same time with the production rate increase and smaller demand of flue gas treatment plants.

In this paper, is approached the implementation of oxygen enriched air on industrial scale incineration plants to demonstrate the validity of technology and reduction of pollutant emissions to the environment using as a study case the MSWI from Arnoldstein Austria and accompanied by a literature review of impact of oxygen in waste incinerators is presented.

IMPACT OF OXYGEN ENRICHMENT ON MSW COMBUSTION

Oxygen boosting

The incineration process that is using oxygen enriched air with an amount of oxygen in range of 22-30% may be referred-to as oxygen boosting. For MSWI the oxygen boosting is used in the primary air supply into or directly above the waste bed. The manner of primary air supply is directly related to the incineration technology. In the grate systems it is supply trough the grate into the waste bed to:

- Bring the necessary air to the different zones of the grate where the reactions occur and ensure the homogenous and sufficient distribution inside the waste bed which improves bottom ash burnout;
- Cooling of the grate bars to prevent slagging and corrosion.

In MSWI grates the primary air flow is determined primarily by the oxygen requirement and not by the grate cooling requirements. Separating the supply of the primary air to the different zones within a grate incinerator, allows the separate control of each of the zone. This allows a flexibility and smooth running on each process that occurs on the grate. (BAT et.al. 2006)

Features of the system

The thermal treatment of waste with grate fired based systems has become the preferred system for the suitable treatment of residential waste worldwide. This is due to the use of the energy content of the waste as well as the quality of the products and residues produced. By using modern technologies of incineration and waste gas cleaning methods, the bottom ash and gaseous emissions are reduced on a minimum. This modern technology presumes to implement the oxygen boosting combustion that incorporates the oxygen-enriched primary air and the recirculation of an amount of the flue gas as secondary air (Kira et.al. 2010). Flow diagram is schematically shown in Fig. 1.

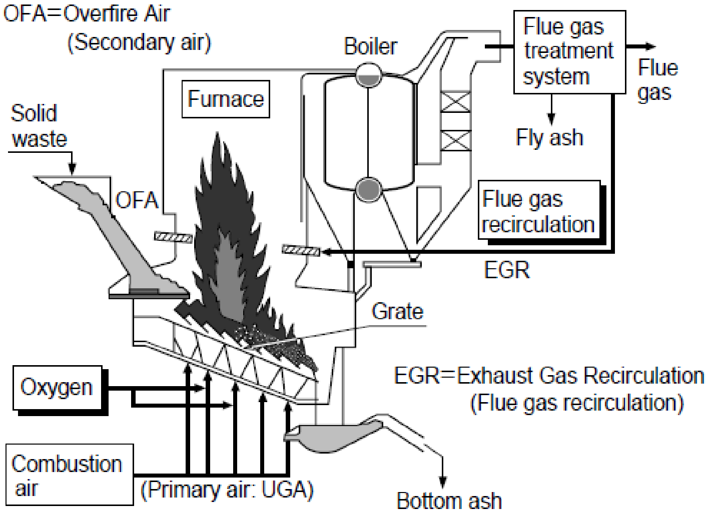

Figure 1. Flow diagram of oxygen enriched combustion system

Typical features are summarized as follows:

- Oxygen boosting air promotes intense firing of solid waste bed on the grate so the residual content of organic pollutants (CO, DXNs, etc.) in the bottom ash is lowered, that leads to a stronger fusion of the bottom ash which yields better elution properties.
- Leached properties of the resulted bottom ash are considerable improved, so on site landfilling is accepted.
- Using the oxygen boosting on the primary air leads to flame stabilization on the grate especially needed when incinerated waste has a low calorific value.

- Recirculation of the flue gas as secondary air improves the mixing of combustion gas in the furnace to complete gaseous combustion and also prevents increase of NOx. (Kira et.al. 2010)
- Substantial decrease in the flue gas flow rate allows compact design of auxiliary equipment such as boilers and flue gas treatment (FGT) facilities. (Kira et.al. 2010)

MSW combustion process

Waste is generally a highly heterogeneous material, consisting essentially of organic substances, minerals, metals and water. Temperature range of oxidation process for grate incinerators is generally between 850 and 1000 °C. For dioxins and furans destruction, the temperature of the combustion should not drop under 850 °C. MSW is mainly constituted by C, H and O elements among minor N, S and other elements. The volatile component and fixed carbon have high content in MSW. (Yuan et.al., 2012). Basically, waste incineration is the oxidation of the combustible materials contained in the waste. Incineration is a complex process, separated in two important stages, namely devolatilization and char oxidation.

The oxygen concentration on combustion reactions has a strong effect on the duration of volatile combustion time. While increasing the oxygen concentrations is reducing the duration of combustion time period. This may indicate that, in order to speed up the combustion process, low oxygen enrichment represents an efficient means (Marin et al., 2003).

The char burnout process is controlled by diffusion mechanisms at high and medium temperatures, and by kinetic mechanisms at low temperatures (Bauer et al., 1988). Char oxidation becomes increasingly difficult in the late stages of the burnout. This phenomenon is due to a reduction in available surface area as well as a drop in the specific reactivity (Hurt et al., 1998). Beeston and Essenhigh (1963) show that impact of oxygen (slope of the char burning time) increases with the particle size; therefore for a large particle the presence of oxygen enriched oxidants is more beneficial.

During the hot period of the year the boiler operation is de-rated by an additional 5-10% due to the low air density. Due to these circumstances, the oxygen boosting reduces the specific flue gas volume, thus potentially increasing the power production. The production of 1 MWh of electricity requires an amount of 0.6 tons of oxygen for a Rankine cycle with and efficiency of 35%. This number may be used to calculate the amount of oxygen necessary to boost the combustion air with oxygen. (Marin et al., 2003).

One conclusion emphasizes the fact that concrete means for oxygen injection plays an important role. This knowledge plays a key role in the process efficiency.

CASE STUDY KRW MSWI ARNOLDSTEIN

The MSWI plant from Arnoldstein has implemented with success modern technologies for waste incineration since 2004. Thermal treatment developed is applied for the nonhazardous wastes, mainly domestic waste and similar industrial waste. To a certain extent, other wastes types that are also included in the domestic waste mix are accepted if are correctly stored. The MSWI Arnoldstein features the highest standard worldwide in terms of its combustion technology and cleaning of the flue gas. The first technical large-scale implementation of the Synthetic Combustion (SYNCOM) process worldwide was implemented on this incineration plant. This technology allows a reduction of the amount of flue gas as well as an increase of the combustion bed temperatures, which leads to an improvement of the bottom ash quality (KRW et.al 2011).

Plant facilities description

The study case incinerator consists of the following facilities:

1. Facilities for delivery, unloading and storage of the waste and operating materials, as well as for the storage, loading and removal materials and other residues for road and railway transport;
2. Combustion plant consisting of a steam boiler with integrated reverse-acting grate;
3. Four stage flue gas cleaning system, consisting of an absorber, fabric filter, activated carbon filter and selective catalytic reduction for nitrogen oxides (SCR);
4. Machinery and auxiliary electro-technical systems as well as air-separation system.

The plant concept is depicted in an overview figure below:

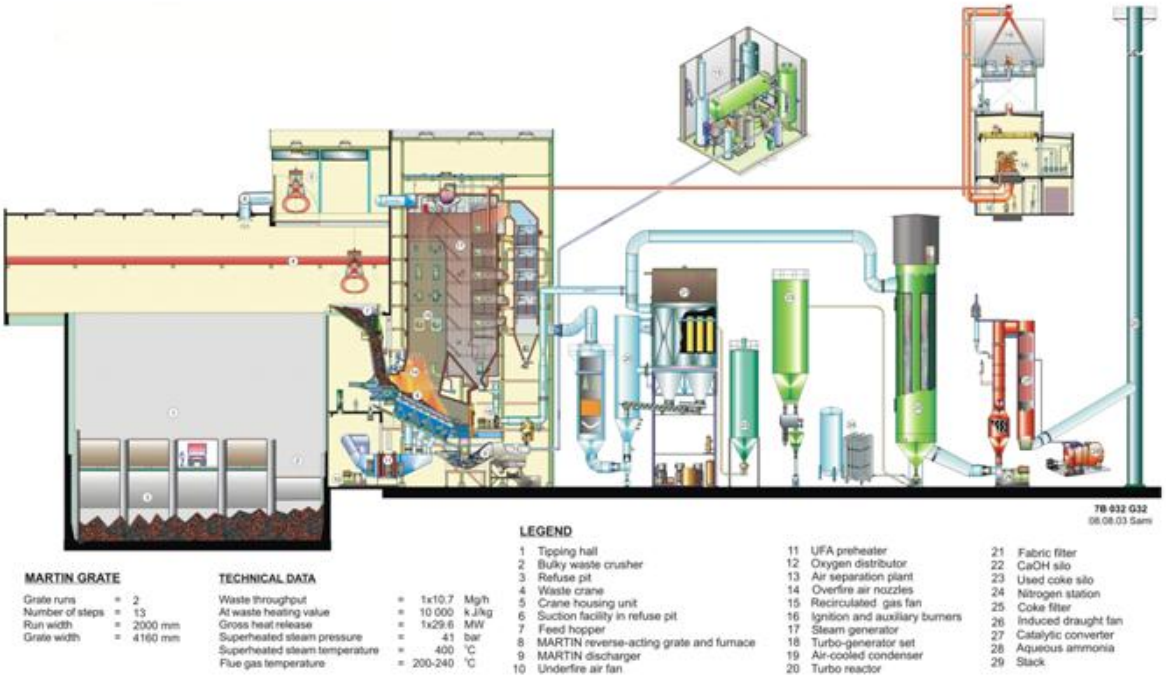

Figure 2. Waste to energy Facility Arnoldstein - Plant concept (KRW et.al 2011)

The applied technology is briefly described below

The income waste received at the "gate" is weight and unloaded from trucks into the bunker, through four unloading stations for domestic waste. For bulky waste is used a separate unloading station with crushing facility (rotary shear), from where the crushed bulky waste goes directly into the waste bunker. For mixing and displacing the waste in the bunker and to feed the dispatch chute for grate feed are used two waste cranes (one running-one reserve).

The waste incineration takes place in a boiler with grate combustion using a grate reverse-acting grate. With this system the waste is automatically agitated back and forth, air is added constantly, the waste is turned over and the red hot mass is mixed with newly fed waste. In order to create ideal combustion conditions the oxygen boosting is used. The combustion bed temperature on the grate is monitored with and infrared camera placed on the top of the boiler, just above the steam drum. Thus the amount of combustion primary air with enriched oxygen is controlled by this infrared camera. Compared with the conventional grate combustion plants, the main advantage is that the flue gas volume is much lower so the emission quantities are also reduced. Furthermore the combustion chamber temperature can be regulated more evenly and smoothly by the way of an infrared monitoring camera.

The combustion primary air incorporates the waste air from the waste bunker as well as fresh air is used. By this way the smell around waste bunker is significantly reduced. The oxygen used for enriching the combustion air is produced through pressure swing adsorption (PSA) in the oxygen separation plant. This technology is used to separate some gas species from a mixture of gases under pressure according to the species molecular characteristics and the affinity from an absorbent material.

In this study case the zeolite is used as filling material for the two adsorbent vessels that attracts nitrogen more strongly that it does oxygen. The PSA process is depicted in figure 3.

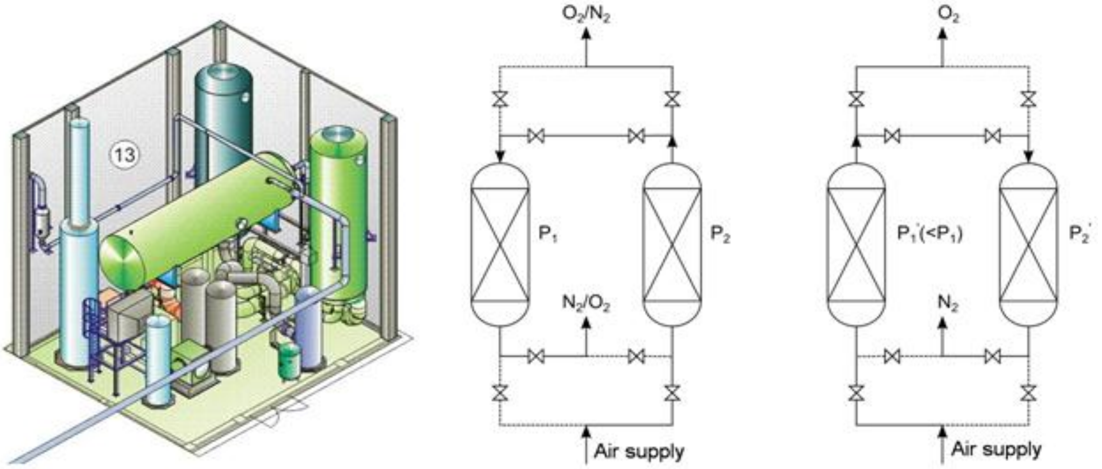

Figure 3. Oxygen production-pressure swing adsorption

The air amount is passed under pressure trough the filling materials of the adsorbent vessel where the nitrogen is kept in this material and the gas coming out the vessel is enriched in oxygen. When the filling material reaches the adsorb capacity of the nitrogen, it can be regenerated by reducing the pressure thus the adsorbed nitrogen is released. The purity of oxygen obtain by this way is around 93%. Using the system with two adsorbent vessels is created the so called pressure equalization, where the gas leaving the vessel being depressurized is used to partially pressurize the second vessel. These results in significant energy saving that make this technology to be possible to implement on industry scale. The amount of oxygen used on the case study MSWI, related to 11.5 to 12.5 t/h incinerated wastes, is 1.800-2.200 m^3/h O2 (~92% purity) (KRW et.al 2011).

The steam generated in the boiler is used for electricity production in a steam turbine. In addition, district heat and process steam are also extracted from the process. The residual heat is discharged through an air condensation system.

The flue gas produced during the thermal treatment is cleaned in a four stage flue gas cleaning system, consisting of an absorber, a fabric filter, activated carbon filter and selective catalytic reduction for nitrogen oxides (SCR). The components of the flue gas cleaning system are depicted in the figure 4.

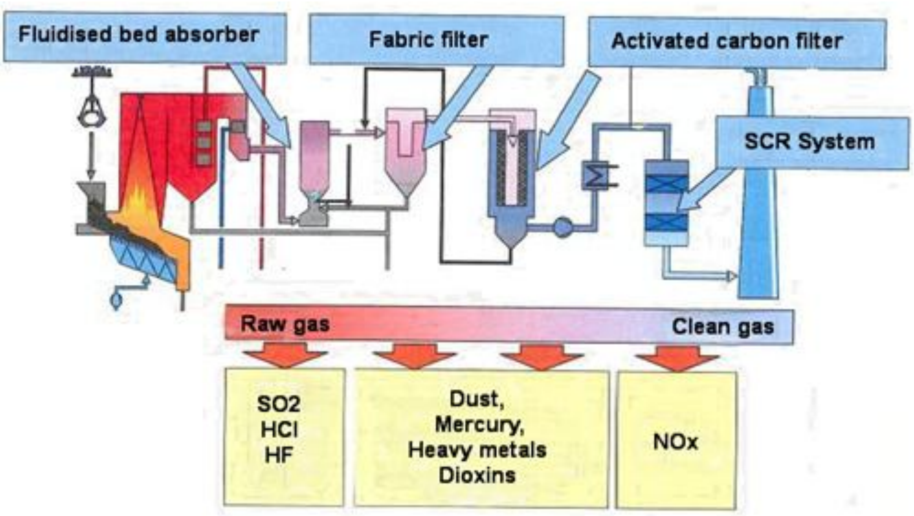

Figure 4. Flue gas cleaning system - MSWI Arnoldstein (KRW et.al 2011)

The flue gas cleaning system is operated waste-water-free. Operating waste water is only continuously produced by the water-steam cycle and is neutralized, if necessary, before discharge into the sewer. The bottom ash is mostly freed from iron metals downstream the wet slag remover and temporarily deposited in a bottom ash container until removal for further usage or final depositing. The separated metals are recycled by the metal industry. The residues from flue gas cleaning, where the pollutants are concentrated, are temporarily stored in a silo until removal. The residual material and other residues that cannot be recycled are deposited at the available landfills according to the legal framework conditions.

Type and quality of emissions

The MSWI Arnoldstein is equipped with state of the art flue gas cleaning system. Emissions limits according to the licensing notification and Waste combustion Decree are summarized in the table 1 (KRW et.al 2011).

Table 1: Emission limits into atmosphere of MSWI Arnoldstein

Half-hour mean values			
Hydrogen chloride	HCl	7	mg/Nm^3
Hydrogen fluoride	HF	0.3	mg/Nm^3
Sulphur dioxide	SO_2	20	mg/Nm^3
Nitrogen oxide, lists as nitrous oxide	NO_2	70	mg/Nm^3
Ammonia	NH_3	10	mg/Nm^3
Carbon monoxide	CO	35	mg/Nm^3
Suspended particle emissions	---	5	mg/Nm^3
Mercury	Hg	0.02	mg/Nm^3
Total carbon	C_{org}	5	mg/Nm^3
Mean value 0.5-8 hours			
Lead, zinc, chrome	Pb, Zn, Cr	0.1	mg/Nm^3
Arsenic, Cobalt, Nickel	As, Co, Ni	0.1	mg/Nm^3
Cadmium	Cd	0.01	mg/Nm^3
Cadmium and thallium	Cd, Tl	0.05	mg/Nm^3
Antimony, Arsen, Lead, Chrome, Cobalt, Copper, Manganese, Nickel, Vanadium, tin	Sb, As, Pb, Cr, Co,Cu, Mn, Ni, V, Sn	0.5	mg/Nm^3
Mean value over 3-16 hours			
Dibenzodioxins, Furans	PCDD/PCDF	0.1	ngTE/Nm^3
All concentrations listed above as well as the flue gas volume flow refer to dry waste gas at 0°C, 1013 mbar and 11 vol.%O_2; NH_3 refers to 0 vol.% O_2			

The flue gas treatment plant operates waste water free. Furthermore, the system does not require the extraction/discharge of any cooling water, because it operates in a close loop cooling system. In a neutralization plant, the PH-value of the waste water from the water/steam cycle is regulated, before the waste is discharged into the plant sewer. The specified limits are summarized in table 2 (KRW et.al 2011).

Table 2: Waste water emission limits into hydrosphere of MSWI Arnoldstein

Parameters	Basis	Unit	Value	Parameters	Basis	Unit	Value
Temperature	AEV-Wa	°C	30	pH-value	AEV-Wa		6.5-8.5
Filterable substances	AEV-Wa	mg/l	30	Arsenic – As	AEV-Wa	mg/l	0.1
Aluminium - Al	AEV-Wa	mg/l	2	Cadmium - Cd	AEV-Da	mg/l	0.05
Lead - Pb	AEV-Wa	mg/l	0.1	Iron – Fe	AEV-Wa	mg/l	2.0
Chrome - Cr	AEV-Da	mg/l	0.5	Nickel – Ni	AEV-Wa	mg/l	0.5
Copper - Cu	AEV-Wa	mg/l	0.5	Zinc – Zn	AEV-Wa	mg/l	2.0
Quicksilver - Hg	AEV-Wa	mg/l	0.01	Hydrazine	AEV-Wa	mg/l	2.0
Ammonium - N	AEV-Wa	mg/l	1.0	Total ligated nitrogen - N	AEV-Wa	mg/l	2.0
Fluoride - F	AEV-Wa	mg/l	10	TOC	AEV-Wa	mg/l	20
Total phosphor - P	AEV-Wa	mg/l	2	CSB	AEV-Wa	mg/l	30.0
Mangan - Mn	AEV-Wa	mg/l	1.0	BSB5	AEV-Wa	mg/l	90.0
Total of hydrocarbons	AEV-Da	mg/l	10	AOX	AEV-Wa	mg/l	20.0
AEV-Da: Decree on the limitation of waste water emissions from cooling systems and steam generators (FLG 1072/1994) AEV-Wa: Decree on the limitation of waste water emissions from water treatment (FLG 892/1995)							

Process input and output flows

The input flows necessary for the described waste incineration plant are basically composed as follows:

1. Nonhazardous waste for thermal treatment
2. Air for combustion process
3. Operating materials for the safe and environmentally sound operation:
    - Service water
    - Industrial salt (NaCl) for the regeneration of the water treatment plant
    - Calcium hydroxide of burnt lime for flue gas cleaning
    - Coke for flue gas cleaning
    - Ammonia water for flue gas cleaning and feed-water conditioning
    - Nitrogen for the manipulation of anthracite coke
    - Sodium carbonate or hydrochloric acid for the neutralization of the waste water
4. Energy
    - Fuel oil (on the startup)
    - Electricity for internal consumption

The output flows resulted after the thermal treatment of non-hazardous waste are:
1. Solid products:
    - Metals scrap
    - Bottom ash
    - Flue gas cleaning residues
2. Energy
    - Process steam
    - District heat
    - Electricity
3. Waste heat in the flue gas and in the air condenser
4. Cleaned flue gas
5. Waste water into the receiving water course of sewer (sanitary waste water).

The lists of hourly input-output streams of the study case waste incinerator, related to incineration of 96,000 t/year are summarized in table 3 (KRW et.al 2011).

Table 3: List of input-output flows based on 96,000 t/year

Input	
Non-hazardous waste	12 t/h
Air	31.000 m^3/h
Service water	5 m^3/h
Calcium hydroxide	150-300 kg/h
Coke	3 – 8 kg/h
Ammonia water (25%)	15 – 25 kg/h
Nitrogen	6 Nm^3/h
Industrial salt	0.75 kg/h
Output	
Cleaned flue gas	50.000 Nm^3/h
Metals	0.12-0.24 t/h
Slag	2.4-3.6 t/h
Residues from flue gas cleaning	0.4-0.6 t/h
Waste water	1.5 m^3/h
Energy production / district heat and process heat extraction	
Supplied heat (waste)	33.33 MW_{th}
	120 GJ/h
Steam parameters (turbine entry)	39 bar
	397 °C
	40 t/h
District heat disengagement	Up to 9 MW_{th}
Process steam extraction	Up to 13.0 t/h
Generation of electricity (net)	Up to 6 MW_{el}

The income waste in thermal treated by grate incineration according to SYNCOM technology with oxygen enriched air as well as automatic monitoring and regulation of the combustion temperature. Compared to other methods, this achieves a combustion temperature that is approx. 150 K higher and yields better combustion proprieties. Thus the bottom ash is already vitrified on the grate, rendering any post-treatment of the slag for safety landfilling disposal.

Downstream the grate combustion system there is a wet slag remover where the slag is cooled off and then discharged without any dust or smell exposure. Due to the fast cooling process, crystallization developed in the melted mass are stopped quickly, and the melted glasses are fixed.

Due to thermal treatment, the pollutants contained in the incinerated waste are concentrated in the flue gas cleaning residues. The residue consists of fractions produced in the process of flue gas cleaning, such as fly ash, desulphurization products and activated carbon. The quantity of the residues ranges between approx. 33 and 50kg per ton of incinerated waste, depending on the pollutant content of the waste that is used. Related to 96.000 t of incinerated waste this means about 3.200 to 4.800 tons. These residues are currently solidified with latent hydraulic binding agents and then disposal landfilled.

CONCLUSIONS

One of significant breakthroughs in waste incinerators has been the introduction of the oxygen boosting. This technology has significantly reduced the emissions and increases the efficiency of grate incinerators. Oxygen enrichment fits perfect for fuels with low calorific values like domestic waste and similar industrial ones. The pressure swing adsorption technology is already implemented on industrial scale facility so the oxygen production is not anymore an impediment.

The increased combustion bed temperature does not lead to a higher grate temperature, due to the self –covering poking. This, in turn, avoids any increased thermal corrosion of the grate bars. Resulted bottom ash through this technology can be disposal landfilled with any further steps.

One conclusion emphasizes the fact that concrete means for oxygen injection plays an important role. This knowledge plays a key role in the process efficiency.

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REFERENCES

European comission. BAT (2006): Integrated Pollution Prevention and Control. Reference document on the Best available Techniques for Waste incineration, 250-251.

Kira M.,Tsuneizumi S., Doi T., Takuma M., Kitta T. (2001): Development of New Stoker Incinerator for Municipal Slolid Wastes Using Oxygen Enrichement. Mitsubishi Heavy Industries, Ltd., 38 (2), 78.

Yuan H, Lu T, Kobayashi N, Huang H, Chen Y, (2012): Th einfluence of Oxygen concentration and Equivalence Ratio on Pyrolysis Gas In Oxygen-Enriched Pyrolisis By Theoretical Calculation, AASRI Procedia 3, p.429.

Marin O, Chatel-Pelage F., Usman Ghani M., Perrin N.. (2003): Low oxigen enrichement in coal-fired utility boilers. 28th International Technical Conference On Coal Utilization & Fuel Systems, 10-13 March.

Bauer C.M, Spliethoff H., Hein K.R.G. (1999). 24th International Technical Conference On Coal Utilization & Fuel Systems, Clearwater, FL, p.517.

Hurt R.H, Sun J.K, Lunden M., (1998): A Kinetic Model of Carbon Burnout In Pulverized Coal Combustion, Combustion and Flame, p.181.

Kärntner Restmüllververwertungs Gmbh, TBA Arnoldstein (2011): Description of the present status

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ADSORPTION OF FE^{2+} AND ZN^{2+} IONS FROM LANDFILL LEACHATE BY NATURAL BENTONITE FROM KRIVA PALANKA(B - KP), REPUBLIC OF MACEDONIA

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ABSTRACT

Due to its typical layered silicate structure, large specific surface area, chemical and mechanical stability, high cation exchange capacity, bentonite has been widely applied as heavy metals adsorbent from aqueous solutions. In this paper the adsorptive properties of natural bentonite from Kriva Palanka, Republic of Macedonia, for the removal of Fe^{2+} *and* Zn^{2+} *ions from landfill leachate were studied. The raw material (B-KP) was characterized in terms of chemical composition (conventional silicate analysis), structural morphology (XRD, FT- IR, TGA-DTA), specific surface area, particle sixe distribution (wet - sieve analysis). It was considered that montmorillonite is dominant phase in B-KP. For adsorption experiments the batch method has been employed using volume of 25* cm^3*, 50* cm^3*, 75* cm^3*, 100* cm^3 *and 125* cm^3 *of leachate with 2 g of bentonite, at 298 K. The initial metal ion concentration in the leachate was 9,25* mg/dm^3 *for* Fe^{2+} *and 0,22* mg/dm^3 *for* Zn^{2+} *and these concentrations as well as the concentrations after adsorption were determined by atomic absorption spectrophotometer (AAS). Applied Freundlich and Langmuir adsorption isotherms showed good fits to the experimental data. The monolayer capacities of bentonite for* Fe^{2+} *and* Zn^{2+} *were determined by Langmuir equation and are 0,4371 mg/g and* $4,1\cdot10^{-3}$ *mg/g, respectively. The removal efficiency for zinc was above 98%.*

Key words: *municipal solid waste leachate,* Fe^{2+}*,* Zn^{2+}*, adsorption isotherms, bentonite.*

INTRODUCTION

Due to the irregular management, municipal solid waste landfills (MSWL’s) are major threat to the quality of the environment in Macedonia as in many other developing countries. Produced and freely released leachate is a source of groundwater and soil pollution. Leachate is highly polluted liquid composed of many inorganic (sulfates, chlorides, heavy metals) and organic (acids, alcohols) pollutants. The MSWL Drisla, does not contain any drainage system for the underground waters protection nor any receiving reservoir for primary treatment. The leachate is freely released into the stream of Meckin Dol. Therefore the presence of heavy metals in leachate is a serious threat for groundwater and nearby fields and accordingly for the health of the population. .

The methods used for removal of heavy metals include chemical precipitation, ion exchange, solvent extraction, membrane processes, adsorption and others. Among all the approaches proposed, adsorption is one of the most popular method and it is considered as an effective, efficient and economic method for wastewater purification. Various materials such as activated carbon (Kouakou et al., 2013; Bernard and Jimoh 2013) natural and synthetic zeolites (Erdem et al., 2004; Shaheen et al., 2012), bentonite (Ghormi et al., 2013; Kaya and Oren 2005) have been used as adsorbents for the removal of heavy metals from water and wastewater.

Among the natural clays of high surface area and eminent cation exchange capacity as well as the adsorption affinity for organic and inorganic ions and a low cost, bentonite is marked as the most promising adsorbent for the removal of heavy metals (arsenic, cadmium, chromium, iron, lead, zinc) from aqueous solutions. Bentonite has a typical layered silicate structure consisting of two silica tetrahedral sheets with a central octahedral sheet. The interlayer space is easily accessible to water and another polar liquids. Bentonite has a good cation exchange capacity due to the presence of hydrated cations as Ca^{2+}, Na^{+}, K^{+}, etc., in their interlayer surfaces, and these cations can be easily exchanged by heavy metals compensating the negative charge.

There are many studies on the adsorption of iron and zinc (Sheta et al., 2003; Bhattacharyya and Gupta 2006; Mishra and Patel 2009) The aim of this work is to study the Macedonian natural bentonite as potential adsorbent for iron and zinc removal from wastewater.

EXPERIMENTAL

The bentonite samples in this study, originate from Kriva Palanka, (Ginevci district) Republic of Macedonia. Bentonite was used in its natural form without any treatment. For bentonite characterization, specific surface, sieve, chemical, XRD, FT- IR and TGA- DTA analysis were performed.

The initial metal ion concentration in the leachate taken from MSWL Drisla was determined by atomic absorption spectrophotometer (AAS) and it was 9,25 mg/dm^3 and 0,22 mg/dm^3 for Fe^{2+} and Zn^{2+}, respectively. The pH value of the leachate was 7,8. The batch method was used for adsorption processes. Volume of 25 cm^3, 50 cm^3, 75 cm^3, 100 cm^3 and 125 cm^3 of leachate with 2 g of bentonite were placed in 5 Erlenmeyer flasks to commence the experiment. Flasks were set in the shaker (CERTOMAT R, B. Braun supplied by Biotech International) at constant temperature of 298 K. 100 rpm shaking was applied in the shaker for 5h and the last 1h at 140 rpm until equilibrium was attained. The solutions were filtered and the filtrates were analyzed for Fe^{2+} and Zn^{2+} by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

In this work specific surface of bentonite was evaluated from data of equilibrium adsorption of water vapor at 298K. The adsorption isotherm at 298K is interpreted by linear form of BET equation:

$$\frac{x}{n^a(1-x)} = \frac{1}{n_m^a C} + \frac{C-1}{n_m^a C}x \qquad (1)$$

where, x is relative pressure ($x = P/P_0$), n^a [mol/g] is amount of adsorbed water vapour, n_m^a [mol/g] is monolayer capacity of adsorbent and C is a constant. The diagram of the linear form of the equation is given in Figure 1. The good fit of the experimental isotherm to the equation is evidenced by the linearity of the plot. The value of regression coefficient is higher than 0,98.

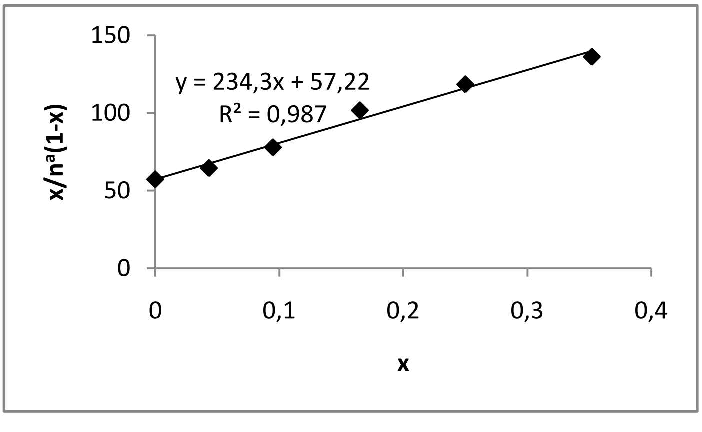

Figure 1. Diagram of linear form of BET equation of adsorption of water vapour on bentonite

The value of monolayer capacity is used to calculate the specific surface area of bentonite by the equation:

$$a_s = n_m^a N_A a_m 10^{-18} \tag{2}$$

where a_s is the specific surface area, a_m is surface of adsorbent occupied by one molecule of adsorbate, which for water is 0,106 nm^2.

The values of the parameters of the equation, monolayer capacity, n_m^a and constant C, and the specific surface area, a_s, are $3{,}43 \cdot 10^{-3}$ mol/g, 5,10 and 219 m^2/g, respectively.

It was proved by XRD analysis on this bentonite, Figure 2, that the dominant component is montmorillonite and the remaining components are muscovite, quartz, feldspar and kaolinite.

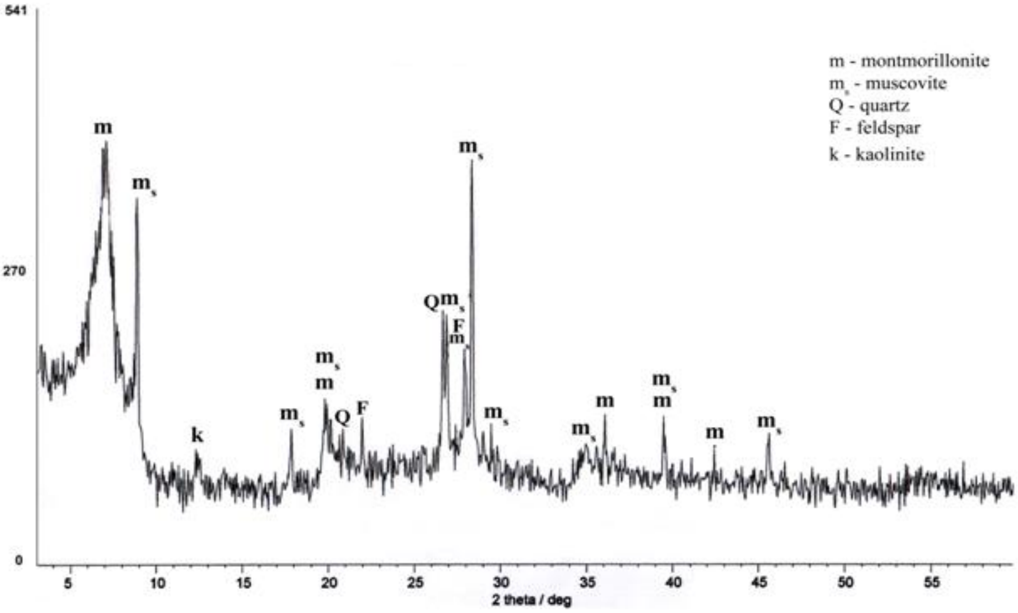

Figure 2. XRD patterns of the bentonite

Structural composition of B-KP revealed by XRD analysis was confirmed by FT-IR results, Figure 3. Namely, the adsorption bands at 467, 517, 783 and 1120 cm^{-1} point to the presence of quartz (Si-O-Si) while the bands at 1034 and 1634 cm^{-1} reveal the presence of SiO$_2$ amorphous. The bands appearing at 617 and 675 cm^{-1} outline the Al-O-Si-O bond (feldspar presence) and at 917 cm^{-1} the Al-Al-OH bond. The presence of adsorbed water is manifested by appearance of bands at 1634, 3442 and 3617 cm^{-1}. OH$^-$ groups considered with bands at 917, 3442 and 3692 cm^{-1} were additionally confirmed by TGA-DTA analysis, Figure 4, that point to the different nature of OH$^-$ groups present in B-KP.

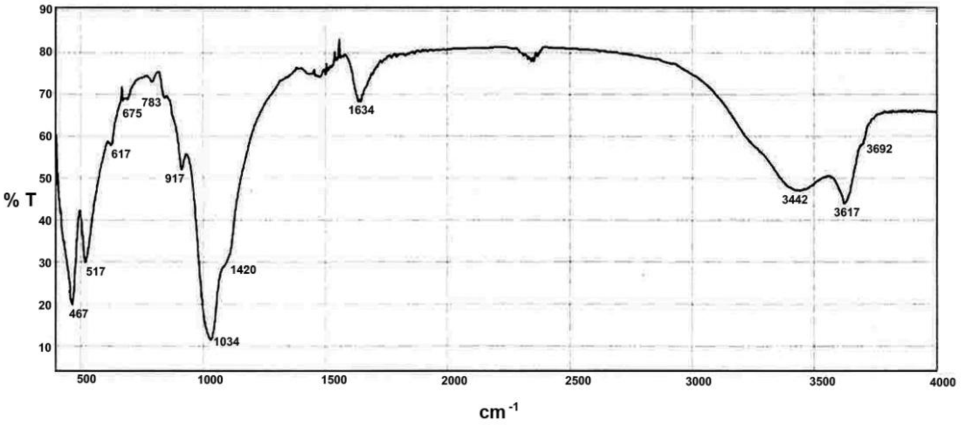

Figure 3. FT-IR spectrum of bentonite

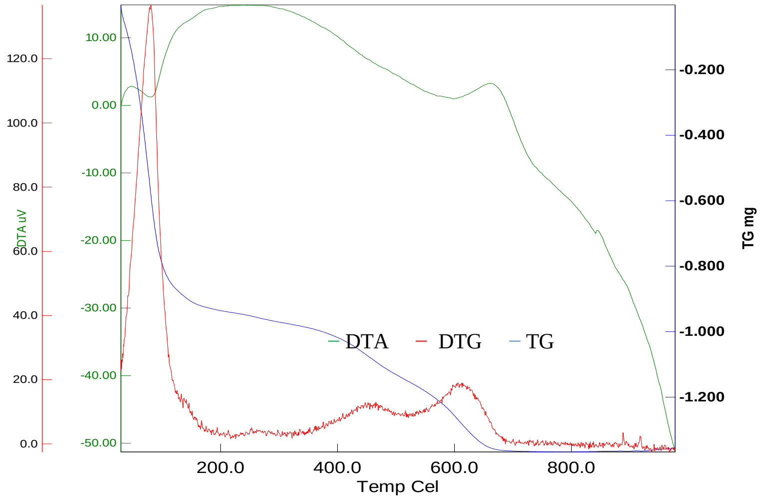

Figure 4. TGA-DTA diagram of bentonite

The results of granulometric sieve analysis and chemical composition of the bentonite determined by conventional silicate chemical analysis are presented in Table 1 and Table 2, respectively.

Table 1: Granulometric sieve analysis of bentonite

Fraction [mm]	Mass [%]
+0,071	3,82
-0,071+0,063	0,55
-0,063+0,040	5,26
-0,040+0,032	1,79
-0,032	88,58
$\sum$	100

Table 2: Chemical composition of bentonite

Composition	Mass [%]
SiO_2	60,82
Al_2O_3	21,32
Fe_2O_3	3,21
MgO	4,15
CaO	2,03
Na_2O	0,40
K_2O	0,40
$H_2O + CO_2$	8,06

Adsorption studies

The adsorbed amount of metal ion per unit adsorbent mass, m^a [mg/g], was calculated as follows:

$$m^a = \frac{(C_0 - C_e)V}{m} \tag{3}$$

where C_0 [mg/dm^3] is the initial heavy metal concentration, C_e [mg/dm^3] is equilibrium heavy metal concentration, m is the amount of the bentonite [g] and V is the leachete volume [dm^3]. Initial concentrations of Fe^{2+} and Zn^{2+} metal ions in leachate were 9,25 mg/dm^3 and 0,22 mg/dm^3, respectively.

Adsorption isotherms are important for adsorption processes research. Langmuir and Freundlich isotherms are the most widely used for practical applications. The Langmuir adsorption isotherm is valid for monolayer sorption onto a surface with a finite number of identical sites (Melichova and Hromada 2013; Al Dwairi and Al Rawajfeh 2012), and it can be defined according to the following linear form:

$$\frac{C_e}{m^a} = \frac{1}{m_m^a b} + \frac{C_e}{m_m^a} \qquad (4)$$

where m_m^a [mg/g] is the monolayer capacity and b is the equilibrium constant.

The dependence of C_e/m^a from C_e, obtained by using experimental results, is shown in Figure 5 for Fe^{2+}, and in Figure 6 for Zn^{2+}.

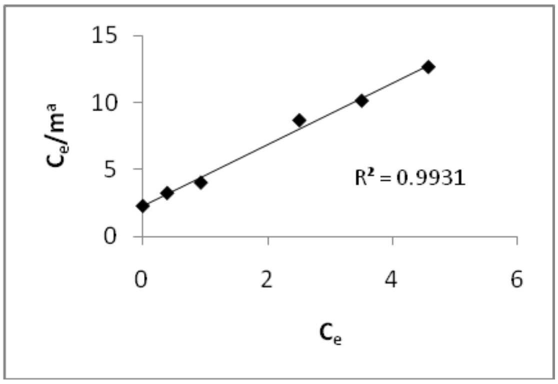

Figure 5. Langmuir adsorption model for Fe^{2+}

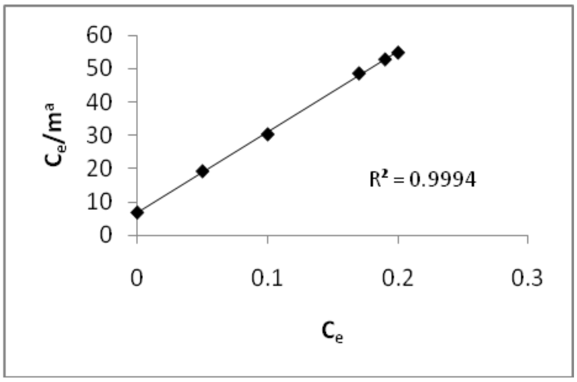

Figure 6. Langmuir adsorption model for Zn^{2+}

The values of m_m^a and b were determined from the linear form of the Langmuir equation and the Langmuir plot. The calculated results and correlation coefficients R^2 are listed in Table 3.

Langmuir isotherm determines the adsorption favorable or unfavorable. To determine the characteristic behavior of adsorption, dimensionless equilibrium parameter, R_L (known as the separation factor) is used (Al Dwairi and Al Rawajfeh 2012; Budsaereechai et al., 2012). This parameter is given by:

$$R_L = \frac{1}{1 + bC_0} \qquad (5)$$

For favorable adsorption R_L value must take place $0 < R_L < 1$. In our results R_L values were found 0,10 and 0,11 for Fe^{2+} and Zn^{2+} respectively, and that confirms that the adsorption process is favorable.

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be explained by the linear form:

$$\log m^a = \log K_F + \frac{1}{n}\log C_e \qquad (6)$$

where K_F is the Freundlich constant [mg/g] and n is an empirical parameter related to the intensity of adsorption. The linear Freundlich plots for iron and zinc are given in Figure 7 and Figure 8.

The parameters of Freundlich equation as well as the correlation coefficients for both metal ions are listed in Table 3.

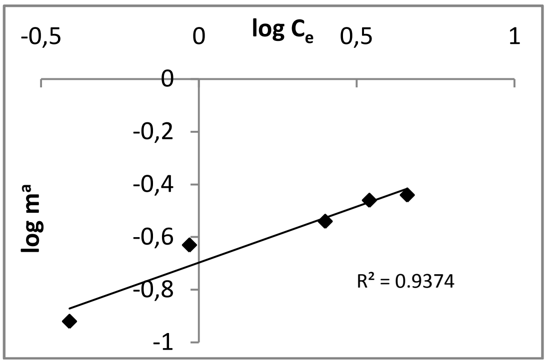

Figure 7. Freundlich adsorption model for Fe^{2+}

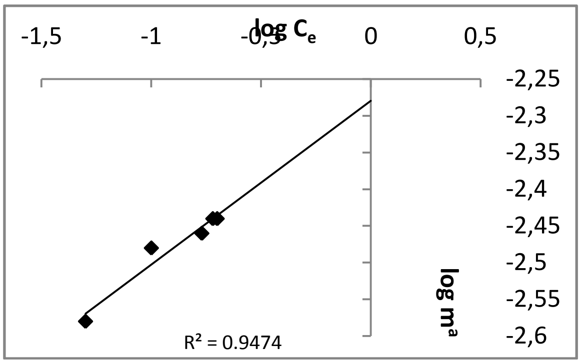

Figure 8. Freundlich adsorption model for Zn^{2+}

Table 3:Parameters of the Langmuir and Freundlich isotherms

Metal	Langmuir			Freundlich		
	m_m^a [mg/g]	b	R^2	K_F [mg/g]	N	R^2
Fe	0,4371	1,01	0,993	0,20	2,35	0,937
Zn	$4{,}1\cdot10^{-3}$	35,7	0,999	$5{,}25\cdot10^{-3}$	4,49	0,947

The linearity of the plots, Figures 5, 6, 7 and 8 and higher values of correlation coefficients show that Langmuir isotherms correspond better than Freundlich isotherms for both metals.

Langmuir monolayer capacity m_m^a and Freundlich constant K_F, that could be considered as the amount of metal adsorbed by solid phase at the equilibrium concentration of unity (Ghasemi-Fasae et al., 2012) do indicate and compare adsorption performance. According to the results for monolayer capacity, m_m^a and Freundlich constant K_F, bentonite shows greater sorption capacity for Fe^{2+} than for Zn^{2+}. According to many literature data (Budsaereechai et al., 2012; Ghormi et al., 2013; Melichova and Hromada 2013) it was expected the bentonite to have higher values for monolayer capacity. In our case, because of the complexity of investigated system (leachate) which is highly polluted with many inorganic and organic pollutants and there is an increase of the competitiveness for bentonite adsorption sites, we have much lower results for sorption capacity.

The adsorption parameter *n* in the Freundlich isotherm which measures preferential adsorption of one adsorbate to other and the intensity of adsorption, compared directly with Langmuir constant *b* a factor which relate to heat of adsorption and affinity to the binding site (Okeola and Odebunmi 2010). As it can be seen from the Table 3 the two constants *b* and *n* are proportionally related for both metals and the higher values of *b* and *n* for Zn^{2+} indicate a stronger bond between bentonite and Zn^{2+} ions than bentonite and Fe^{2+} ions. Using mathematical calculations *n* values between 1 and 10 indicate effective adsorption (Al-Shahrani 2012) Our results show effective adsorption for Fe^{2+} and Zn^{2+} according to the *n* values which are 2,35 and 4,49 respectively.

From economic point of view it is necessary to define the optimal ratio between amount of used bentonite and dose of leachate. For that purpose the removal efficiency of Fe^{2+} and Zn^{2+} metal ions adsorption on bentonite was calculated by the following equation and the results are listed in Table 4.

$$\text{Removal }\% = \frac{C_0 - C_e}{C_0}\cdot 100 \qquad (7)$$

Table 4: Removal efficiency of bentonite for Fe^{2+} and Zn^{2+}

Amounts of leachate/bentonite	Removal [%]	
	Fe	Zn
25 cm^3 / 2g	95,78	98,82
50 cm^3 / 2g	89,95	98,50
75 cm^3 / 2g	72,86	98,41
100 cm^3 / 2g	62,05	98,36
125 cm^3 / 2g	50,49	98,34

The results show that to keep removal percentage above 90% for Fe metal ions the ratio between amount of leachate and bentonite should be 25 cm^3 / 2g because using the bigger volume of leachate drastically decreases the removal percentage. But, as it can be seen from the table, for Zn ions by increasing the leachate volume, percentage of removal, almost, do not change at all, and it is 98%.

CONCLUSION

The natural bentonite from Kriva Palanka, Republic of Macedonia (B-KP), belongs to the group of clay minerals with montmorillonite as main constituent. Bentonite has high specific surface area of 219 m^2/g.

The linear form of Langmuir and Freundlich equations were used to describe the adsorption isotherms. The experimental results were well fitted with both isotherms, but the values of the correlation coefficients show that Langmuir model correspond better. The monolayer capacities of bentonite for iron and zinc were determined by Langmuir equation and are 0,4371 mg/g and $4{,}1\cdot10^{-3}$ mg/g, respectively. This values are very low because we investigated a real system which is highly polluted and there is an increase of competitivety for superficial sites in bentonite.

The results for removal percentage indicate that in that conditions bentonite is more effective as adsorbent for zinc and the removal efficiency above 98% is economically reasonable.

The further investigations would be conducted to examine adsorption characteristics of Macedonian bentonite under various operating variables like initial metal concentration, solution pH, contact time, clay dosage and temperature. Further studies would be dedicated to the investigations under which conditions the bentonite is no longer reusable as well as to determine the expected lifetime of the bentonite.

REFERENCES

Al Dwairi, R. A. & Al Rawajfeh, A. E. (2012). Removal of cobalt and nickel from wastewater by using Jordan low – cost zeolite and bentonite. *Journal of the University of Chemical Technology and Metallurgy*, 47(1), 69 – 76

Al – Shahrani, S. S. (2012). Treatment of wastewater contaminated with nickel using Khulays activated carbon. *International Journal of Engineering & Technology*, 12(4), 14 – 18

Bernard, E. & Jimoh, A. (2013). Adsorption of Pb, Fe, Cu and Zn from industrial electroplating wastewater by orange peel activated carbon. *International Journal of Engineering and Applied Sciences*, 4, 95 – 103

Bhattacharyya, K. G. & Gupta, S. S. (2006). Adsorption of Fe(III) from water by natural and acid activated clays: studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Adsorption*, 12(3), 185 - 204

Budsaereechai, S., Kamwialisak, K. & Ngernyen, Y. (2012). Adsorption of lead, cadmium and copper on natural and acid activated bentonite clay. *KKU Res. J.*, 17(5), 800 – 810

Erdeme, E., Karapinar, N. & Donat, R. (2004). The removal of heavy metal cations by natural zeolites. *Journal of Colloid and Interface Science*, 309 – 314

Ghasemi – Fasae, R. Gafari – Haghigh, M., Mousavi, S. M. & Dehghan, M. (2012). Sorption characteristics of heavy metals onto natural zeolite of clinoptilolite type. *International Research Journal of Applied and Basic Sciences*, 3(10), 2079 – 2084

Ghormi, F., Lahsini, A., Laajeb, A. & Addaou, A. (2013). The removal of heavy metal ions (copper, zinc, nickel and cobalt) by natural bentonite. *Larhyss Journal*, 37 – 54

Kaya, A. & Oren, A. H. (2005). Adsorption of zinc from aqueous solutions to bentonite. *Journal of Hazardous Materials,* 183 – 189

Kouakau, U., Ello, A. S., yapo, J. A. & Trokourey, A (2013). Adsorption of iron and zinc on commercial activated carbon. *Journal of Environmental Chemistry and Ecotoxicology,* 5(6), 168 - 171

Melichova, Z. & Hromada, L. (2013). Adsorption of Pb^{2+} and Cu^{2+} ions from aqueous solutions on natural bentonite. *Pol. J. Eniron. Stud.,* 22(2), 457 – 464

Mishara, P. C. & Patel, R. K. (2009). Removal of lead and zinc ions from water by low cost adsorbents. *Journal of Hazardous Materials*, 168(1), 319 - 325

Okeola, F. O. & Odebunmi, E. O. (2010). Freundlich and Langmuir isotherms parameters for adsorption of methylene blue by activated carbon derived from agrowastes. *Advances in Natural and Applied sciences,* 4(3), 281 – 288

Shaheen, S. M., Derbalah, A. S. & Moghanm, F. S. (2012). Removal of heavy metals from aqueous solution by zeolite in competitive sorption system. *International Journal of Environmental Science and Developmen,* 3, 362 – 367

Sheta, A. S., Falatah, A. M. Al – Sewailem, M. S., Khaled, E. M. & Sallam, A. S. (2003). Sorption characteristics of zinc and iron by natural zeolite and bentonite. *Microporous and Mesoporous Materials* 61, 127 - 136

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ENVIRONMENTAL EFFECTS OF GLASS FORMATION FROM METALLURGICAL SOLID WASTE

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ABSTRACT

This paper is concerned with environmental effects of the vitrification process of solid metallurgical waste (filter dust, FD, slag from electro-furnace, SEF and slag from converter, SC) from ferronickel production industry. Chemical and mineralogical characterization of the waste materials was done. The waste mixture (FD : SEF : SC = 1 : 10 : 1) contains SiO_2 amount enough for glass forming. Vitrification process was performed at 1250 ^oC for 3h and at 1450 ^oC for 1 h. Standard TCLP (Toxicity Characteristic Leaching Procedure) test was performed on the waste materials as well as on the produced glass. Metallurgical waste contains several heavy metals (Fe, Ni, Mn, Zn, Cr) which can be potential hazard to the soils. The content of hazardous heavy metals in the glass produced from the metallurgical waste mixture is far bellow the applied limits.Thermal characteristics of the glass point out that transformation to glass-ceramic can be performed by traditional two-stage method.

Key words: *metallurgical solid waste, filter dust, slag, vitrification, glass.*

INTRODUCTION

Industrial capacities in R. Macedonia in the field of extractive metallurgy and power production generate considerable amount of filter dust and slag. They are consisted mainly of acid oxides (SiO_2, Al_2O_3), alkaline oxides (CaO, MgO), oxides of heavy (Fe, Pb, Zn, Cu, etc.) and radioactive (Ra^{226}, U^{235}, Pb^{202}, Pb^{214} etc.) metals. Average annual production of filter dust is the following: 100–150. thousand tons in TEC Oslomej, 780.000 tons in REK Bitola, 100.000 tons in FENI INDUSTRY, Kavadarci, 6.000 tons in MAKSTIL, Skopje (European Commission, 2007). Average annual production of metallurgical slag is 1.250.000 tons in FENI INDUSTRY, Kavadarci, 40.000 tons in MAKSTIL, Skopje and 850.000 in JUGOHROM, Jegunovce. According to European legislation (Waste Directive, 2008), filter dust and metallurgical slags are considered as hazardous materials and previous processing (neutralization/inertization) before final disposal on landfills should be done. But, waste disposal should be the last alternative after previously recovery of useful components. European practice has shown that filter dust and metallurgical waste are valuable raw material for civil engineering, fillings the roads (Feuerborn, H-J, 2001; Fatih, T. and Umit, A., 2001) and production of glass and glass-ceramic of high quality (Rawlings, R. D. et al., 2006; Boccaccini, A. and Rawlings R., 2002; Isa H., 2011; Barbieri, L. et al., 2002; Zimmer, A. and Bergmann, C.P., 2007). In Europe, only 7% of the filter dust is disposed on landfills after corresponding inertization procedures (Feuerborn, H-J, 2001).

Vitrification is considered as an ultimate method for immobilization of hazardous wastes, because during glass melting, the harmful elements are chemically bonded in a durable amorphous network (Vogel, W). On the other hand, the produced glass can be transformed to glass- ceramic with quality comparable or better than commercial ones (Chinnam R. K. et al., 2013; Fredericci C. et al., 2000; El-Alaily N.A., 2003; Ferreira E. B. et al., 2002). Therefore, by this procedure for treatment of metallurgical waste, considerable environmental and economical effects can be achieved.

Metallurgical waste from steel and ferroalloys production contains increased amount of iron oxides. The research on iron-reach glass and glass-ceramic highlight good chemical, physical and mechanical properties of the produced glass or glass-ceramic, close or even better than those produced from virgin raw materials (Karamanov A. et al., 1999; Karamanov A. et al., 2002; Pisciella, P. et al., 2001). In principle, the glass-ceramics produced from iron-reach glass are characterized by an appearance similar to that of natural stones, because during the heat treatment the crystallization starts from the surface to the inside of each grain. The crystal size is on the order of millimetres and the different particles can be easily distinguished in the structure of the materials. Pyroxene is formed preferentially in the bulk while hematite (Fe_2O_3) is formed on the surface as a result of the oxidation of FeO. Magnetite (Fe_3O_4) also crystallizes in the bulk of the glass but its formation is influenced by the initial ratio Fe^{2+}/Fe^{3+}, by the particle size distribution, and by the sintering conditions (Karamanov A. et al., 1999).

The aim of this study is vitrification of solid waste from ferronickel smelting plant, such as filter dust (FD), slag from electro-furnace (SEF) and slag from converter (SC). Standard TCLP (Toxicity Characteristic Leaching Procedure) test was performed on the waste materials as well as on the produced glass. Characterization of waste materials and produced glass was done in order to estimate their possibility for further production of glass-ceramic.

MATERIALS AND METHODS

The used metallurgical waste originates from the technological line of ferronickel smelting plant FENI INDUSTRY, Kavadarci (Fig. 1). In the first stage of pre-reduction of the ores in rotation kiln filter dust (FD) is produced. In the next stage of reductive smelting in electro-furnace the main amount of slag (SEF) is produced. In the final stage of refination of the produced ferroalloy in converter, lower amount of slag (SC) is produced. Their annual production is approximately in ratio FD : SEF : SC = = 1 : 10 : 1 (see Table 1).

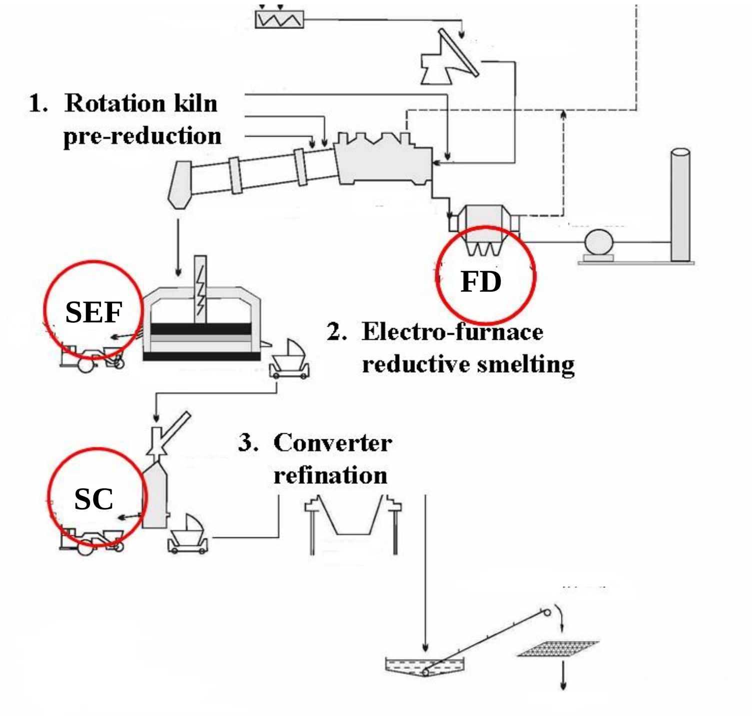

Figure 1. Scheme of the technological line of FENI INDUSTRY, Kavadarci

Table 1: Annual production of waste materials in FENI INDUSTRY for 2012

Waste material	Quantity, tons
Filter dust, FD	102 000
Slag from electro-furnace SEF	1 135 000
Slag from converter, SC	109 000

Chemical composition of the waste materials was determined by X-ray fluorescence (XRF) spectrometer (Model XRF ARL 9900). Mineralogical analysis was carried out by X-ray diffraction method using Philips APD 15 diffractometer, operating at CuKα-radiation. Diffraction data were collected at a constant rate of $0.02^{o}\cdot s^{-1}$ over an angle range of $2\theta = 5–90^{o}$.

The content of different type of waste was in this ratio within the waste mixture aimed for vitrification. To correct the content of MgO and Cr_2O_3 in the waste mixture (WM), standard glass (SG) powder was added in ratio WM : SG = 7 : 3. Waste materials and the standard glass were homogenized and melted in chamber furnace at 1250 ^{o}C for 3 hours and 1450^{o}C for 1 hour.

To determine environmental impact of the waste materials and further the produced glass, standard leaching test – TCLP (Toxicity Characteristic Leaching Procedure) was performed (Van der Sloot H. A. et al., 1997). The leaching setup is shown in Fig. 2. In Table 1 the leaching test conditions are summarized. Concentrations of heavy metals after testing were measured by atomic absorption spectroscopy (AAS) using the instrumentation Perkin Elmer AA400.

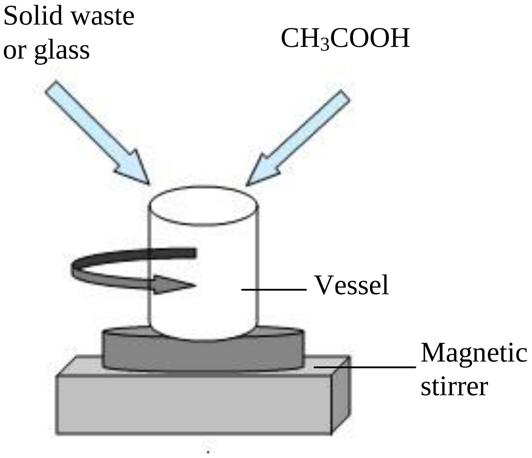

Figure 2. Equipment for performing the TCLP test

Thermal characteristics of the produced glass were studied by means of differential thermal analysis (DTA). DTA measurements were performed using a Perkin Elmer PYRIS Diamond Thermogravimetric/Differential Thermal Analyzer. The studied material was heated in the temperature interval of 25^{o}C–900 ^{o}C by heating rate of $20^{o}C\cdot min^{-1}$ in atmosphere of nytrogen.

RESULTS AND DISCUSSIONS

Chemical composition of the waste materials is shown in Table 2. All waste materials contain high quantity of Fe, especially slag from converter (SC). On the other hand, the dust and slag from electro-furnace contain high enough SiO_2 – the main glass forming component. SiO_2 in the converter slag is very low, but, the waste mixture in the previously mentioned ratio has appropriate content of SiO_2 (47.8%) for glass forming. MgO and Cr_2O_3 is high in the whole waste mixture (15.9 and 2.2 % respectively) and can cause spontaneous uncontrolled crystallization. Cr_2O_3 in lower amount can improve the nucleation during transformation of glass to glass-ceramic. In order to reduce the content of MgO and Cr_2O_3, standard glass (SG) was added in the waste mixture in ratio WM : SG = 7 : 3.

Table 2: Composition of dust (D), slag from electro-furnace (SEF), converter slag (SC)

Item	D	EFS	CS
SiO_2	37.5	53	1.9
MgO	14.5	16.9	6.2
CaO	2.3	2.4	15.9
Al_2O_3	1.8	2	0.3
Cr_2O_3	1	2.5	0.7
CoO	0.1	0.1	0.1
NiO	2.7	0.1	0.45
Fe_2O_3	30	14	60
FeO		9	19

Table 3: Mineralogical composition of the waste materials

	Mineral	Chemical formula	Crystal lattice
FD	Akermanite	$Ca_2MgSi_2O_7$	Tetragonal
	Hematite	Fe_2O_3	Rhombohedral
	Copper zinc chrome iron oxide	$Cu_{0.5}Zn_{0.5}Cr_{1.1}Fe_{0.9}O_4$	
	Forsterite	Mg_2SiO_4 или $2MgO{\cdot}SiO_2$	Orthorhombic
	Magnesium silicate	$MgSiO_3$ или $MgO{\cdot}SiO_2$	Orthorhombic
	Quartz	SiO_2	Hexagonal
	Calcium aluminum silicate	$Ca_{1.95}Al_{3.9}Si_{8.1}O_{24}$	
SEF	Forsterite, Ferroan	$Mg_{1.42}Fe_{0.58}Si_{0.99}Al_{0.01}O_4$	Orthorhombic
	Albite	$NaAlSi_3O_8$	Triclinic
	Maghemite	$Fe_{1.966}O_{2.963}$	Tetragonal
	Quartz	SiO_2	Tetragonal
SC	Hematite	Fe_2O_3	Rhombohedral
	Wuestite	$Fe_{0.925}O$	Cubic face-centered
	Magnetite	Fe_3O_4	Cubic face-centered
	Calcium iron oxide	$CaFeO_3$	Orthorhombic
	Willemite	Zn_2SiO_4	Tetragonal

According to XRD analysis (Table 3), iron is present as hematite (Fe_2O_3, i.e. Fe^{3+} form) and as non-stoichiometric mixed oxide with Cu, Zn and Cr ($Cu_{0.5}Zn_{0.5}Cr_{1.1}Fe_{0.9}O_4$) in the filter dust. The similar mineralogical form of iron is in slag of electro-furnace – non-stoichiometric mixed silicate (forsterite) and non-stoichiometric Fe^{3+} oxide – maghemite. Converter slag contains Fe^{3+} as hematite and calcium iron oxide ($CaFe_2O_4$), Fe^{2+} as wuestite and mixed Fe^{3+} and Fe^{2+} oxide – magnetite (Fe_3O_4). SiO_2 as the glass forming component is present as pure oxide quartz and silicates with other metals, mainly with Mg and Ca. According to the Fe content and appearance, it is expected to produce glass similar to basalt based one (Hlavac J., 1983).

Next step in this study was vitrification of the waste mixture. As was mentioned above, due to higher amount of MgO and Cr_2O_3, standard glass was added in ratio WM : SG = 7 : 3. The composition of the waste mixture, standard glass and the final mixture aimed for vitrification is shown in Table 4. The amount of MgO was reduced to 12.1 %, while Cr_2O_3 to 1.5 %. To ensure transformation of the mixture in liquid state, vitrification was performed at 1250 ^{o}C for 3 hours and 1450 ^{o}C for 1 hour. After cooling at ambient temperature, the produced glass was undergone to thermal investigations. In Fig. 3, som detals from vitrification in chamber furnace are given.

Table 4: Composition of waste mixture (WM) in ratio D : SEF : SC = 1 : 10 : 1, standard glass(SG) and overall glass mixture (GM) in ratio WM : SG = 7 : 3

Item	WM	SG	GM
SiO_2	47.8	71.4	55
MgO	15.9	3.3	12.1
CaO	3.5	9.8	5.4
Al_2O_3	1.9	0.6	1.5
Cr_2O_3	2.2		1.5
CoO	0.1		0.1
NiO	0.3		0.2
Fe_2O_3	19		13.3
FeO	9		6.5
Na_2O		13.3	4
K_2O		1.3	0.4

Figure 3. Vitrification of metallurgical waste in chamber furnace

The results of TCLP test are summarized in Table 5. In the waste materials there are several metals which exceed the applied limits and can be potential hazard to environment if the waste materials would be disposed at landfill. Ni, Mn, Zn, As and Cu are hazardous components in the filter dust, in the slag from electric-furnace slag are Fe, Ni and Mn, while in converter slag are Fe, Ni and Cr. Concentration of Fe and Ni are to much over the applied limits. Also, TCLP test of the produced glass was performed. The results show the vitrification procedure is successful and that the obtained glass demonstrates high chemical durability, corresponding to an inert material. The concentration of all heavy metals are to much bellow the applied limits.

Table 5: Concentration of heavy metals ($mg \cdot dm^{-3}$) in the solution after TCLP test

Item	D	SEF	SC	Glass	Applied limits
Fe	1	202	1155	0.416	2
Ni	6,1	2.7	19.2	0.311	2
Co	0.4	0.14	1.1	< 0.005	2
Cd	< 0.005	< 0.005	< 0.005	< 0.005	0.02
Cu	0.15	0.093	0.07	0.011	0.1
Mn	4.7	14.6	1.5	< 0.005	2
Pb	0.026	0.031	0.086	0.017	0.2
Zn	3.6	0.29	0.42	< 0.005	2
Cr	0.22	1.1	2.9	< 0.005	2
Sb	0.020	0.038	0.023	0.023	
As	1.2	0.011	0.18	0.009	5

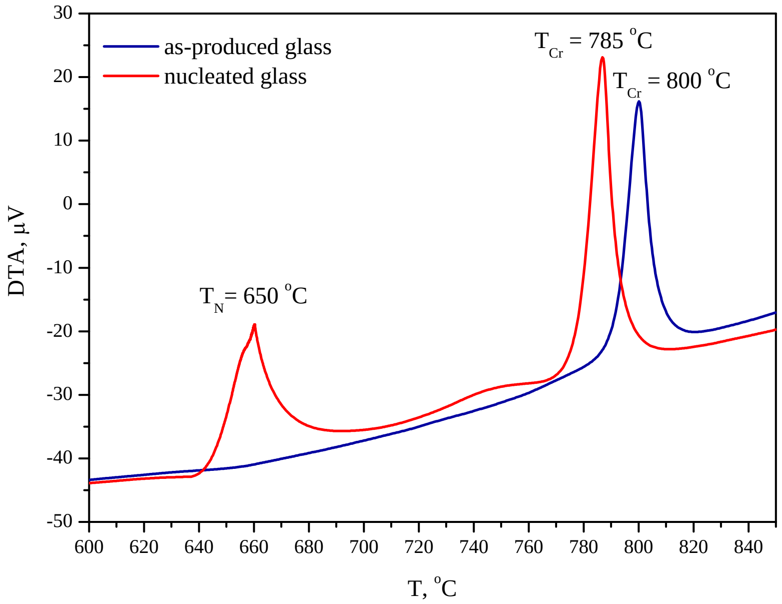

Figure 4. DTA spectra of the as-produced and nucleated glass

In order to determine how and at which temperature the studied glass crystallize, DTA analysis was performed at temperature region from ambient to 900 °C by heating rate of 20 $^{o}C \cdot min^{-1}$. Crystallization of the waste based glass occurs at 800 °C. The shape and the intensity of peak indicate intensive bulk crystallization. If we previously perform nucleation of glass with retention of heating at 650 °C for 1 hour, the temperature of crystallization shifts to lower temperature of 785 °C, while the intensity of the bulk crystallization increases. Those points out that the waste based glass is appropriate for production of glass-ceramic and can be performed by two-stage process: firstly heating at 650 °C to perform nucleation and crystal growth at 785 °C.

CONCLUSIONS

Within this study, characterization of metallurgical waste oroginated from ferronuckel industry as well as its vitrification and characterization of the produced glass was done. The obtained results point out on the following conclusions:

- Waste materials from ferronickel production process contain components which can be potential hazard to environment.
- Waste materials are appropriate for vitrification and further transformation of the produced glass to glass ceramic due to sufficient content of the glass forming components, mainly SiO_2.
- TCLP test of the produced waste based glass has shown that it is environmental friendly, i.e. the quantity of the heavy metals in the leachate is much below the applied limits.
- The as-produced glass has shown intensive bulk crystallization at 800 °C. Nucleation at 650 °C for 1 hour decreases the crystallization temperature to 785 °C, as well as increases the intensity of the bulk crystallization.

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REFERENCES

Barbieri, L., Corradi, A., Lancellott, L. (2002). Thermal and chemical behaviour of different glasses containing steel fly ash and their transformation into glass – ceramics, *J. Europ. Ceram. Soc*. 22, 1759-1765.

Boccaccini, A., Rawlings R. (2002). Glass-ceramics glass – ceramics from waste materials. *Mater. World. 10*, 16-18.

Chinnam, R.K., Francis, A.A., Will, J., Bernardo E., Boccaccini, A.R. (2013). Review. Functional glasses and glass-ceramics derived from iron rich waste and combination of industrial residues. *J. Non-Crystalline Solids*. 365, 63-74.

El-Alaily, N. A. (2003). Study of some properties of lithium silicate glass and glass ceramics containing blast furnace slag. *Glass Technology*. 44, 30-35.

European Commission (2007). Project no. PL 517574 - PREWARC, Strategic Plan for the Prevention of Regional Water Resources Contamination from Mining and Metallurgical Industries in Western Balkan Countries, Final Report.

Fatih, T., Umit, A. (2001). Utilization of Fly-Ash in Manufacturing of Building Bricks, International Ash Utilization Symposium, Center for Applied Research, University of Kentucky.

Ferreira, E. B., Zanotto E. D., Scudeller, L. A. M. (2002). Glass and glass-ceramic from basic oxygen furnace (BOF) slag. *Glass Science and Technology*. 75, 75-86.

Feuerborn, H-J. (2001). Coal Combustion Products in Europe – un update on Production and Utilization, Standardization and Regulation. World of Coal Ash (WOCA) Conference, Denver , CO, USA.

Fredericci, C., Zanotto E. D., Ziemath, E. C. (2000). Crystallization mechanism and properties of a blast furnace slag glass. *J. Non-Crystalline Solids*. 273, 64-75.

Hlavac J. (1983). *The Technology of Glass and Ceramics: An Introduction*. Elsevier, Amsterdam.

Isa, H. (2011). A review of glass-ceramics production from silicate wastes, *Int. J. Phys. Sci*. 6, 6781-6790.

Karamanov, A., Aloisi, M., Pelino, M. (2007). Vitrification of copper flotation waste. *J.Hazar. Mater.*, 140, 333-339.

Karamanov, A., Di Gioacchino, R., Pisciella P., Pelino, M. (2002). Viscosity of iron rich glasses obtained from industrial wastes. *Glass Technology*. 43, 34-38.

Karamanov, A., Taglieri G., Pelino, M. (1999). Iron-Rich Sintered Glass-Ceramics from Industrial Wastes. *J. Am. Ceram. Soc*. 82, 3012-3016.

Pisciella, P., Crisucci, S., Karamanov, A., Pelino M. (2001). Chemical durability of glasses obtained by vitrification of industrial wastes. *Waste Management*. 21, 1-9.

Rawlings, R. D., Wu, J. P., Boccaccini, A. R. (2006). Glass-ceramics: Their production from wastes - A Review. *J. Mater. Sci*., 41, 733–761.

Van der Sloot H. A., Heasman L. and Quevauviller Ph. (1997). Harmonization of leaching/extraction tests. *Elsevier*, Amsterdam.

Vogel, W. (1994). Glass Chemistry. *Springer-Verlag*, Berlin, Heidelberg.

Waste Directive (2008/98/EC) of the European Parliament and the Council of 19 Nov. 2008 on waste and repealing certain Directives, Official Journal of the European Union (L312/3), 22.11. 2008.

Zimmer, A., Bergmann, C.P. (2007). Fly ash of Mineral Coal as Ceramic Tiles Raw – Materials. *Waste Management*. 27, 59-68.

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STRATEGY OF MUNICIPAL WASTE MANAGEMENT

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ABSTRACT

Waste management is an activity of public interest which involves implementation of prescribed waste treatment measures within collection, transport, storage, treatment and disposal of waste, including surveillance over these activities and maintenance of the facilities after their closure. A separate "Waste Treatment Hierarchy" principle defines the priorities within the waste management praxis, such as waste generation prevention, waste generation reduction, separation-primary selection, reuse of products, recycling, secondary raw materials, composting (fertilizer), combustion with and without energy use or waste disposal by deposition, if there is no alternative solution available. Inadequate management of different waste types is the main cause of pollution of air, water and soil. Thus, the decision on waste management technology is a task of high importance that has to be resolved for each concrete system.

Key words: *Solid Waste, Management, Planning, Polluter pay principle, Primary selection, Recycling.*

INTRODUCTION

The EU legislation has produced several directives in the field of waste management. The main goal of the thematic strategy of the European Union on prevention and waste recycling, known as thematic strategy of waste, is to prevent the generation of waste, as well as to promote the usage of waste as a resource, primary in order to obtain secondary raw materials and energy. In the EU waste framework directive, the member states are obliged to produce the plan of the waste management. Council directive 99/31/EC on the landfill of waste has the purpose to reduce the negative effects of waste disposal on the environment, especially concerning soil, ground and surface waters, as well as effects on the population health, by introducing the rigid technological demands.

In the paper of Šooš and Murgašová (2013), EU directives have been classified into three levels. The first level deals with the basics that represent the basic principles, definitions and strategic goals. The second level defines the waste treatment activities, including waste incineration and disposal. The third level contains specific waste flow regulations.

Growth of the waste production represents a cost for the community and a burden for the environment, but, at the same time, a valuable deposit of usable resources. Here arises the demand for development of innovative and sustainable strategies for prevention and management in urban areas, as well as improvement of scientific-based decision making and waste management planning, risk prevention and the usage of land as an integral part of urban planning.

SUSTAINABLE WASTE MANAGEMENT

A sustainable waste management solution should represent a balance between the economic effects, environmental protection and social balance for present and future generations. These complex goals are being expressed by criteria functions and the task of the management is been defined as the problem of multicriteria optimization.

The basic parameters for forming the alternative waste treatment concern the following activities:

- Primary selection,
- Recycling and separation of secondary raw materials,
- Composting,
- Mechanical-biological treatment (MBT),
- Incineration and energy production
- Disposal of non-usable materials

The general opinion is the municipal waste should be treated as a natural resource for secondary raw materials or for energy production, and not to be transported and deposited at the landfills. Nowadays in some EU countries less than 5% of total collected solid waste is been disposed at the landfills, while the rest is been used either as secondary raw material or for energy production. This amount is even more than 50% in certain developed EU member states, while incineration takes about 10%. An average of deposition for less developed EU countries is 90% (see Tables 1 and 2)

On the example of Sweden one can see how the recycling percentage grew and disposal percentage decreased over time (observed since 1975).

The waste generation is constantly increasing due to several factors such as growing population and industrial development, as well as changes in the consumer habits (Solomon, 2010). The objective is to develop the methodology to assess the efficiency of alternative programs both environmentally and from the economic and social perspectives.

Waste represents a considerable loss of resources both in the form of materials and energy. Reducing the material intensity of production and consumption of goods and services is essential to environmental protection and resource conservation. Reductions in intensity of material use can be achieved by more efficient use of natural resources in production and consumption, by recycling used and waste material, and by shifts in consumption patterns to less material intensive goods and services. The treatment and disposal of the generated waste may cause environmental pollution and expose humans to toxic substances and bacteria, and therefore impact on human health. The proper treatment and disposal of waste is important from an environmental and social viewpoint but can be an economic burden on industries, municipalities and households. The amount of waste recycled and composted reduces the demand for raw materials, leading to a reduction in resource extraction. There may also be a benefit of increased income generation for the urban poor through recycling schemes.
Environmental performance at waste management is achieved by consuming less, emitting less,

Table 1: Production and Management of Solid Waste in developed EU Countries kg/inh./year

Country	Communal Solid Waste (kg/inh.)	Landfilling (%)	Incinerated or energy production (%)	Recycling (%)	Composting (%)
EU27	524	40	20	23	17
Belgium	493	5	36	35	25
Denmark	802	4	54	24	18
Germany	681	1	35	48	17
Netherlands	622	1	39	32	27
Austria	601	3	27	29	40
Sweden	515	3	49	35	13
Average	619	2,83	40	38,8	23,3

Table 2: Production and Management of Solid Waste in developing EU Countries kg/inh./year

Country	Communal Solid Waste (kg/inh.)	Landfilling (%)	Incinerated or energy production (%)	Recycling (%)	Composting (%)
EU27	524	40	20	23	17
Bulgaria	467	100	0	0	0
Cyprus	770	87	0	13	0
Latvia	331	93	0	6	1
Lithuania	407	96	0	3	1
Poland	320	87	1	9	4
Romania	382	99	0	1	0
Slovakia	328	83	10	3	5
Serbia	318	85	0	15	0
Average	415,37	91,25	1,37	6,25	1,37

by reusing, achieving financial objectives, protecting the environment, complying with all rules and regulations.

Widely accepted hierarchy of priorities is as follows:

- prevention of waste material being created
- reduction by appropriate technologies and products
- separation of waste materials
- reuse of waste materials
- recycling of waste materials by reprocessing into new products
- incineration or thermal treatment to generate heat or electricity (energy)
- composting to decompose organic waste material, recycling as compost/fertilizer
- disposal of waste in a landfill

The aim of this hierarchy is to extract the maximum practical benefits and to generate the minimum amount of waste.

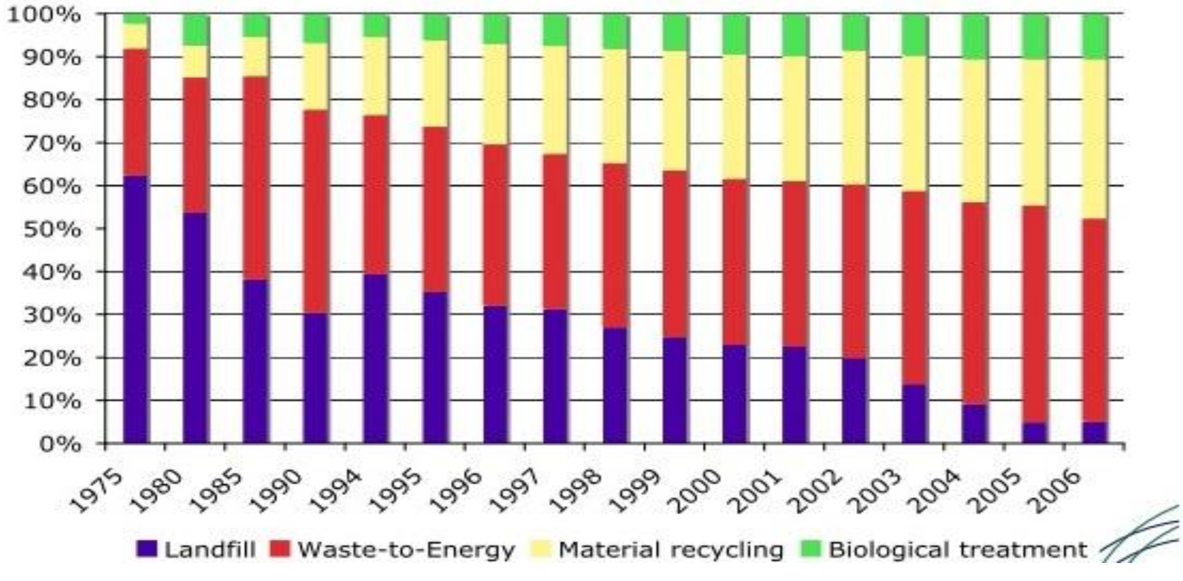

Figure 1. Treatment of municipal solid waste in Sweden (1975-2006)

MUNICIPAL WASTE MANAGEMENT PLANNING

The municipalities have responsibility and authority for planning the collection and transportation of municipal waste and of source-separated recyclables. The county (or the authority at planning area) has the power and duty to prepare and implement plans for the treatment (processing) and disposal of municipal waste generated in the county. A waste management plan should propose the optimal complementary use of a variety of management technologies, including waste reduction, recycling, waste processing, waste-to-energy, and landfilling. In addition, the plan should consider implementing agency, implementation documents, implementation schedule, method of funding the system, and public participation in the development of the plan.

The following long-term treatment (processing) and disposal options could be considered:

- Process of separation and recycling method,
- Composting method,
- Waste-to-energy facility (heat or electricity) for one or a few counties,
- Refuse derived fuel (RDF) / composting processing option
- Publicly owned and operated landfill option,
- Out-of-region disposal options.

A plan should consider the feasible management alternatives. The collection alternatives are differentiated according to the degree of municipal involvement and, conversely, the role of the private sector. Two transportation alternatives could be considered: direct system where municipal waste is conveyed by collection vehicles from the collection site directly to the final treatment/disposal site, and transfer system where the collection vehicles convey the wastes from the collection site to a transfer station facility. A combination of direct and transfer system may also be cost effective. The physical location of these treatment and disposal facilities should be selected. A detailed evaluation of solid waste treatment and disposal alternatives has to be done according to the environmental, regulatory, economic, and harms/benefits aspects. Solutions are based on environmental assessment, ability to meet national targets, and minimizing costs. Critical evaluation of municipal solid waste composting and potential compost markets is presented in (Farrell & Jones, 2009). An analytic network process approach for shifting a municipal solid waste plant in the Metropolitan area of Valencia (Spain) is presented in Aragonés-Beltrán et al. (2010).

The following planning tasks should be performed as the part of the plan:

- Select process of separation waste
- Select recycling facilities
- Select treatment facilities
- Select plants and landfill locations
- Provide adequate disposal capacity for the planning period for generated municipal solid waste.
- Execute Agreements with qualified facilities for municipal waste disposal services, and provide the administration of these agreements
- Maintain and improve services for safe, reliable, effective and efficient solid waste management system
- Propose and execute method of funding the management system

Each appropriate solution of above mentioned tasks should contribute to the technological development in the field of waste management. Defining the appropriate, most optimal solution should be conducted based on achieving the goals of environmental protection, improvement of system efficiency, together with increase of benefit and decrease of costs. These goals are usually in conflict so the tasks are been solved by applying the multicriteria optimization method.

WASTE MANAGEMENT FUNDING

Nowadays are been studied the sources and modes of waste management financing, the collection and treatment taxes, financial benefits from recyclable waste, as well as stimulating instruments for primary selection and recycling.

The service price should cover all the labor costs, as well as costs of the system shutdown. The “polluter pays” principle defined by the law is important, however, it has been never applied in the praxis in the full sense of this provision. Namely, the polluters should pay for the full economic price caused by their activities, i.e. the total price of specialized activities on the pollution removal. If the waste management solution exists, they should finance all the costs of collection, treatment and disposal of waste. Unfortunately, this principal has never been applied in Serbia. Waste management costs, as well as (more or less) all the costs of environmental protection are been treated as a social issue, so the prices of environmental pollution or, in this case, waste management, are been estimated on the basis of actual financial ability of the polluter to pay for the costs of their activities. Consequently, it occurs that sanitary landfills, build with the financial help of the EU, are not being used, because the municipal communal enterprises have no financial means to pay for the disposal costs, while the waste is still been disposed at either illegal or legal but non-sanitary landfills, so the polluters still the environment without having to pay any taxes for environmental pollution.

Next, the funding sources are being concerned at local, regional, national level. Until recently, the Autonomous Province of Vojvodina was able to finance the construction of the waste management facility from its own Fond for Environmental Protection; however, in the meantime, this Fond has been banned. The similar case is with local governments that used to have their own waste-management-dedicated resources, but these resources do not exist anymore as well. From these facts one can conclude the waste management funding in Serbia is severely jeopardized since it represents a social problem and since neither the citizens nor the economy can afford the investments in this activity.

All until decision makers (politicians, government and local municipality bodies) realize no environmental protection and waste management can be provided by making economically unjustified favors for the sake of keeping the social peace, the issue of environmental protection will not be solved. It is necessary to approach to the question of solving the waste-and- environmental issues in a manner defined by the law, so the polluter is forced to pay for elimination of pollution they have produced. If the payment is not possible, then the caused damage should be recompensed in an alternative way. This could be easily achieved by introducing the compulsory primary separation of secondary raw materials at the place of their generation and by introducing taxes charged to all the citizens and enterprises, so the acquisition of garbage containers system for segregation of all the usable waste types (secondary raw materials) could be conducted separately for each building or enterprise.

Municipal waste contains a significant amount of secondary raw materials, as listed in the Table 3 (see below). Practically one third of waste, in bigger settlements and towns, is been made of secondary raw materials. If this group is been complemented by domestic appliances (refrigerators, cooking stoves, laundry machines etc.), worn out furniture, light bulbs and out-of-date PC equipment, partially collected by private entrepreneurs, one can realize how much of useful material is been wasted and, besides that, how the environment is been polluted. Next, about 36% of communal waste in Serbia is been made of biological waste that can be partially easily recycled in the composting reactors, while the other part (i.e. the gardening waste) could be used for energy production, i.e. for heating. Secondary raw materials and biological waste together make about 75% of useful waste while only 25% is been made of other waste types which requests greater financial means to be recycled and used.

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Table 4: Waste production listed by types in the East European countries

Country	Waste type	Year	Materials (%)						
			Paper	Plastic	Glass	Metal	Textile	Food	Other
Croatia	USW*	1995	19.6	7.3	3	2.3	—	31.2	46.6
Czech Republic	USW	1994	8	4	4	2	—	18	64
Estonia	USW	1994	8.1	3	7.4	4.3	5.1	53	19.1
Hungary	USW	1997	19	4.4	3	3.8	3.6	32.3	33.9
Latvia	USW	1998	5	12	7	8	—	50	18
Lithuania	USW	1998	16.9	8	4	2.5	—	50	18.6
Russia	USW	1997	31.9	4.3	5.5	3.6	3.9	33.8	17
Serbia	USW	1998	13.57	12.73	5.44	1.38	5.25	36.72	24.91
Average			**15,26**	**6.97**	**4,92**	**3.48**	**2,23**	**38.12**	**30.26**

*USW stands for useful solid waste

Municipality assemblies should bring the decisions for introducing the waste separation system at the place its generation, as well for all the citizens and enterprises to conduct the part of the process on their own for which they are unable to pay due to low incomes. In this way, the construction of separate waste separation (recycling) unit for the waste that is been produced by themselves would become unnecessary. If the citizens and companies do not accept this kind of treatment process system, than it would be necessary to the economic prices of communal services covering all the expenses of produced waste collection and separation, not letting the price remain on the social level.

Figure 2. System of containers for waste separation at its source (an example from Japan)

CONCLUSIONS

- Waste management is an activity of public interest which involves implementation of prescribed waste treatment measures within collection, transport, storage, treatment and disposal of waste.
- The EU legislation has produced several directives in the field of waste management. The main goal of the thematic strategy of the European Union on prevention and waste recycling, as well as to promote the usage of waste as a resource.
- A sustainable waste management solution should represent a balance between the economic effects, environmental protection and social balance for present and future generations.
- The general opinion is the municipal waste should be treated as a natural resource for secondary raw materials or for energy production, and not to be transported and deposited at the landfills. Nowadays in some EU countries less than 5% of total collected solid waste is been disposed at the landfills, while the rest is been used either as secondary raw material or for energy production.
- In Serbia, as well as in many other East European countries, the situation is quite different. Over 90% of collected solid waste ends up at illegal or legal but non-sanitary landfills, causing pollution of soil and water, since the waste collection price is not an economic but social category.
- The service price should cover all the labor costs, as well as costs of the system shutdown. The “polluter pays” principle defined by the law is important, however, it has been never applied in the praxis in the full sense of this provision.
- Consequently, it occurs that sanitary landfills, build with the financial help of the EU, are not being used, because the municipal communal enterprises have no financial means to pay for the disposal costs, while the waste is still been disposed at either illegal or legal but non-sanitary landfills, so the polluters still contaminate the environment without having to pay any taxes for environmental pollution.
- The service price should cover all the labor costs, as well as costs of the system shutdown. The “polluter pays” principle defined by the law is important, however, it has been never applied in the praxis in the full sense of this provision.
- Consequently, it occurs that sanitary landfills, build with the financial help of the EU, are not being used, because the municipal communal enterprises have no financial means to pay for the disposal costs, while the waste is still been disposed at either illegal or legal but non-sanitary landfills, so the polluters still the environment without having to pay any taxes for environmental pollution.
- Municipal waste contains a significant amount of secondary raw materials, as listed in the Table 3. Practically one third of waste, in bigger settlements and towns, is been made of secondary raw materials.
- Municipality assemblies should bring the decisions for introducing the waste separation system at the place its generation, as well for all the citizens and enterprises to conduct the part of the process on their own for which they are unable to pay due to low incomes.
- If the citizens and companies do not accept this kind of treatment process system, than it would be necessary to the economic prices of communal services covering all the expenses of produced waste collection and separation, not letting the price remain on the social level.

REFERENCES

Aragonés-Beltrán, P., Pastor-Ferrando, J.P., García-García, F., &Pascual-Agulló, A. (2010).An analytic network process approach for siting a municipal solid waste plant in the Metropolitan area of Valencia (Spain), *Journal of Environmental Management,* 91(5), 1071-1086.

Ćurić, N. (2013). Additional Information Toward Inter Municipal Agreement Effectiveness, Proceedings of the III International Conference «*Ecology of Urban Areas*», Zrenjanin

Farrell, M & Jones, D.L. (2009).Critical evaluation of municipal solid waste composting and potential compost markets.*BioresourceTechnologym,* 100 (19), 4301-4310.

Miloradov M., (2012). Integralno, optimalnoiodrživoupravljanjeotpadom, Pristupnabeseda VANU, Akademskebesede, Novi Sad

Miloradov, M., Opricović, S., Stanisavljević, N. (2013).Multicriteria Decision Making for Sustainable Environmental Protection, Proceedings of the III International Conference «*Ecology of Urban Areas*», Zrenjanin, pp. 406-415.

Opricovic, S., &Tzeng, G.H. (2004).The Compromise solution by MCDM methods: A comparative analysis of VIKOR and TOPSIS,*European Journal of Operational Research*, 156(2), 445-455.

Solomon, U. (2010). A detailed look at the three disciplines, environmental ethics, law and education to determine which plays the most critical role in environmental enhancement and protection. *Environment, Development and Sustainability*, 12(6)

Strategija UO, (2010). Strategijaupravljanjaotpadomza period 2010-2019, VladaRepublikeSrbije, Beograd, Službeniglasnik RS

Strategija O-RAZ, (2008). Nacionalnastrategijaodrživograzvoja, Službeniglasnik RS, broj 57/08.

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ECO-FRIENDLY SOLUTION FOR THE PROBLEM OF THE INDUSTRIAL WASTE FLY ASH

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ABSTRACT

Fly Ash (FA) waste particles, obtained as a combustion by-product from the fero-nickel production process as well as from the coal mine, were used like reinforcements of plastic matrices. In this work, FA was chemically modified and used in Poly Vinyl Chloride (PVC) composites aimed for geomembranes. Plasticized PVC was used as a matrix. Concentration of the fly ash was varied in the range of 5, 10 and 20 %. FA/PVC composite samples were prepared using two different types of FA. The FA surface was modified by NaOH and HCl treatment. The obtained samples were analyzed by TGA/DTA, FTIR, SEM and swelling test. Uniform reinforcement dispersion in the polymer matrix is very important in order to ensure that there was a good interactions between both constituents that will result in good composite's properties. SEM microphotographs of the obtained FA/PVC composites have shown region of well dispersed FA particles, but also and FA agglomerations in the composites. Thermal parameters of the PVC composites decreased in the presence of both types of FA. Lower values were obtained due the HCL treatment of FA particles compared to NaOH treated FA. Generally, all the FA/PVC composites have shown higher swelling degree than PVC.

Key words: *Fly Ash, Polymer Composites, TGA/DTA analyze.*

INTRODUCTION

Fly ash is a puzzolanic material generated from the fero-nickel production process as well as coal-burning thermal power plants. Though a significant fraction of coal fly ash is used as a cement and concrete additive in the world, only a very small portion of the million tons of fly ash generated is re-utilized in Macedonia. Fly ash contains a range of heavy metals of different mobilities in its structure (Polat et al., 2002). Since it is usually disposed of in the form of slurry in the vicinity of the power plant, fly ash possesses significant environmental risk due to the possibility of leaching of these metals into environment (Polat et al., 2002; Baba A, 2004). This risk has led to extensive studies on the physical-chemical properties and leaching behavior of fly ash (Vassilev et al. 2005; Singh et al., 2003). There is a large body of work on the use of fly ash in cement and brick production (Demirbas A.,1996). In one study, the Derjaguin–Landau–Verway–Overbeek (DLVO) theory for dispersion–flocculation of heterogeneous particles with different surface potentials was applied to explain the effect of fly ash on the rheology of cement paste containing naphthalene sulfonate superplasticizer. The fly ash and ordinary porland cement were compared. The fly ash–cement paste without superplasticizer resulted the sign of zeta potential of fly ash was different from ordinary Portland cement. So, the extent of the potential energy barrier between particles was small or showed negative value, and the change in the rheology of the fly ash–cement paste was mainly dependent on the bulk solid volume of fly ash. The fly ash–cement paste with naphthalene sulfonate superplasticizer, fly ash and cement had the same sign and dispersed well due to higher potential barrier. The extent of potential energy barrier depended on the absolute value of surface potential, which was represented by a function of the amount of adsorbed superplasticizer. The bulk solid volume of fly ash also affected the change in flow ability.

The purpose of this study was to investigate the application of fly ash as an alternative filler material in PVC past sols aimed for geomembrane.

EXPERIMENTAL

Composite films based on PVC and Fly ash were prepared by solvent-casting method in 1,4-Dioxin with the total mixing time of 30 min. Plasticized PVC was used as a matrix. Concentration of the fly ash was varied in the range of 5, 10 and 20 %. FA/PVC composite film-samples were prepared using two different types of FA (FA from fero-nickel production and FA from coal mine). The FA surface was modified by 2M NaOH and 1M HCl treatment. The obtained samples were analyzed by TGA/DTA, SEM and swelling test. TGA/DTA measurements were performed using a Perkin Elmer Pyris Diamond Thermogravimetric/Differential Thermal Analyzer. The studied material was heated in the temperature interval of 25oC÷1100oC by heating rate of 20oC·min−1 air atmosphere. SEM analyses were performed using FEI Quanta 200 FEG system.

RESULTS AND DISCUSSION

Chemical composition of both types of Fly ash used in the preparation of the PVC based composite films was analyzed and the obtained data are shown in Table 1. As it was expected, in the fly ash from Oslomej dominant were SiO_2 and Al_2O_3 oxides, while in the fly ash from FENI, Fe_2O_3 and MgO oxides dominate.

Table 1: Chemical composition of Fly Ash samples

Elements	FA-Oslomej [%]	FA-FENI [%]
SiO_2	50	37,5
Al_2O_3	30	1,8
Fe_2O_3	13	22,5
MgO	1,5	14,5
CaO	3,0	2,3
TiO_2	1,0	/

Uniform reinforcement dispersion in the matrix materials is very important in order to ensure that there was a good interactions between both constituents that will result in good composite’s properties. Scanning electron microscope (SEM) was used to take pictures of the powder materials to determine the general look of particles such as shape. Characteristic SEM picture of FA is shown in Figure 1. As it is seen from Figure 1, the shape of fly ash is not regular and uniform. There are large and small particles. This is expected due to the mixed composition of ash content.

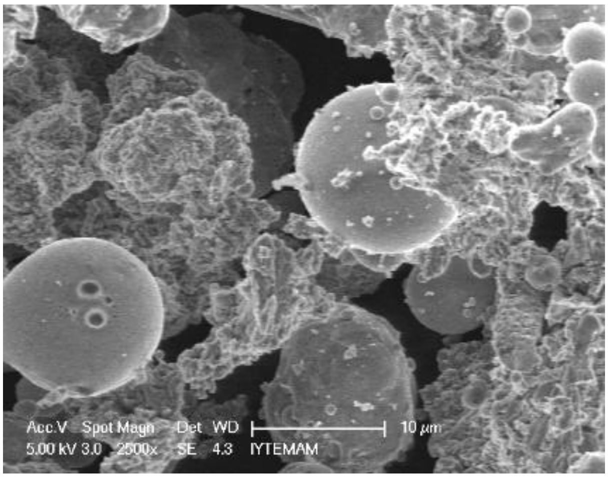
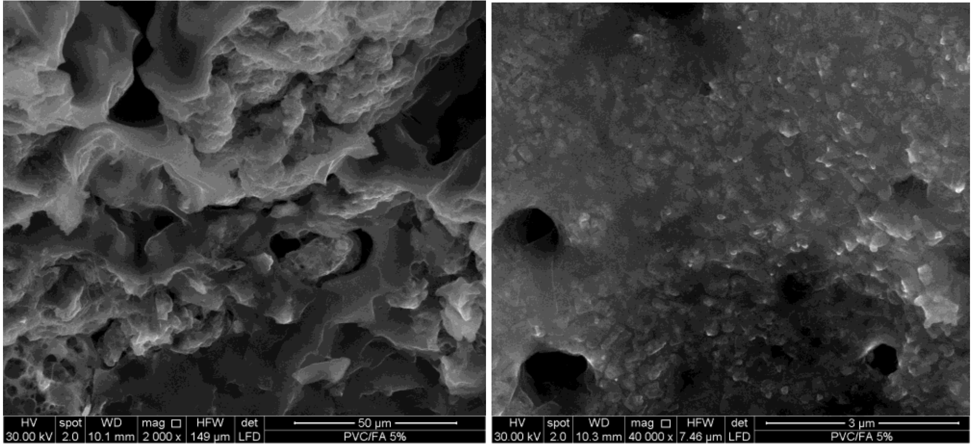


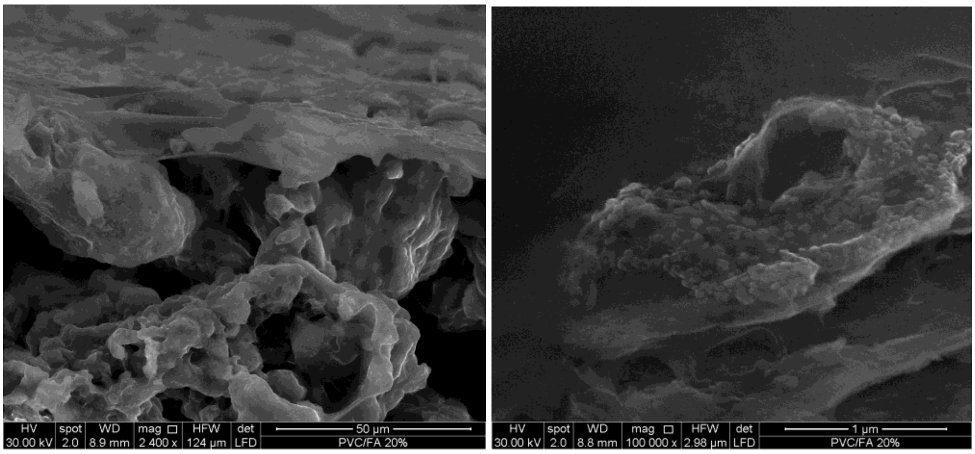
Figure 1. SEM photos of Fly ash (x2500)

SEM microphotographs of the obtained FA/PVC composites are shown in Figure 2 and Figure 3. They have shown region of well dispersed FA particles, but also and FA agglomerations in the composites. Besides information for the FA dispersion in the polymer matrix, SEM photos have shown that voids and micro pores were present in the obtained composites.



(a)(x2000) *(b) (x40000)*

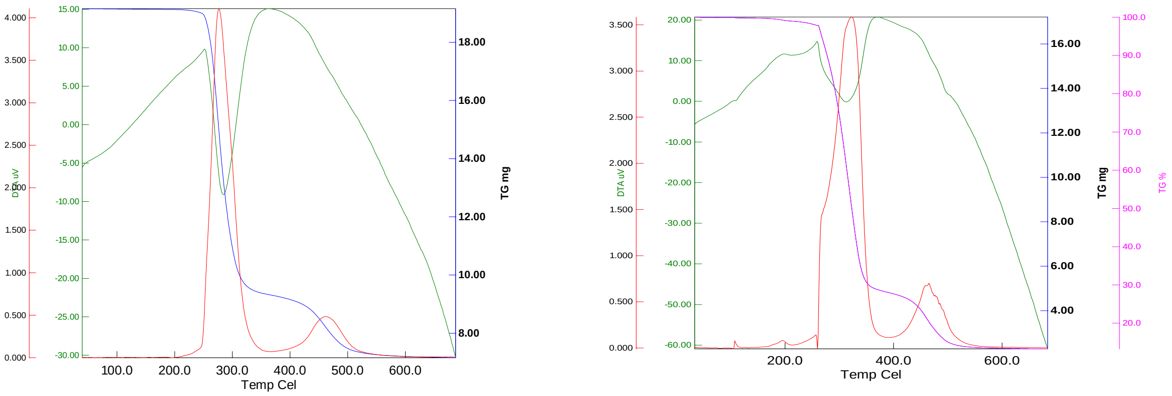
Figure 2. SEM photos of 5% FA/PVC



(a) (x2400) *(b) (x100000)*

Figure 3. SEM photos of 20% FA/PVC

Thermal stability and all the other characteristic thermal parameters of the PVC composites decreased in the presence of both types of FA. Lower values were obtained due the HCL treatment of FA particles compared to NaOH treated FA. Characteristic TGA/DTA thermogram for FA/PVC is shown in Figure 4.



(a) 10% FA/PVC *(b) 20%FA/PVC*

Figure 4. Characteristic TGA/DTA for FA/PVC composites

Generally, all the FA/PVC composites have shown higher swelling degree than PVC. Swelling degree increase by increasing the flay ash content. Higher values were obtained for composites with NaOH treated FA particles. Swelling behavior was studied for both types of FA used. Characteristic curves are shown in Figure 5 and Figure 6.

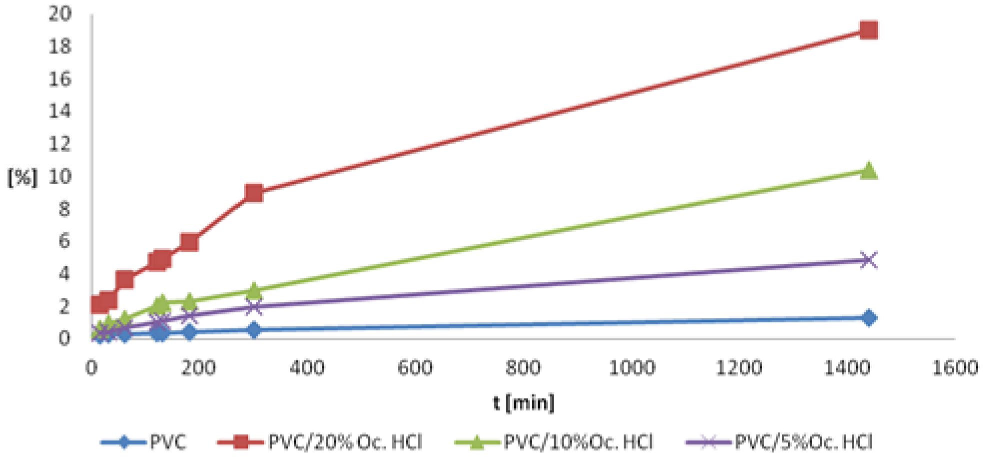


Figure 5. Swelling behavior of PVC/FA Os-HCl treated

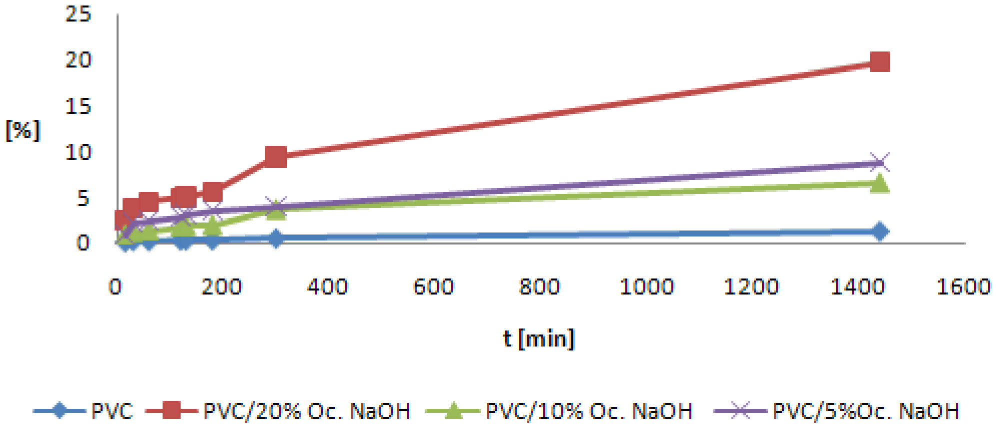


Figure 6. Swelling behavior of PVC/FA Os-NaOH treated

CONCLUSIONS

Composite films based on PVC and Fly ash were sucsefully prepared by solvent-casting method. Plasticized PVC was used as a matrix and various concentration of fly ash (5, 10 and 20 %). FA/PVC composite film-samples were prepared using two different types of FA (FA from fero-nickel production and FA from coal mine). The FA surface was modified by 2M NaOH and 1M HCl treatment. The obtained samples have shown imprved thermal stability. Higher content of fly ash has resulted in higher % of swelling.

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REFERENCES

Polat M., Guler E., Akar G., Morogan H., Ipekoglu U., Cohen H.J., (2002) ,Feasibility of using fly ash, lime and bentonite to neutralize acidity of pore fluids, *J. Chem. Technol. Biotechnol*., 77, 372

Baba A., (2004) Investigations of leaching characteristics of ash wastes from thermal power planits in western Turkey, *19th World Energy Congres*, Sydney, Australia

Vassilev S.V., , Vassieva C.G., (2005) Methods for characterization of composition of fly ashes from coal fired power stations: a critical overview, *Energy Fuels*, *19*, 1084 (2005)

Singh N., Ramachandran R.D., Sarkar A.K., (2003) Quantitative estimation of constituents in fly ash by lithium tetraborate fusion, *Int.J.Environ.Anal.Chem.*, *83*,891

Demirbas A., (1996) Optimizing the physical and technological properties of cements additives in concrete mixture, *Cement and Concrete Res., 26*, 1737

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ECOLOGICAL-ECONOMIC ANALYSIS OF RECYCLING PROCESS MEDICAL WASTE IN THE CASE ON NORTHEAST REGION OF BOSNIA AND HERZEGOVINA

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ABSTRACT

On the way to establish a system of sustainable development recycling activities are based on the conservation of existing natural resources. In this paper, the collected data on the quantity and volume of medical waste generated in health care facilities in the Northeastern region of Bosnia and Herzegovina, as a basis for the development of ecological-economic model of the treatment of medical waste based on the recycling of non-hazardous waste as part of the primary process.Featured results can significantly contribute to the understanding of the problem and improve the situation in the field of integrated medical waste management in order to build better environmental policies, and programs of more efficient and more realistic model treatment of medical waste generated in Bosnia and Herzegovina.

Keywords: *Medical waste, recycling activities, the amount and category of medical waste, treatment model.*

INTRODUCTION

Consequence of the continuous and dynamic growth of the level of economic wealth and demographic growth in the developed countries but also in developing countries, generating an increasing amount of medical waste. Health care institutions do not conduct adequate medical waste management system, which is in line with the recommendations of the World Health Organization (WHO) and EU Directives. Hospitals as a major generators of medical waste are not made segregation of waste at source and in most cases the waste is collected together with the MSW and ends without proper treatment at the landfill, which disrupts the quality of the environment. The main problems relate to the lack of separation operation of hazardous and non-hazardous medical waste, lack of plans for medical waste management in health institutions and monitoring the amount of waste generation. (Stankovic, A.et. al., 2008).

The World Health Organization (WHO) has classified medical waste to hazardous and non-hazardous medical waste. Between 75% and 90% of medical waste generated in the health field, can be compared with the solid waste (non-hazardous waste), and the remaining 10% to 25% of the total amount of waste, it is potentially dangerous.

Based on the statistical data of the World Health Organization (WHO), the average structure of the generated medical waste in a health care facility is shown in Figure 1. Non hazardous waste (general waste) takes up about 80% and hazardous waste around 20% (pathological and infectious waste 5%, chemical and pharmaceutical waste 3%, blades 1% and special hazardous waste 1%). (Chaerul M. et. al.2007).

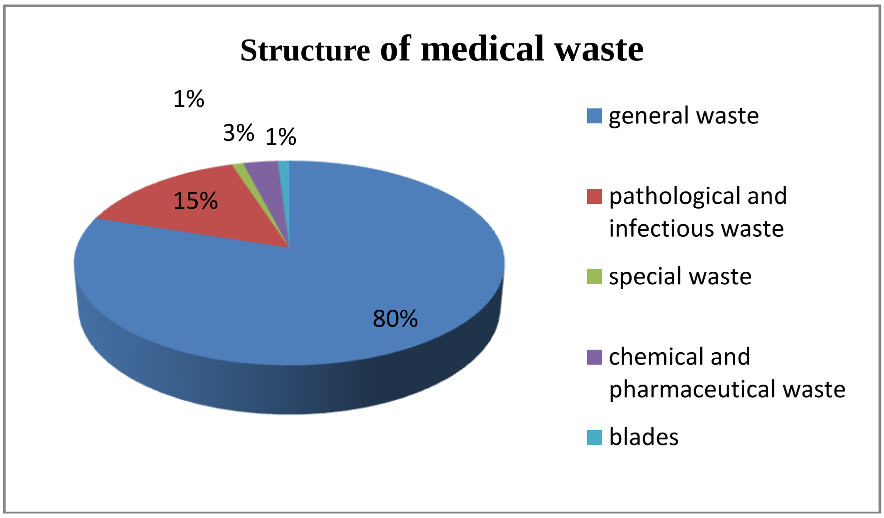

Figure 1. Structure of medical waste (WHO)

In order to establish a process of recycling medical waste, it is necessary to determine the mass and volume percentage of recyclable components from non-hazardous part of waste. Separation of recyclable components from the total quantity of hazardous medical waste, reducing the amount and volume of waste that is landfilled and waste management costs, and on the other hand it is possible to achieve financial gain from the sale of recyclable materials on the market.

RESEARCH METHODOLOGY

The research is based on the data collected through written surveys on the territory of North-East region of Bosnia and Herzegovina, where it is concentrated around 650,000 people and 42 health centers, which are organized at the primary and secondary health care level.

From a technical point of view written survey was related to collection of data on the total amount and volume of medical waste generated in health care facilities in the area of research.

Area of research

The study was conducted in medical institutions in the city of Bijeljina and Tuzla, the municipality Ugljevik, Lopare, Zvornik, Vukosavlje Odzak, Samac, Modrica, Gracanica, Lukavac, Srebrenik, Han Sand and Brcko District. (Figure 2.)

Figure 2. Map of Europe and the Regional map of Bosnia and Herzegovina, showing areas of research

RESULTS

The existing practice of irresponsible collection and disposal of medical waste without sorting and detoxification leads to the loss of natural resources, as well as the rapid spread of infectious diseases, transmission of microorganisms through water, soil and air. Good practice in the treatment of medical waste includes its classification at the place of occurrence on hazardous and non-hazardous (general) medical waste, with the opportunities created by the application of specialized treatment methods for hazardous waste and non-hazardous waste from the separation of recyclable components. This reduces the cost of subsequent sorting and increases the quality of recyclable materials.

Results of the survey of health facilities

The result of the survey of health facilities in the area of research, showing the approximate quantity and volume of generated medical waste. Weekly surveys on a monthly basis, undertook an assessment of the total amount and volume of medical waste generated in each department in each facility of greater healthcare institutions. The absence of a system for monitoring the quantity and volume of waste generation leads to imprecise data, so they need to be interpreted with some caution. Data obtained estimates were reduced statistically to municipalities and cities with the goal of improving the precision of estimates, as well as qualitative impact on the prediction of the quantity and volume of medical waste generation.

According to the data, the total amount of medical waste generated in health care facilities is 440 tons, with a capacity of 2,635 beds and an average bed occupancy of 69.79%.

It is notable that the medical waste is mainly generated in the diagnosis, treatment or immunization of patients and the amount of waste vary depending on the type of services provided in health facilities.

Identified the following types of hazardous waste under the Waste Catalogue: pathological and infectious waste, sharps, pharmaceutical products, pressure vessels, chemical waste and inert (general) waste. Table 1. summarizes the average total amount of medical waste on a monthly basis, which is generated by various medical institutions.

Table 1: Overview of evaluation the average amount of generated medical waste obtained by written survey in the area of research

Type of health care facilities	Evaluation of the total volume of medical waste **(*t/month*)**
Health Centers	56,9
Dialysis Centers	71,4
Polyclinics	132,1
Hospitals	155,1
Ambulances	24,5
Total:	440,0

According to the World Health Organization (WHO), it can be assumed that the total amount of medical waste generated by 440 t on a monthly basis, reduced to 80% inert (non-hazardous) waste and 20% of hazardous waste, as in the study is 352 t and 88 non-hazardous tonnes of hazardous waste per month. (Figure 3.)

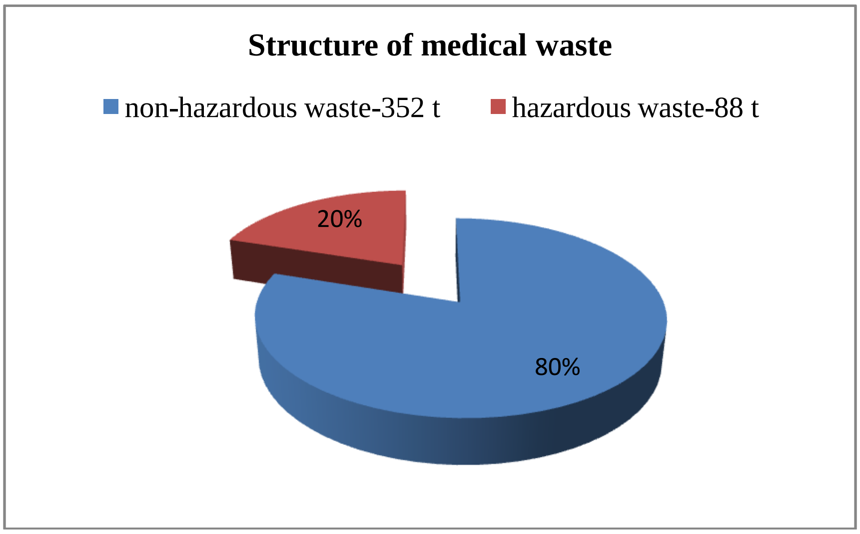

Figure 3. Percentage composition of the total amount of generated medical waste

Based on World Health Organization (WHO), it can be compared an average structure of non-hazardous medical waste, and reduced to a secondary raw material mass and volume share: paper, plastics, organic waste, diapers, metal, glass, yard waste, and more. (Table 2.)

Table 2: Participation of raw materials in the structure of non-hazardous medical waste

Raw materials	Mass participation	Volume participation
Paper	53	20
Glass	2	2
Plastics	14	35
Metals	3	2
Diapers	4	1
Organic waste	17	36
Yard (plant) waste	2	2
Other	5	2
Total:	100%	100%

For estimated amounts of non-hazardous medical waste were adopted medium density waste by type of recyclable components in order to define volume part of waste (Table 3). Adopted medium density were recommended by consulted literature, although the value of the density generally depends on several influencing factors.

Table 3: Average density of certain recyclable components

Reciklabilna komponenta	Average density (t/m^3)
Paper	0,070
Glass	0,330
Plastics	0,140
Rubber	0,195
Textile	0,175
Metal	0,700
Organic waste	0,400
Other	0,500

Table 4 shows the structure of the total weight and volume of generated hazardous medical waste in the survey on a monthly basis, where it clearly shows the potential amounts of raw materials in order to establish a recycling activity.

Table 4: Mass and volume of raw materials

Raw material	Mass (*t*)	Volume (*m*^{3})
Paper	187	2.671
Glass	7	21,5
Plastics	50	357
Metals	11	16
Diapers	14	80
Organic waste	60	150
Yard (plant) waste	7	17,5
Other	16	32
Total:	352	3.345

Reduction in the total volume of non-hazardous medical waste

Separation of recyclable components from non-hazardous medical waste, that are easily available on the site generation reduces the volume of waste that is landfilled.

The initial volume of non-hazardous medical waste on a monthly basis of 352 t and 3,345 m^3 on average amounts to about 2,364 m^3 of waste per month, after the separation, as shown in Table 5.

Table 5: Possible reduction in waste volume on a monthly basis

Raw material	Volume partition (%)	Monthly volume (*m*^{3})	Utilization coeficient	After separation (*m*^{3})
Paper	20	2.671,0	0,3	801,5
Glass	2	1,5	0,3	6,5
Plastics-non classified	35	357,0	0,3	107,0
Metal	2	16,0	0,8	15,0
Organic waste	36	167,5	0.3	51,0
Total:		3.233,0		981,0

If it is assumed, that a part of waste that can theoretically be extracted, remain mixed with the rest of the waste for final disposal, it is possible to decrease the volume of waste by 30%, thus the service life of the landfill effectively extended.

Economic and financial analysis

Analyzing the possible financial gains shown in Table 6. of the separated recyclable components, we get the revenue on a monthly basis in the amount of € 2,491.50 and the annual income amounts to € 29,900.00.

Table 6: Possible monthly financial effects

Raw material	Mass partition (%)	Monthly amount (*t*)	Possible to extract (*t*)	Sale price (€/*t*)	Income (€/monthly)
Paper	14	187	56,1	25,0	1.402,00
Glass	2	7	2,1	15,0	31,50
Plastics-non classified	12	50	15	50,0	750,00
Metal	2	11	8,8	35,0	308,00
Total:		255	82		2.491,50

Funds obtained by the sale of raw materials in the market, health care institutions in the region on one side would settle utility bills and purchase of supplies, and on the other side significantly slows the depletion of natural raw resources. Investment funds in the present, to the revenues and benefits in a long number of years in the future, thereby reducing the high level of uncertainty and achieve the expected ecological and economic performance of these investments.

DISCUSSION

Establishing a process of recycling medical waste, consequently, enables the decrease in the degree of degradation of water, air and soil, and represents a significant step forward in preserving the quality of the environment Northeastern region of Bosnia and Herzegovina.

Separation of the total amount of medical waste generated at the site (in-situ) is environmentally friendly solution and would be used as pre-treatment, followed by a separate non-hazardous medical waste needed to be sent to a recycling center, and the rest must be disposed to landfill complex.

Proposal represents an interim solution, which fits well into the future final solution - the construction of incineration or purchase equipment for the destruction of hazardous medical waste.

CONCLUSION

On the basis of this study it can be concluded that there is a possibility of establishing a recycling activities in health care institutions in the example of North-East region of Bosnia and Herzegovina on the basis of potential recyclable components of medical waste.

Management of health institutions Northeastern region of Bosnia and Herzegovina, it is necessary to make a decision on mandatory separation and selection of medical waste at the source in order to establish a recycling process, preserve natural resources and save energy.

The total amount of non-hazardous medical waste prior to landfilling is reduced by separating the place of generation by 30% (approximately 12,000 m^3/y), which represents a significant saving on the level of the entire lifetime of the landfill complex.

Ranking separated recyclable waste components in the market raw materials, can achieve an annual income of about € 29,900.00 and create basic conditions for job creation.

The work opens new directions of research of medical waste management in Bosnia and Herzegovina, based on the principles of sustainable development and European integration requirements.

REFERENCES

Askarian M. Vakili M. Kabir *G. Results of a hospital waste survey in private hospitals in Fars Province,* Iran, Waste Management 24, 347-352.

Bdour A. Altrabsheh B Hadadin N. Al-Shareif M. *Assessment of medical wastes management practice: a case study of the Northern Part of Jordan*,Waste Management 27, 746-759.

Fisher S. *Healthcare waste management in UK:the challenges facing healthcare waste producers in light of changes in legislation and increased pressures to manage waste more efficiently,* Waste Management 25, 572-574.

Kanazir Jasmina, Vojinović-Miloradov Mirjana, Bašić Đorđe, ECOLOGY AND RISK MANAGEMENT OF HAZARDS IN PHARMACEUTICAL INDUSTRY ENVIRONMENTAL, HEALTH AND HUMANITY ISSUES IN THE DOWN DANUBIAN REGION: MULTIDISCIPLINARY APPROACHES, (2009), vol. br. , str. 255-263.

Kudumović M. Kudumović A. *Economic analisis of health*, HealthMed, 2008, 2 (2): 100-103.

Mohee R. *Medical wastes characterization in healthcare institutions in Mauritius.* Waste Management 25, 575-581.

Pravilnik o upravljanju medicinskim otpadom (Sl. novine FBiH 77/08 i Sl. Glasnik RS 90/06).

Stanković, A., Nikić, D., Nikolić, M., *Treatment of medical waste in Nišava and Toplica districts, Serbia,* Waste Manag Res, June 2008, vol. 26, 3. pp.309-313.

Svraka, A. V,. Vučina, Z., Filipović-Hadžiomeragić A., Mulaomerović, M.,(2008) *Methods of removing infectious and laboratorys'waste in clinic centers,* HealthMed, Vol.2, no. 4, p. 265-272.

Zakon o zaštiti okoliša/ Zakon o zaštiti životne sredine (Sl. novine FBiH 33/03 i Sl. Glasnik RS 53/02).

Velma (Tahmaz) Pijalović, Mensura Kudumović *Analysis of health expenditure in the EU8 countries and Bosnia and Herzegovina*, HealthMed, 2010,4 (4): 822-828.

Chaerul M. Tanak M. Shekdar A. V. *A system dynamics approach for hospital waste management,* Waste Management 28, 442-449.

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PROBLEMS OF RECYCLING AND SUSTAINABLE MANAGEMENT OF ELECTRIC AND ELECTRONIC WASTE

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ABSTRACT

Recycling of electrical and electronic waste is a very complex problem. The waste itself is massive, but it is also contained in many other products, such as automobiles, aircrafts, agricultural machinery, industrial equipment, military equipment, toys, and so on. Today, electrical and electronic equipment and devices are used in all life domains and they raise a number of serious problems that are related to the end of their life cycle. So, the first question is how to ensure the systematic collection of this type of waste and its selection? A special problem is the collection of e-components from complex products at the end of their life cycle, for example a car? Of course, there are the problems of their dismantling and subsequent selection and recycling. On the other hand, this waste is very toxic and it should be handled with care during collection, disposal, and transportation to its dismantling and recycling. Also, a special attention should be paid to the development of new electrical and electronic products and components in order to replace the highly toxic materials and new materials that are environmental and human friendly. However, this is not always possible, especially when it comes to military equipment and telecommunications. E-waste is a major source of valuable and rare materials such as gold, platinum, silver, germanium, rare earths, and many other metals and metalloids. By recycling it, we save the already poor resources of many strategically important materials. This is the waste that has a very high growth trend. It is influenced by massive growth of application of e-products, and short product life, primarily due to obsolescence, due to the extremely rapid technological development of this field. The recycling of materials and specific substances that are contained in e-waste require the use of complex and expensive technologies. The establishment of an effective system of sustainable management of e-waste, with appropriate innovation, is the right way for its efficient recycling, environmental protection and ensuring of economic viability.

Key words: *electrical and electronic waste, e-waste, sustainable recycling, toxic materials, life cycle, the end of the life cycle.*

INTRODUCTION

With rapid application of electronics in a variety of areas (from children’s toys to the security system of houses and flats), there is an increasing accumulation of electrical and electronic waste (e-waste) and the accumulation is exponential. On the other hand, with the explosive innovations in this area, there is a rapid replacement of the product, long before the end of their lives (e.g. mobile phones), leading to multiple increasing of e-waste. Electronic waste is accumulated nearly 3 times faster than regular household garbage. Thus, the growth rate of this waste ranges from 5% to 10%. Of course, that e-waste is an important resource for obtaining strategic materials, but it is also a potential pollutant of the environment. E-waste contains a large number of precious and heavy metals, rare earths and radioactive materials, plastics, glass and a variety of other materials that can be recycled. In addition, it contains a number of toxic and harmful substances that may enter the water, contaminate soil, etc., which leads to contamination of the environment and contamination of food in the food chain.

The soil contamination is permanent, which causes serious damage to the environment and human health while reducing the resources for food production. It is therefore very important to establish an efficient system operation and management of e-waste in order to avoid these consequences, and the waste has become an important resource for the production of precious and strategic materials.

Bearing all this in mind, many countries have passed legislations (directives, laws, recommendations), which regulate the area of e-waste management and the design and production of electrical and electronic products. As an example, the most commonly listed EU directives in the world are under the name of RoHS - Restriction of use of certain hazardous substances in electrical and electronic equipment, and WEEE - Waste Electrical and Electronic Equipment.

However, in spite of all efforts in the treatment and management of e-waste, there are obvious problems. They can be grouped into several sections:

- the presence of electric and electronic components in a large number of other products that are usually not the subject of dismantling, selection and collection of recycling of those products,
- collection of certain e-products such as batteries, bulbs (especially energy saving bulbs), mobile phones, toys, etc.
- the complexity of processes of recycling of certain materials or neutralization of toxic substances and their cost
- specific requirements for handling and recycling of certain toxic substances contained in e-waste (pyrolysate, mercury, radioactive cobalt, etc.).
- location of the facilities for the recycling of e-waste and its impact on the environment and human health
- the problem of recycling of composite materials contained in modern e-devices (for super magnets, dielectrics, fibers, etc.).
- disposal of final e-waste.

Of course this does not exhaust the set of issues surrounding e-waste and its recycling, but these problems are the most evident.

Electronic waste is divided into several types of waste and that is the following:

- computer products
- audio-visual products
- communication products
- radio and television equipment
- devices and household appliances
- lighting equipment
- all types of accumulators and batteries
- instruments and devices for monitoring and measuring,
- power tools
- wires and cables
- electronics for motor vehicles and other transport equipment
- energy devices and equipment
- industrial electronics
- electronics for military resources, devices and systems
- medical equipment and devices
- traffic signalization and systems
- laboratory and scientific equipment
- other electronics.

The listed waste should include all electronic and electrical waste resulting from regular replacement of materials, parts and components of products or the aforementioned are changed due to defect. The quality of electronic products is diverse and complex and it is affected by the quality of materials, the origin of products (company, state) and the conditions of use.

Regardless of all the above, the electronic waste should be treated as a very important resource because many metals and materials that are in it are very limited in nature (gold, platinum, germanium, zirconium, rare earth, etc.). Of course, neither copper nor silver can be found in abundance. It is therefore very important to pay great attention to collection and recycling of e-waste.

RECYCLING SITUATION

So far, no country in the world has established a sustainable recycling of e-waste (Vinod Kumar, Ruchi Garg, Zillur Rahman, A.A.Kazmi, 2011; Deepti Mittal, Navnish Goel, Renu Rani 2012). Yet many laws and regulations governing this area were passed, and the whole series of concrete measures were taken in order to improve the recycling of e-waste. However, in Serbia very little has been done in this area and is mainly confined to the recycling of non-ferrous metals (accumulators, electric cables), and to a lesser extent, components that contain a significant amount of silver, gold and platinum are exported. There is no systematic approach to the collection and recycling of e-waste. In Serbia, the observed negative trends can be seen in: Unofficial estimates show that from the total amount of generated waste from electrical and electronic products (approximately 70,000 tons per year) less than 10% is recycled. This negative statistics inevitably leads to the conclusion that the highest percentage of e-waste ends up in dumps along with other materials or in illegal dumps, which is absolutely unacceptable (S. Chatterjee, 2012)! Monitoring the quantity and type of generated e-waste and the monitoring of its flow practically did not exist prior to the laws and regulations; There is no organized system of collection, selection, recycling and disposal of e-waste; Little or no knowledge about the negative consequences of improper treatment and disposal of e-waste in landfills; Exports of selected recyclable waste from electrical and electronic products for further recycling to countries that have recycling centers for each component for which there is no possibility of recycling in Serbia presents an expensive investment for operators, and the possibility of using these materials in Serbia is underdeveloped (cathode ray tube as the material for paving, etc.). Construction of the facility for treatment of hazardous components of e-waste (although more expensive short-term investments) produces significant long-term savings that would allow operators to invest in the promotion of recycling technologies (Lozica Ivanović, Danica Josifović, Blaža Stojanović, Andreja Ilić, 2012). The absence of a systemic solution for financing of the collection of e-waste at the local level results in the ignorance of some of the actors for more serious involvement in the process (P. Gramatyka, R. Nowosielski, P. Sakiewicz, 2007); The absence of cross-sector partnerships in addressing the challenges that arise during the management of waste from electrical and electronic equipment makes the process inefficient, costly and unsustainable.

Providing representation reflects the real situation, and not the one that is defined by law and strategies of waste management and intentions that can only be seen on paper.

What's the status of recycling of e-waste in the world? EU, Japan, South Korea and other countries now have their own systems for the processing of e-waste. There the analysis of the current collection of e-waste, reusing, recycling and applicable regulations is done, in order to study their functioning and assess their effectiveness (Matthias Buchert, Andreas Manhart, Daniel Bleher, Detlef Pingel, 2012; Suraj S., 2010).

1) European Union

In 28 member states a number of regulations related to e-waste is adopted, which is intended to preserve, protect and improve the quality of the environment, protect human health and ensure sustainable use of natural resources (European Commission-WEEE Directive, 2003 updated 2012). It included five key categories: the design of e-products, e-waste, e-waste recovery, treatment, and the financing of e-waste treatment and awareness of users of e-products. Directive includes the recovery, recycling and reuse of e-waste. The regulation aims to raise awareness about the factors end of life span during product design. These factors include the removal of parts and recycling of materials, system for proper collection, which requires separate collection of e-waste, in order to decrease waste in the general waste flow and the best practice for treatment, recovery and recycling of e-waste (DIRECTIVE 2012/19/EU).

The implementation was not an easy task. Although some EU countries are already implementing the directive (the Netherlands, Greece) other, mostly countries without system for e-waste management required changes or the right to a temporary deviation from the regulations. The two main factors that have delayed the full implementation of the Directive are: (1) the transition from previous regulations, (2) negotiations with interested parties regarding the responsibility for the process. Adaptation of the directive in 2012 included both factors, for the purpose of real consideration of the practical application of the requirements of the directive.

2) Japan

Japanese law on e-waste requires manufacturers and importers to include end of life electronics to be recycled and to manage this waste, in order to ensure the separation of e-waste from municipal solid waste. Thus, the law on recycling of home appliances, which is fully in force since 2001, forces manufacturers and importers to recycle four types of e-waste from households: TVs, refrigerators and freezers, washing machines and air conditioners. In addition, in 2001, Japan has started mandatory recycling business PCs, and in 2003 the requirement was extended to home computers, by adoption of the Law on Promotion of Effective Utilization of Resources. The system was initially managed by local authorities, and since 2003, products are grouped PC3R promotional center that is responsible for the collection and recycling / re-use of computers. Ticketing system for the recycling of home appliances was developed, which ensures that the relevant parties: consumers, retailers and manufacturers comply with the activities for the recycling of household appliances, and according to the Law on recycling of home appliances.

Figure 1 shows the flow of concrete recycling system of home appliances in Japan.

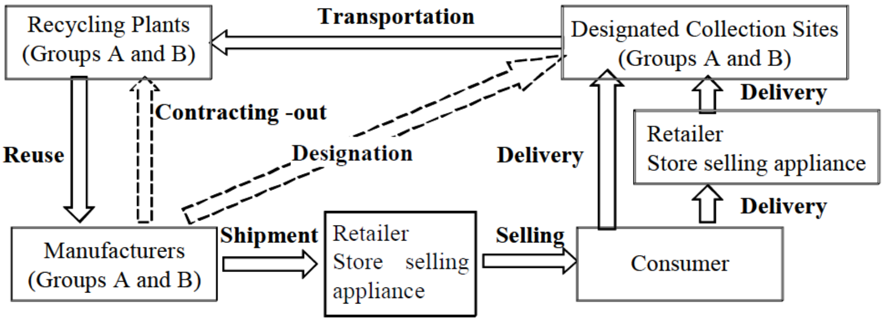


Figure 1. E-waste recycling system in Japan
Source: World Academy of Science, Engineering and Technology 38 2010, Bi Bo and Kayoko Yamamoto

3) China

Figure 2 shows a system of recycling of e-waste in China. On the above graph, we can see that the system of recycling e-waste is not fully developed. Both e-wastes, the one that is generated in the country and the one that is imported from other countries, are collected and treated mainly as it is shown in Figure 2.

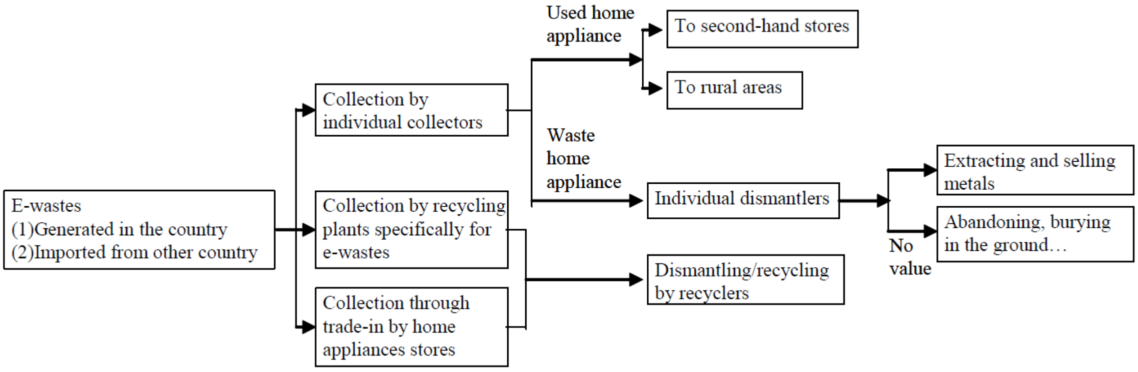


Figure 2. E-waste recycling system in China
Source: World Academy of Science, Engineering and Technology 38 2010, Bi Bo and Kayoko Yamamoto

The first way is to collect e-waste from individual collectors. Individual collectors are buying e-waste from consumers and treating it in two different ways: (1) Certain repair and / or reconstruction is still usable (mostly home appliances) for sale in second-hand shops or sales in rural areas, and (2) Selling E -waste without the use value and function from household to disassembly crew. Individual disassembly personnel does not have special equipment for the treatment of e-waste, but disassemble it by hand with simple tools to extract substrates of heavy metals and other components made of rare metals. They throw away or bury in the earth unnecessary, remaining parts after the treatment of e-waste. In China there are a number of facilities for individual removal in which e-waste is incorrectly treated, which leads to the deterioration of the environment, such as pollution of air, water and land. Another way of collecting is to collect for the recycling facility of e-waste and the waste is collected through shops of home appliances. In fact only some e-waste is collected in this manner.

4) USA

In USA, e-waste is the fastest growing component of municipal solid waste, because people buy new and discard old electronic products much more frequently than ever before. This trend is likely to continue, given the pace of technological progress and the decrease of the lifetime of e-products.
The problem of e-waste focuses on:

- waste in landfills in the U.S.
- waste that is exported.

According to the data, the majority of e-waste ends up in landfills. It can be seen from Table 1. Here the question is how many landfills are environmentally safe place for e-waste?

Table 1: E-waste retirement estimates by management method (thousands of metric tons)

Year	Recycled		At the landfill		Burned		Total	
2003	315,5	20%	1234,9	78%	35,1	2%	1585,5	100%
2004	326,5	20%	1281,9	78%	36,5	2%	1644,8	100%
2005	243,8	20%	1353,7	78%	38,5	2%	1736,0	100%

Source: US EPA, 2007b

Many states of the USA have started with their own activities to collect e-waste (given the free collection of e-waste) from the commercial and residential sectors and its recycling. Some states (California, Washington, etc.) have enacted legislation and built a system for recycling of personal computers, monitors, televisions and laptop computers, which to some extent alleviates the problem of e-waste. Some of the major companies took part in it: AT&T, Dell, Hewlett Packard, Motorola, Sony, and others.

Activities of Member States and major companies are very important for a sustainable approach, but not enough to solve the problem of e-waste. It is necessary at the federal level to create a regulatory framework, in combination with an industrial approach that should provide a comprehensive system solution for the collection and recycling of e-waste.

The presented system of management of e-waste inevitably raises the debate about the likelihood of success of their application in other countries. But the success of a system in one country does not necessarily mean it will be successful in another. Therefore, these systems are built on the principles of sustainable development and as such can only present a stage in the development of sustainable e-waste treatment. Developing a sustainable culture begins with understanding the flows of materials, energy and information. A sustainable system must recognize the physical flows, ICT infrastructure and incentives (Mathias Schluep at al., 2009; Mmereki D, Li B, Wang L, 2012).

Of course, the analysis of the existing systems of treatment of e-waste can identify good and bad sides of solutions and can on the basis of the practical experience build an effective recycling system without repeating the mistakes that are present in these systems.

KEY PROBLEMS

The problems of collection and selection of e-waste are multiple and complex. This is directly related to recycling, primarily, with the motivation for recycling. On the other hand, it is very difficult to establish reversible logistics. Also, a large number of e-products was developed without an analysis of the life cycle (from mining, material production, manufacture, operation, at the end of life cycle, the collection and recycling and return of recycled materials in the production process). The obligation of the manufacturer to ensure the recycling of their e-products is often just a wish and a piece of paper, not a reality (usually from logical and legitimate reasons). It is obvious that an important link is missing in the chain, and it is the role of the state. It can not only be regulatory, advisory and enforced. It has to be creative. Developed countries resolve these problems normatively (directives, laws), and the most pressing problems are transferred in underdeveloped countries (dirty production technology and recycling), and they seemingly meet their standards. This solves several difficult problems: a strenuous recycling organization, financial problems, recycling, environmental pollution and disposal of final waste.

The problems of collection can be divided into several categories.

(1) In reality a difficult problem occurs with collection of small e-waste, including:
- small batteries (watches, cameras, toys, remote controls, flashlights, etc.)
- energy saving light bulbs, light bulbs in general
- mobile telephones
- electric clocks
- toys
- remote controls (for TVs, players, etc.)
- flashlight, etc.

This is logical, because who among users (citizens) can be expected to diligently separate small objects and place them in special containers that do not exist. Even if you put them in a container or bag for metal, which is there, who will in further process carry out the selection of such small objects. Of course, these are extraordinary pollutants of environment and the planet in general.

(2) Power electronic products used in household
- appliances (large, small)
- computers, printers, web cams, discs, etc.
- TV sets, radio, players, and so on.

The problem is that there are no collection points for collecting e-waste from households and that the issue of costs to transport of heavy equipment (washing machines, freezers, refrigerators, etc.) is not resolved.

(3) E-components in complex products
- means of transport (cars, trucks, buses, trains, airplanes, ships, etc.)
- working machines (excavators, loaders, bulldozers, etc.)
- agricultural machinery (tractors, combines, pickers, cultivators, etc.)
- machinery and equipment manufacturing (machinery for wood, metal, plastic, leather, etc.)
- Handy tools (drills, grinders, etc.), and others.

The key issue is organized separation and selection of e-components from complex products. This requires additional analysis of cost-effectiveness of this procedure by the manufacturer and recycling of complex products. In other words, the state must find a way to motivate them to diligently manage e-waste in own domain.

(4) E-components and equipment in large systems
- industry (plant, assembly line, paint shop, automated assembly lines, etc.)
- e-equipment and components in energy (hydropower, thermal power, nuclear power systems, power transmission, oil, gas (automatic), power plants, and so on.
- e-equipment in information and communication systems
- e-components in the construction (electrical, air conditioning, security and surveillance systems, optical fiber cables, ventilation, solar heating system, etc.)
- e-components and equipment in other large systems.

The problem of collecting e-waste also occurs in maintaining of these systems, and in replacement or renovation of entire systems (replacing the old with a new production line, closing nuclear power plants, demolition of old buildings, and so on.). How to collect e-waste in these cases?

(5) E-components and equipment in military and safety systems and resources
In these systems there is the most modern and complex electrical and electronic equipment. It contains the highest amounts of heavy metals and hazardous substances. These are primarily electronic systems for monitoring and control of the sky, sea and land borders, military vehicles, military equipment, tanks, missile systems, military aircrafts, radars, military ships, the cosmic weapons, and so on. Unfortunately, there is no knowledge about the structure of e-content materials or components in them. The only thing we know is that in these systems and tools are no legal restrictions.

Also, the selection of e-waste by similarity of material is not simple or easy. Since these are relatively small amounts of heavy metals in the product, e-equipment manufacturers do not mark products that contain, for example, cadmium, mercury, etc. Only on the basis of productive and constructive documents the composition and quantity of materials can be determined, and based on that the selection of waste collected can be performed.

In order to establish process of collecting e-waste some countries have introduced incentives for collectors; payment of fees or allowances per ton of waste collected. The fee increases with the increasing of mass of collected e-waste and its delivery to the further recycling process. (Figure 3). Progression of compensation may take into account the environmental priorities. For example, for the e-waste containing hazardous materials or precious resources, payment can begin at a higher level and progress at a steeper rate, triggering greater efforts for collection; fee-green line (Figure 3).

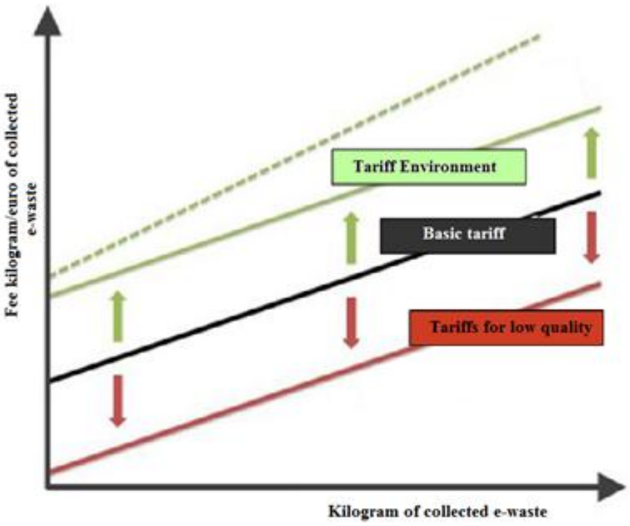


Figure 3. Compensation model to encourage the collection of e-waste
Source: Recommendations on Standards for Collection, Storage, Transport and Treatment of E-waste, Otmar Deubzer, United Nations University, 2012

It would be ideal if in a single geographical area continuous collection of e-waste could be provided and the actual amount of waste could be calculated each year with a realistic comparison. Of course this mainly applies to 10 categories of waste covered by the WEEE Directive (listed in Annex D).

The objectives of the collection can also be contracts signed with collectors on a fixed amount of e-waste per year, as proposed in the WEEE Directive (2003): four pounds of e-waste per inhabitant per year. The amount of e-waste collected in previous years can be used as a basis for setting realistic goals of the collection. The goal is for the collection to be periodically adjusted in order to be sure that it remains in balance with generation of quantities of e-waste per year (Anwesha Borthakur, Pardeep Singh, 2012; Ricardo Montero, Alicia Guevara, Ernesto de la Torre, 2012).

Of course, it should be worked intensively on the problem of collection and selection of e-waste and it cannot be dismissed with only legal norms but also by continuous education of all in the chain of lifecycle of e-equipment, including the entire population of the region or state, as well as to provide the necessary infrastructure (organization, equipment, labeling, recycling centers, the necessary technology to minimize environmental impact). This is serious business of one state and the responsibility that cannot be transferred to the well-established principles of the market economy and its self-organization.

Recycling of e-waste has the following goal:

- to increase the reuse, recycling and other forms of recovery, leading to the reduction in the amount of waste disposed in landfills or being incinerated
- to improve the environmental performance of all the actors involved in the life cycle of electrical and electronic equipment
- to reduce the depletion of natural resources (metals, metalloids, petroleum, etc.).

As noted above, there are two approaches in recycling of e-waste:

- first, which does not require any removal or separation of waste and which is crushed, and then selects certain types of materials (magnetic and other forms of separation)
- second, which requires a certain degree of disassembly/reassembly and application of appropriate technologies for recycling each material separately (aluminum, copper, silver, gold, platinum, etc.).

Both procedures require expensive and complex technology and optimum quantity of waste to ensure the cost-effectiveness of recycling. On the other hand, it is about very dirty technologies (examples of recycling of lead, cadmium, mercury, etc.) that regardless of the high ecological standards significantly pollute the environment in which the plants are located.

When looking at the content of the material in any e-product, Table 2 and Figure 4 (mobile phone), it becomes clear why the prior removal of the components is necessary, as well as their selection (Perrine Chancerel, 2010).

Table 2: Concentration of metals in electronics (2007)

Elektronic	Copper (% by weight)	Silver (ppm)	Gold (ppm)	Palladium (ppm)
Televisio (TV)	10%	280	20	10
Personal Computer (PC) Board(1)	20%	1000	250	110
Mobile Phone(1)	13%	3500	340	130
Portable Audio Scrap(2)	21%	150	10	4
DVD Player Scrap(2)	5%	115	15	4

(1) Source: Umicore Precious Metals Refining Recovery from e-scarp in a global environment. Geneva, Septembar 7, 2007 htpp//archive.basel.int/industry/sideevent030907/umicore.pdf
(2) Source: Jirang Cui and Lifeng Zhang, Metallurgical Recovery of Metals from Electronic Waste, Journal of Hazardous Materials 158 (2008) 228 – 256.

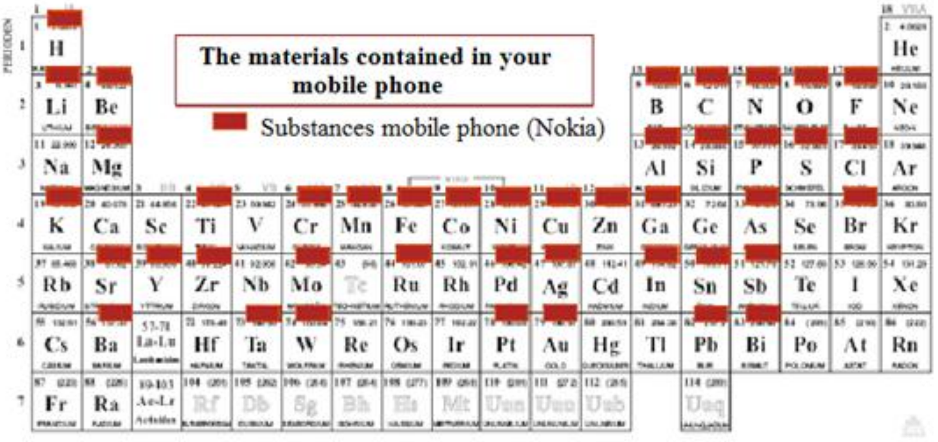


Figure 4. The materials contained in a mobile phone
Source: Umicore 2008

It should also be borne in mind that a large number of rare metals contained in e-waste are in relatively small quantities and for their recycling significant amounts of pre-selected waste is needed, in order to provide economical recycling. Yet the content of these metals in e-waste is generally higher than in the ore from which they derive.

Research work in the recycling of e-waste is far from being completed, especially when you consider the fact that e-waste in the near future will be the main source of strategically important and rare metals.

THE IMPACT OF E-WASTE ON A GLOBAL LEVEL

Electric and electronic waste currently has the highest growth rate. It is a dangerous, complex and expensive for treatment in an environmentally sound manner. Today, most of the e-waste gets thrown into the general waste. E-waste in developing countries that is going to be recycled, usually 80% of it (often illegally) shifts to developing countries such as China, India, Ghana and Nigeria, where it is recycled. Recycling of e-waste in these countries is done in a rather primitive way, in order to obtain many valuable materials. Such globalization of e-waste has negative consequences for the environment and human health. Thus, developing countries bear a disproportionate burden of global problems without adequate technology. Besides that, they themselves generate more e-waste. The problem can be solved by the present practice and illegal trafficking of waste, provide economic stimulus. It is important to identify local and regional contexts and social implications for this issue; application of high technology and capital intensive recycling process have appropriate results for each country or region.

The main risks for human health is the presence of heavy metals, organic substances and chemicals with unknown properties and other potentially hazardous materials in e-waste. There are also three sets of hazardous substances in recycling of e-waste, and that the materials contained in products (lead, mercury, etc.), materials used in the recycling process (cyanide, etc.), and substances generated during the recycling process (dioxins, etc.). If recycling of e-waste is poorly managed, those substances present a risk to humans and the environment, either it is about e-waste or about recycling. Toxic substances can be found in the following types of emissions or outputs:

- by drainage of water from lanfills
- particles from the process of dismantling (coarse and fine particles)
- flying particles of ash and ash from burning
- emissions from heating , soldering and other forms of combustion of mercury amalgam
- waste water from the plant for dismantling and crushing
- wastewater from cyanide leaks and spills of other substances

Ecological recycling of e-waste consists of the following steps:

- removal of parts and components - this includes manual removal of devices and components and their recovery
- removal of harmful substances - removal and separation of individual materials / substances to allow them to be handled separately and minimize their impact, including batteries, fluorescent lamps and cathode ray tubes (CRTs).
- separation of materials - manual separation and preparation of materials for further processing
- mechanical processing of individual materials - this includes processing of compatible plastic resin, metal or glass of CRTs for the market - the quality of raw materials
- mechanical processing of mixed materials - this includes processing of entire sections, followed by technology of separation
- refining / smelting - after being sorted into components or crushed, metals are sent to smelting or refining. At this stage, using thermal and chemical processes to extract the metal.
- In this phase thermal and chemical processes are used in order to extract the metal.

E-waste is a complex and difficult form of recycling waste, and problems are such as increasing the concentration of heavy metals in the air, and that are contained in leading technological equipment developed countries. Workers and local residents are exposed to toxic chemicals through breathing, swallowing dust, touch through the skin and entering through the mouth. Inhalation of dust or ingestion causes a number of occupational diseases including silicosis.

Especially important are the pathways of human exposure to: dioxins, lead, copper, cadmium, polybrominate diphenyl ethers, polychlorinate biphenyl, chromium, mercury and other metals and carcinogens. Generally, the health risks to humans from e-waste include shortness of breath, respiratory irritation, cough, dyspnea, pneumonitis, tremors, neuropsychiatric problems, convulsions, coma or even death. Workers who work with e-waste are exposed to other risks that lead to physical injuries and chronic diseases, such as asthma, skin diseases, irritation of eyes and stomach. Substances that are deposited in the collection of e-waste for recycling can lead to inflammatory response, oxidative stress and DNA damage.

Unfortunately, the number of illnesses and injuries caused by irresponsible behavior (dispose anywhere), and treatment of e-waste is far greater than the foregoing so to managing this type of waste has an exceptional weight. Also very important is the indirect impact of e-waste to the atmosphere, water and soil, and the environment and human nutrition. Of course, the work space does not permit a detailed analysis of the impact of e-waste on human health.

Components and substances that are commonly found in e-waste, and containing mercury are relays, switches and lamps with gas and batteries containing mercury, cadmium, lead and lithium. Printed circuit boards contain a number of substances of concern, such as lead, antimony, beryllium and cadmium. Plastics often contain brominated flame retardants and PVC in isolation and during the combustion releases dioxins and furans. CRT (in older desktop computers and TVs) contains a large quantity of substances of concern, such as two to three pounds of lead in each unit. However, the newer liquid crystal display (LCD) contains a mixture of 10-20 substances suspected to be dangerous (such as indium). In addition, the LCD screens are hard to dismantle, and to prevent mercury emissions when breaking up the parts of the backlight. To date, the optimal recycling of these devices have not yet been resolved.

Little is known about the toxicity and environmental properties of over a thousand chemicals listed in the flow of e-waste. This is largely associated with a rapid change of production processes, product designs, materials and chemicals. Some pollutants in e-waste are unusual or completely new and there is almost no studies done on their impact on the environment. Examples include lithium (used in batteries), beryllium (contact materials), antimony (fire suppression), gallium and indium (used for silicon chips and LCD monitors).

In addition, the composition of e-waste is rapidly changing in operational technological development, government regulations and NGOs. Thus, replacing CRT monitors with LCD screens significantly reduces the lead contained in the CRT, but LCD screens contain mercury, indium and zinc. Also, the optical fibers that replace some copper conductors may contain fluoride, lead, yttrium and zirconium (Otmar Deubzer, 2012; Jonathan Butler, 2012).

Also, the composition of rechargeable batteries has changed drastically from the nickel-cadmium and nickel hydride to lithium ion batteries.

On the other hand, the problem is complicated due to large amounts of epoxy resin, fiberglass, PVC, thermoplastic, lead, tin, copper, silicon, beryllium, carbon, iron and aluminum, as well as the increasing presence of germanium, tantalum, vanadium, terbium , gold, titanium, ruthenium, palladium, manganese, bismuth, niobium, platinum, rhodium, carbon, americium, arsenic, antimony, barium, boron, cobalt, europium, gallium, lithium, indium, nickel, manganese, selenium, silver , tantalum, molybdenum, thorium, yttrium and others.

Cocktail interaction effects of chemicals on the environment and human health may be greater than the effect of individual chemicals. However, there is still a large gap in the understanding of the potential impact of exposure to chemical mixtures. Cocktail of chemicals can disrupt the hormonal system, adversely affect reproductive functions and cause different types of cancer. Although nearly all toxic and polluting substances are tested on chemical and biochemical basis, so far no one has included more pollutants simultaneously in testing. A cocktail effect is especially evident when the chemicals are mixed with water and exposed to sunlight and air, or scattered on the ground.

If chemicals are not deposited in the body they are metabolized and excreted. This happens mostly in the liver and in the skin, lungs, intestines and kidneys. Products of metabolism are known as metabolites, and they may be more or less toxic than the original chemical. Metabolites form in enzymes - by catalyzed reactions and naturally occurring in the cell.

Unfortunately, the effects of toxic metabolites are not well studied.

Bearing in mind all the above, it becomes clear just how globally prominent environmental problem of e-waste is, and of entire e-industry. If we start from the principle of sustainability and analyze the total life cycle of e-products, from the mining, production of raw materials, production of materials and components and to the final e-products, its use and end of life, and then the recycling of e-waste and reproduction of the starting materials and by analyzing the entire cycle, disturbing facts about the harmful effects on the environment and human health can be found. On the other hand, e-products, and thus the e-waste, arrive in the remotest parts of the world and carry out an attack on the environment of the entire planet. In long term this will lead to unpredictable consequences for the planet, because pollutions from e-waste are long and with very serious consequences. Also, this applies to the sources of rare metals and materials, which are rapidly drained and will in a short period of time be permanently exhausted.

SUSTAINABLE RECYCLING SYSTEM

Here is presented a brief overview of the impact of electrical and electronic equipment and their waste (at the end of life) on the environment. The reason is to show the importance and necessity of establishing an organized and efficient recycling of e-waste. Figure 5 gives a systematic approach to recycling e-waste.

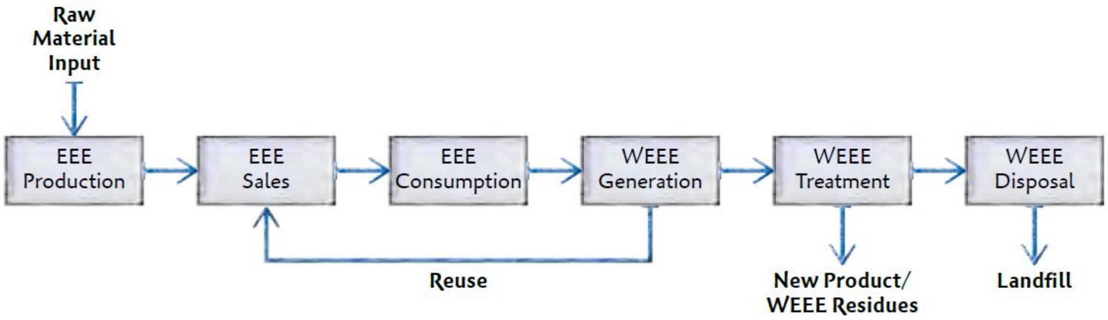


Figure 5. Life cycle of e-waste (UNEP, DTIE, 2007a).

Plastic example is the production and use of computers. Here we have direct and indirect impacts on the environment and people. When considering the entire cycle computer from the production of materials, use of a delay at the end of the life cycle and recycling.

A. Direct impact

(1) The impact on the environment during the production process
Energy consumption, many materials, many chemicals
exposure of workers to harmful and dangerous substances
negative impacts during the production of metals, materials and chemicals, which are the components of a computer or used during its manufacture.
(2) Energy consumption during use
(3) Impact of deferred computers on the environment (at the end of life)
heavy disassembly
heavy metals, hazardous materials

B – Indirect impact

(1) The impact on the health of users
damage to the joints, eyes and spinal cord
Lack of exercise - obesity and obesity related diseases
dependence on computer games - bad test results
(2) The impacts with industrial activities
long-term impact of aggressive and toxic substances on the health of workers
pollution of the environment in place where the facility / factory is located
(3) the impact during use
paper use (cutting of forests, ..)
(4) Impact after disposing of used computers (e-waste dumps)
long-term contamination of soil, water (surface water, groundwater)

Of course, you can similarly analyze other electric and electronic equipment and their e-waste. What is missing in the EU directives and normative acts of other countries is the lack of standardization of military e-waste, which is both in quantity and in effect even greater polluter because electrical and electronic equipment used for military purposes contain much higher concentrations of heavy metals and hazardous substances. It also contains radioactive material, because much of the equipment is exposed to radiation (nuclear bombs, nuclear storage, nuclear munitions, transport means and use this ammunition, etc.). All of the above applies to the equipment used in nuclear power plants, which are often replaced because of the shortened life span because it's used in extreme conditions. On the other hand, due to the ongoing work of powerful radars and other military equipment that uses electromagnetic fields, we have a strong influence of electromagnetic radiation on the environment and on all living beings. It remains an open question how to handle the equipment after the end of its life span, because for reasons of confidentiality and security the content of materials and chemicals is not revealed. This greatly hampers its dismantling and recycling. The foregoing requires the establishment of an adequate and sustainable e-waste management, which includes:
(1) Re-use of functional e-products
(2) Overhaul and repair of e-products
(3) Recovery and reuse of e-components
(4) The End - processing in order to recover materials and part of energy
(5) Disposal to landfill (ultimate waste)

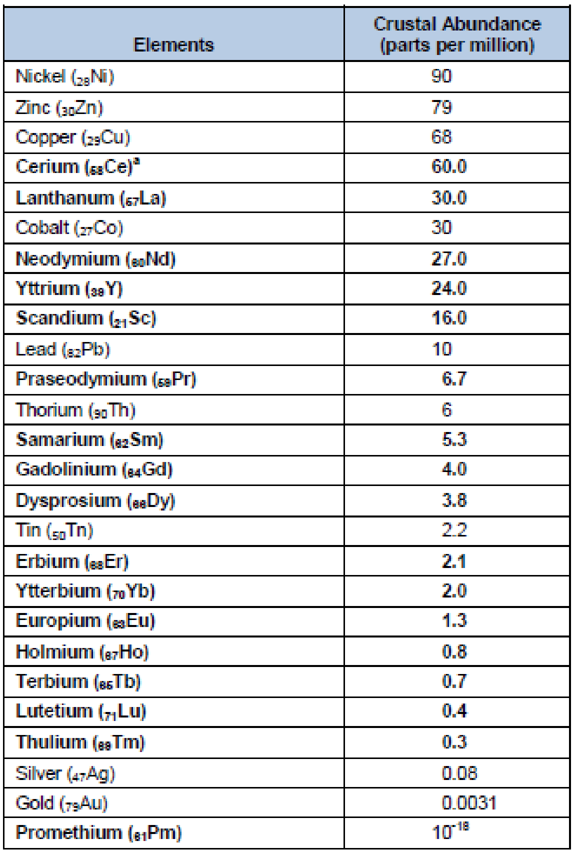
The process of recycling of e-waste is very complex if you want to restore much of the strategic materials contained therein. This, first of all, refers to precious metals (gold, silver, platinum), as well as to important strategic materials (metals, metalloids) which fall in the group of few countries whose resources on the planet are very limited and critical in the aspect of exploitation. The complexity of the recovery of these materials consists of:

- the complex and expensive technologies of recycling
- very small concentration of these materials in present e-waste
- high toxicity of the recycling process.

For these reasons, the developed countries shift their e-waste to countries in development (India, Nigeria, China, etc.), often in illegal ways.

Table 3 presents the content of elements in the earth's crust, but many of them are so scattered that their obtaining is very difficult and is not economical.

Table 3: Abundance of Elements in the Earth’s Crust (Wedepohl, 1995)



Elements	Crustal Abundance (parts per million)
Nickel ($_{28}$Ni)	90
Zinc ($_{30}$Zn)	79
Copper ($_{29}$Cu)	68
Cerium ($_{58}$Ce)^{a}	**60.0**
Lanthanum ($_{57}$La)	**30.0**
Cobalt ($_{27}$Co)	30
Neodymium ($_{60}$Nd)	**27.0**
Yttrium ($_{39}$Y)	**24.0**
Scandium ($_{21}$Sc)	**16.0**
Lead ($_{82}$Pb)	10
Praseodymium ($_{59}$Pr)	**6.7**
Thorium ($_{90}$Th)	6
Samarium ($_{62}$Sm)	**5.3**
Gadolinium ($_{64}$Gd)	**4.0**
Dysprosium ($_{66}$Dy)	**3.8**
Tin ($_{50}$Tn)	2.2
Erbium ($_{68}$Er)	**2.1**
Ytterbium ($_{70}$Yb)	**2.0**
Europium ($_{63}$Eu)	**1.3**
Holmium ($_{67}$Ho)	**0.8**
Terbium ($_{65}$Tb)	**0.7**
Lutetium ($_{71}$Lu)	**0.4**
Thulium ($_{69}$Tm)	**0.3**
Silver ($_{47}$Ag)	0.08
Gold ($_{79}$Au)	0.0031
Promethium ($_{61}$Pm)	**10^{-18}**

Lanthanides (lanthanoids), scandium, and yttrium are presented in boldface type.

Figure 6 demonstrates the use and participation of few countries in e-products, which indicates that the rapid development of new advanced technologies increasingly depletes natural resources and that these materials will become critical for further technological development in the near future. On the other hand, due to the low content of most elements in e-waste (often in trace amounts) it will be very difficult to develop technology for their return through the recycling processes.

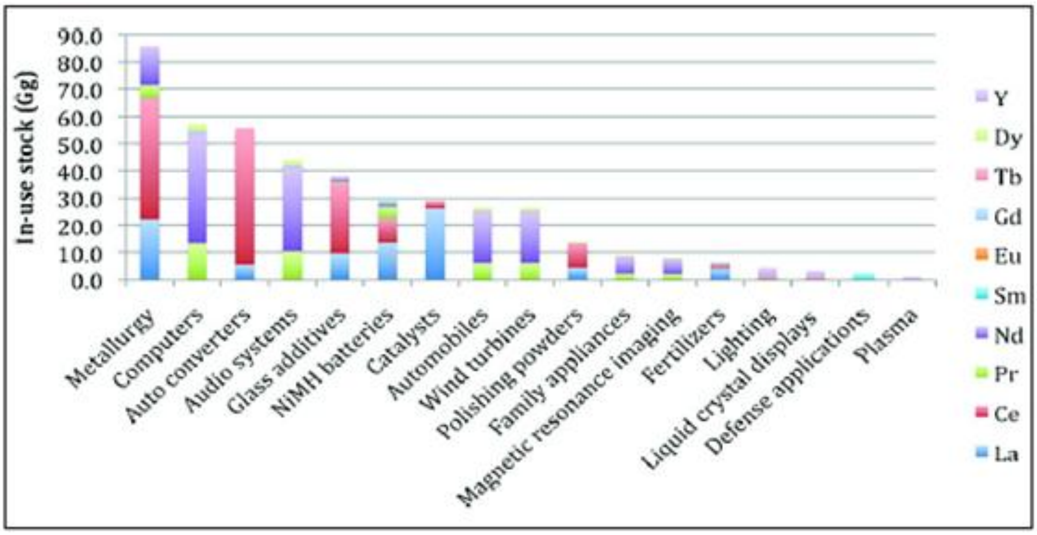


Figure 6. In-use stocks of selected REEs by specific application or industry (in gigagrams) (Du and Graedel, 2011)

Figure 7 gives an example of using the utilization of e-components in four product groups. What is new is that since 2011 metals Ma, Co and Ni have become critical materials for further technological development. Of course, one of the solutions is obtaining them from e-waste.

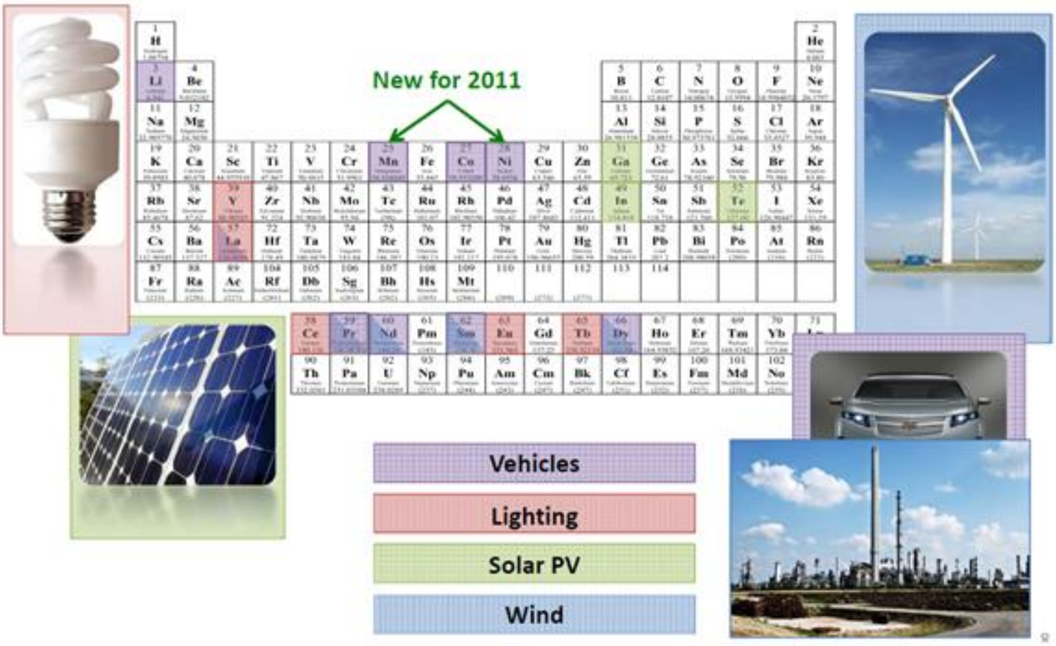


Figure 7. Application of elements in e-products and new critical metals since 2011 (US Department of Energy)

Figure 8 presents a level of critical materials used in e-products. They slow or restrict the further technological e-waste. It requires development and require new approaches and methods for obtaining them. One of them is the recovery of materials from adequate recycling technologies and their cost-effectiveness. If production is not economical, appropriate incentives must be provided, because it is related to critical strategic materials.

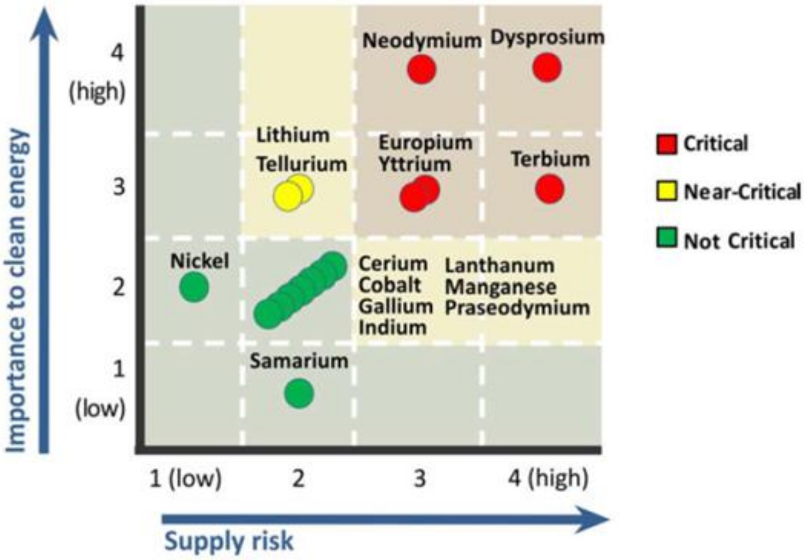


Figure 8. Materials Medium-Term Criticality (2015-2025) (US Department of Energy)

Having in mind all aforementioned complexity of e-waste and its recycling, appropriate recycling models that attempt to reconcile the need for recovery of materials and cost of obtaining them are developed. One model of management and recycling of e-waste used in Brazil is shown in Figure 9.

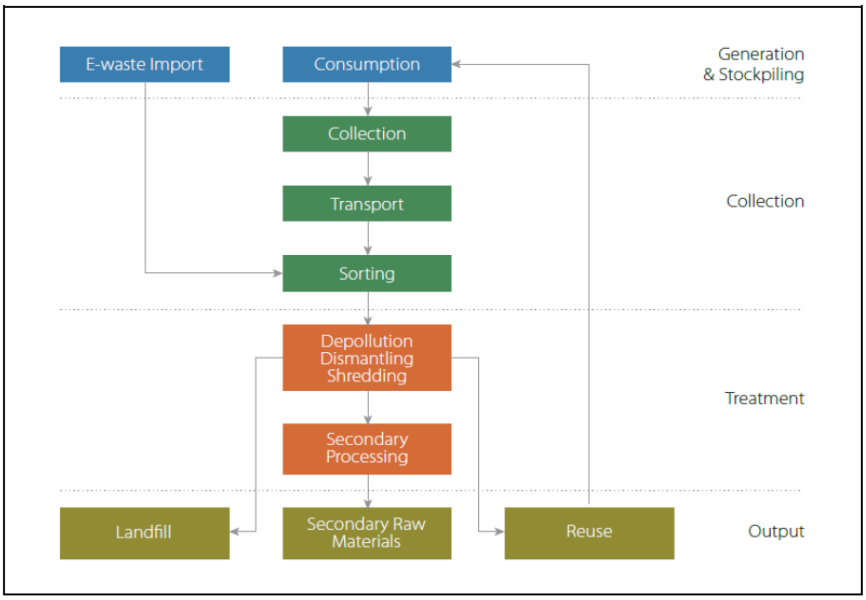


Figure 9. E-waste Processing Steps
Source: infoDev (The World Bank Group). Wasting No Opportunity: The case for managing Brazil's electronic waste. April 2012. Web. 22 January 2013.

If in the model the problem of collection and initial selection of e-waste is resolved, in the next step the dilemma is encountered, whether to crunch worn gear without dismantling or remove it to a certain level, to make a selection according to the materials contained and only then send them to recycling centers? The second procedure is more natural and better in all aspects, but the second is more cost-effective. For now the second process is dominant, but it is limited and selective in relation to the types of e-waste, with the key determinant: economic viability. Again, the role of the state is missing.
In the process of dismantling there are two separate processes:

- dismantling of electrical and electronic equipment - disconnection of parts, of sub-assemblies with separation of liquids and substances (e.g. pyralene, mercury)
- dismantling of complex products and systems that include e-components with its building components and separation.

Many things are not contained in this part of the process in directives and in laws. We also know that the recycling of cars takes place at a low level of dismantle and the shell with many pertinent parts and assemblies is sent to the shredder where it is crushed. Little is taken into account about e-components. This is also the case with other complex products from trucks to electric locomotives and aircrafts. The basic principles that play the main role in all these processes are the market economy, the economic benefit.

All other aspects are reduced to the instructions and requirements which are powerless to solve the basic problems of environmental pollution and exploitation of natural resources (primarily refers to the rare and limited resources of strategic metals and metalloids).

Figure 10 presents a part of e-components of a modern passenger car. Of course, that's only one part of the equipment mounted on the car.

Figure 10. Assistance in driving a car - IT support

Maximum disassembly of complex products with mandatory separation of e-components, their selection and routing to collection centers for e-waste is extremely important.

Also, dismantling of electrical and electronic equipment for separation of components with toxic materials and substances is very important, as well as the components that consist of precious and rare materials, such as silver, gold, platinum, palladium, germanium, zirconium, tungsten, and others. By applying of crushing of the complete e-products significantly hinders or prevents the recycling of these metals.

The very selection of electronic components has been significantly hampered by the lack of accurate information about the structure of the material of the components. All these present challenges for future research and for finding of optimal solutions for dismantling and the selection of e-waste.

DEVELOPMENT OF NEW E-PRODUCTS

The development of new electrical and electronic products must be subjected to detailed analysis and at the same time many aspects of the entire product life cycle must be taken into account. Above all, environmental requirements, requirements for sustainable use of natural resources, the requirements for the toxic products and wastes and requirements for complete recycling of waste generated after the use of e-products must be taken into account.

Requirements for the development of new electrical and electronic products can be divided into several groups:

- reduction/restriction of hazardous substances in e-products - RoHS directive
- definition of power used by the product during the entire life cycle through the design of the product - EuP directive
- Registration, Evaluation and Authorization of Chemicals in e-equipment - REACH directive
- Waste, Electrical and Electronic Equipment - WEEE directive, which implies an effective recycling of e-equipment, which must be taken into account in the process of design.

In accordance with the requirements of relevant directives, options should be thoroughly investigated in order to reduce the toxicity of e-products, and the processes for their production. This includes, in particular:

- Replacement of materials with a negative impact on the environment with alternative materials that are less harmful, neutral or have a positive impact on the environment
- Avoiding specifications that require the inclusion of heavy metals
- Avoiding using coatings that contain heavy metals
- Reduction of toxic waste by reducing the amount of toxic substances
- Establishing a system for monitoring of toxic materials/substances during the entire life cycle of e-products
- Choice of technologies that use new methods to reduce the use of toxic chemicals and substances and wastes in the production of e-products and recycling at the end of their life cycle.

Of course, in the coming decades a number of surveys should be done in order to facilitate an effective system of e-products in their entire life cycle and in recycling of their waste and residue without any environmental pollution and negative impacts on human health.

CONCLUSIONS

In the recycling of electrical and electronic waste in the world there has been significant progress. The most advanced are in the field of normatives, much less is realized in practice. Evident problems in the recycling of e-waste are reflected in the following: Even with very good normative acts (EU directives, laws of other countries) military means and systems are not covered, as well as other major systems of national importance (energy, telecommunications, etc.). There are no optimal solutions for collection and selection of e-waste, especially small equipment and components (batteries, light bulbs, etc.). There is no optimal solution for e-waste contained in complex products (motor vehicles, trains, airplanes, ships, industrial facilities and equipment, and so on.). There is no valid system of marking of content material on e-products which causes big problems in the collection and selection of e-waste. A system of continuous monitoring of e-waste is not created and it is still not treated as integrated and sustainable. Development of new e-product is still not followed by the logic of the entire life cycle of optimal reversible processes, as well as by the logic of sustainable use of natural resources. The growing use of e-products in all areas and activity of human, the increasing computerization and automation lead to the sudden enlargement of e-waste, which increase is at this time two to three times higher than with other types of waste. This waste is extremely toxic and intense with a rare and strategic metals and materials, it is necessary to pay special attention to the waste in the coming decades.

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REFERENCES

Vinod Kumar, Ruchi Garg, Dr. Zillur Rahman, Dr. A.A.Kazmi, Sustainability and E-waste Management Scenario in India, The First International Conference on Interdisciplinary Research and Development, 31 May - 1 June 2011, Thailand

S. Chatterjee, Sustainable Electronic Waste Management and Recycling Process, American Journal of Environmental Engineering 2012, 2(1): 23-33

Deepti Mittal, Navnish Goel and Renu Rani, E-Waste: A Hidden Threat to Global Environment & Health, VSRD-IJCSIT, Vol. 2 (3), 2012, 271-275

Lozica Ivanović, Danica Josifović, Blaža Stojanović, Andreja Ilić, Improving product design for recycling electronic waste, 39. Nacionalna konferencija o kvalitetu (sa međunarodnim učešćem), Kragujevac, June 2012

P. Gramatyka, R. Nowosielski, P. Sakiewicz, Recycling of waste electrical and electronic equipment, Journal of Achievements in Materials and Manufacturing Engineering, Volume 20 Issues 1-2 January-February 2007

Matthias Buchert, Andreas Manhart, Daniel Bleher, Detlef Pingel, Recycling critical raw materials from waste electronic equipment, Oeko-Institut e.V., Darmstadt, Germany, 24.02.2012

Suraj S., E--waste and Environmental Degradation, The Frank Anthony Public School Cambridge Layout Bangalore, 2010

Otmar Deubzer , (2012), Recommendations on Standards for Collection, Storage, Transport and Treatment of E-waste, United Nations University, 22 June 2012

Jonathan Butler, PLATINUM 2012, published in May 2012 by Johnson Matthey, www.platinum.matthey.com

DIRECTIVE 2012/19/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL, of 4 July 2012 on waste electrical and electronic equipment (WEEE), Official Journal of the European Union

Mathias Schluep, Christian Hagelueken, Ruediger Kuehr, Federico Magalini, Claudia Maurer, Christina Meskers, Esther Mueller, Feng Wang, RECYCLING FROM E-WASTE TO RESOURCES, Federal Laboratories for Material Testing and Research, Berlin, Germany, July 2009

Mmereki D, Li B, Wang L, Estimation of waste electronic and electrical equipment arising in Botswana-A case study of Gaborone City, INTERNATIONAL JOURNAL OF ENVIRONMENTAL SCIENCES Volume 3, No 1, 2012

Anwesha Borthakur, Pardeep Singh, Electronic waste in India: Problems and policies, INTERNATIONAL JOURNAL OF ENVIRONMENTAL SCIENCES Volume 3, No 1, 2012

Ricardo Montero, Alicia Guevara and Ernesto de la Torre, Recovery of Gold, Silver, Copper and Niobium from Printed Circuit Boards Using Leaching Column Technique, Journal of Earth Science and Engineering 2 (2012) 590-595

Perrine Chancerel, Substance flow analysis of the recycling of small waste electrical and electronic equipment, Institut für Technischen Umweltschutz, Berlin 2010

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DETERMINING THE MORPHOLOGICAL COMPOSITION AND QUANTITY OF WASTE FOR KOLUBARA WASTE MANAGEMENT REGION

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ABSTRACT

Landfilling is a dominant method of waste management practice in Serbia. Collection and transportation of waste, as an activity, has a greatest economic cost. In order to minimize the costs, forming of Kolubara waste management region is required, in which current waste management system must be upgraded. In order to upgrade waste management system of all municipalities in the region, exact measurements and planning is required. This paper presents methodology for determining quantity and morphological composition of waste in Kolubara region, and shows results of the implemented methodology.

INTRODUCTION

According to the National Waste Management Strategy from 2009, closure and recultivation of existing landfills, and the construction of 29 regional landfills is estimated (National Waste Management Strategy, 2009). It is planned to build regional landfills with the centers for separation of recyclable materials and transfer stations.

Recommendations for establishment of regional landfills on the territory of the Republic of Serbia are given in the framework of the National Waste Management Strategy. Regional concept of waste management (covers a minimum of 200,000 inhabitants) is accepted in order to minimize cost per ton of disposed waste and with the aim of rational investment of resources in the construction and operation of sanitary landfills (Faculty of Technical sciences, 2013). Good traffic connection between municipalities is required for the successful system of collection, transportation and disposal of waste. Kolubara region is a region that needs regional centre for waste management, because it has all of characteristics mentioned above. Kolubara region consists of 11 municipalities, namely: Barajevo, Valjevo, Lazarevac, Ub, Lajkovac, Obrenovac, Mionica, Koceljeva, Ljig, Osečina and Vladimirci.

In order to start the construction of the regional center, data of the quantity and composition of waste are required. The current situation in Serbia, as well as in the Kolubara region is characterized by unreliable data in this field. There are no continuous measurements, so obsolete data is used for future plans in the field of waste management plans. Due to the necessity for these data and exact results, the measurements were carried out in 11 municipalities that establish the region. Results of the measurements will help local authorities and utility companies to determine the current situation and it represent base guiding for further decisions in the field of waste management. Waste management system will be improved, and it will be determined whether it is economically feasible to invest in more advanced forms of waste management, such as recycling or incineration.

METHODOLOGY

The first objective of this study was to measure the amount of waste generated in a period of one week in these municipalities. The measurement was conducted in the following manner – firstly empty trucks for waste collection were measured (it represents the tare weight of the truck). After that, the trucks measured after the end of its regular route, when they were full (it represents gross weight). All measurements were conducted at weighbridges. When the gross weight is noted, collected waste is deposited by the usual procedure, and truck continues with its work. Trucks come to measurement after every waste collecting route, according to their schedule. The results are written down, and mass of generated waste is obtained by subtracting the tare weight from the gross weight, and the results for the entire week are summarized (Batinić i dr, 2009). Combining obtained results from measurements with the number of residents that are covered by waste collection services, information such as the average waste generation per capita per day can be obtained, as well as the generated amount of waste per year.

Determination of the morphological composition of the waste is the second objective of this research. It is based on the collection of waste bins / containers that are found in certain areas, in such way that the weight of the sample is approximately 300kg. Sampling zones within the municipality are as follows:

- Urban zone – individual type of residence
- Urban zone – collective type of residence
- Rural zone

Waste from each zone waste is collected by usual practice. Buckets/containers from one zone are chosen randomly and they were emptied into truck. When the truck collected a sufficient amount of waste for one sample, it went to a site that is predefined for sampling. Sampling site must have concrete base. Besides that, 15 bins for divided fractions from sample should be prepared, as well as a digital scale for measurement of fractions (Vujić i dr, 2010).

When everything is prepared, sampling can begin according to regulation. According to regulation, sample is divided into 15 fractions, namely: garden waste, other biodegradable waste, paper, glass, cardboard, tetra pack, ferrous- and non-ferrous metals, plastic packaging waste, plastic bags, hard plastic, textile, leather, diapers and fine elements. Sorting of waste is carried out by hand, and each fraction is measured separately. Results are written in tables, and are analyzed later. Waste is sorted on the grid. Grid is specially designed for this purpose, and it consists of a three-part grid. Grid with the biggest holes is placed on the top, and the grid with the tiniest holes is placed on the bottom. Waste that falls through the smallest grid is considered as fraction „fine elements“.

ANALYSIS OF THE RESULTS

Amounts of waste generated in Kolubara waste management region

Values of measurements of generated municipal solid waste for a period of 7 days, for each of the 11 municipalities are shown in table 1. Measurements were conducted in two seasons, spring and summer. Results are separately shown in columns marked with April and July (average value is also shown). Besides this, if the data of number of people that are covered by organized waste collection are known, average amount of waste generated by one resident per day can be calculated.

Table 1: Overview of waste quantities results for all municipalities

Municipality	**Measured amount [t/week]**			**Collected waste amount [t/month]**			**Collected waste amount [t/year]**		
	April	July	**AVERAGE**	April	July	**AVERAGE**	April	July	**AVERAGE**
Barajevo	141	161	**151**	706	807	**757**	7.366	8.424	**7.895**
Valjevo	436	484	**460**	2.178	2.422	**2.300**	22.723	25.268	**23.996**
Lazarevac	354	257	**306**	1.517	1.101	**1309**	18.460	13.398	**15.929**
Ub	195	90	**143**	975	449	**712**	10.177	4.686	**7.432**
Lajkovac	96	72	**84**	478	361	**420**	4.986	3.766	**4.376**
Obrenovac	577	321	**449**	3.462	1.927	**2.695**	30.123	16.761	**23.442**
Mionica	36	21	**29**	216	124	**170**	1.612	1.075	**1.344**
Koceljeva	27	32	**30**	161	190	**176**	1.402	1.651	**1.527**
Ljig	21	22	**22**	127	133	**130**	1.107	1.158	**1.133**
Osečina	25	31	**28**	151	186	**169**	1.318	1.622	**1.470**
Vladimirci	23	24	**24**	136	143	**140**	1.182	1.246	**1.214**
Total	1.930	1.515	**1.723**	10.108	7.843	**8.976**	100.455	79.057	**89.756**

Based on obtained results, it is evident that larger municipalities as Valjevo, Lazarevac and Obrenovac have the greatest values regarding amount of collected waste, thereby share of their amount in relation to the whole region is the largest. Those three municipalities together generate even more than 70% of total generated waste in Region (Figure 1). Specifically, in annual terms, leading is the city of Valjevo and municipality of Obrenovac with 23,996 tons and 23,442 tons respectively, followed by Lazarevac with almost 16,000 tones of collected waste. Other municipalities collect far less waste, where municipality Ljig has lowest value in this respect.

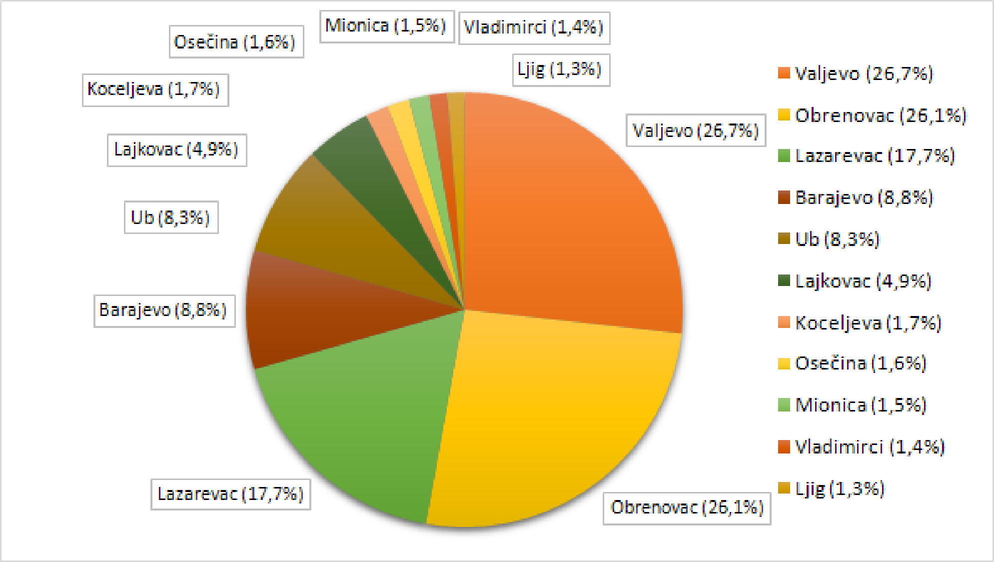

Figure 1. Share of collected waste amounts in municipalities compare to whole Region

If we look at a share of population for each municipality in the region (Table 2) and their waste generation, information about waste generation level expressed by the average inhabitant of the region may be obtained. The results show that the average resident of the region, which includes 11 municipalities, generates 1.04 kg per day, or 379 kg per year.

Table 2: Share of population in municipalities compare to region

Municipality	**Share compare to region**
Barajevo	7,46%
Valjevo	24,85%
Lazarevac	16,13%
Ub	8,01%
Lajkovac	4,26%
Obrenovac	19,96%
Mionica	3,95%
Koceljeva	3,61%
Ljig	3,51%
Osečina	3,45%
Vladimirci	4,81%
Total	**100%**

For easier insights and possibilities of comparison of results on amount of generated municipal waste, usually generation rate is expressed in form of average per capita on annual or daily basis. Regarding this, data presented in graph below indicate that the inhabitants of municipality Lajkovac have the highest rate of generation with 1.19 kg/capita/day, which is considering its size, level of development and the purchasing power of the population, unexpected result (Figure 2).

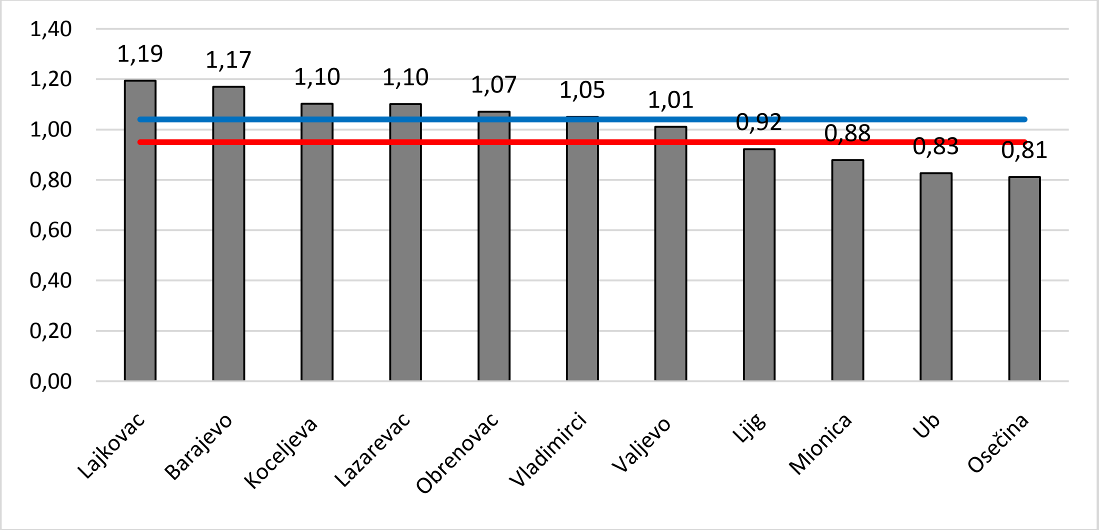

Figure 2. Waste generation in municipalities (kg/cap/day); blue line - Region average; red line - national average

According to recent research, the average resident in the Republic of Serbia generates 0.95 kg of waste per day, which the group of municipalities above the national average according to these measurements in addition to the already mentioned Lajkovac constitute Barajevo (1.17 kg), Koceljeva (1.10 kg), Lazarevac (1.10 kg), Obrenovac (1.07 kg), Vladimirci (1.05 kg) and Valjevo (1,01).

Four municipalities with waste generation rate below the national average are Ljig with 0.92 kg, Mionica with 0.88 kg, Ub with 0.83 kg and Osečina with 0.81 kg, which is also municipality with the least waste production in the region observed in this way.

Morphological composition of waste in Kolubara waste management region

All of 11 municipalities that were cover by this research had measurements of a morphological composition of waste on their territory. Measurements were conducted in one day, in every municipality, and the procedure stated in earlier part of this paper was followed. Results of the measurements of morphological composition of waste are shown in table 3.Values of measurements of generated municipal solid waste for a period of 7 days. As well as in case of measurements of quantities of waste, measurements of morphological composition were conducted in two seasons, spring and summer. Results are separately shown in columns marked with April and July. Total value is also shown, and it represents sum of all fractions of waste in all municipalities.

Table 3: Average waste composition for all municipalities

MUNICIPALITY WASTE CATEGORY	BARAJEVO	VALJEVO	LAZAREVAC	UB	LAJKOVAC	OBRENOVAC	MIONICA	KOCELJEVA	LJIG	OSEČINA	VLADIMIRCI
Garden waste	16,3%	6,7%	16,6%	14,6%	11,8%	28,3%	15,1%	37,8%	19,7%	7,3%	26,3%
Kitchen and other	22,3%	42,6%	34,6%	22,7%	20,5%	24,3%	35,3%	19,8%	24,1%	44,8%	36,2%
Paper	4,0%	6,0%	5,0%	3,9%	4,3%	4,2%	4,0%	2,3%	5,1%	3,4%	2,5%
Glass	4,0%	2,3%	2,7%	3,5%	2,9%	1,5%	6,6%	3,0%	5,0%	6,8%	2,6%
Cardboard	3,4%	3,3%	4,1%	4,9%	2,8%	4,3%	2,6%	5,1%	3,5%	2,9%	1,9%
Composite materials	1,2%	1,1%	1,1%	0,8%	0,5%	1,0%	1,3%	0,4%	1,6%	0,6%	0,5%
Metal - packaging and other	0,9%	1,3%	0,6%	0,3%	0,7%	0,2%	1,0%	2,7%	0,5%	0,9%	0,8%
Aluminum cans	0,3%	0,4%	0,6%	1,1%	0,4%	0,5%	0,7%	0,2%	0,5%	0,8%	0,4%
Plastic packaging	4,2%	3,2%	3,8%	7,3%	4,6%	4,5%	5,7%	3,4%	4,2%	4,7%	5,9%
Plastic bags	11,7%	9,6%	8,3%	8,6%	7,1%	8,5%	6,5%	7,2%	7,0%	4,7%	5,5%
HDPE	2,3%	2,0%	1,2%	2,1%	5,4%	1,5%	1,3%	1,3%	2,6%	2,8%	1,9%
Textile	7,9%	4,3%	5,9%	9,8%	6,6%	12,1%	5,1%	4,3%	11,7%	7,2%	3,5%
Leather	1,6%	0,2%	0,3%	0,2%	0,4%	0,4%	1,7%	1,2%	1,0%	0,4%	0,4%
Diapers	2,2%	3,7%	3,8%	8,5%	5,3%	2,7%	6,1%	2,5%	8,5%	5,3%	1,8%
Fine fraction (<20mm)	17,9%	13,5%	11,5%	11,8%	26,8%	6,2%	6,9%	8,7%	5,1%	7,4%	9,8%

Plastic packaging waste, as a fraction with the highest recyclable potential, generally doesn’t have a large share in waste composition for the observed municipalities. The highest share of PET was recorded in Ub with 7.3% and Vladimirci with 5.9%, and also higher amounts were in municipality Mionica (5.7%), Osečina (4.7%) and Lajkovac (4.6%), while for other municipalities amounts were in range from 3 to 4.5%.

Plastic bags are the most dominant light fraction for majority of municipalities. The highest amount was recorded in Barajevo (11.7%) and Valjevo (9.6%), while the lowest amount was in Osečina (4.7%). High density plastic shows similar values for all municipalities and it is in range from 1.2 to 2.6%, except in municipality Lajkovac (5.4%). Unlike from the aforementioned fraction, textile has greater variations depending on the observed municipality. In municipality Vladimirci, it takes only 3.5% share in waste composition, while in Obrenovac it reaches 12.1%.

In waste composition, leather is the lowest represented fraction for all the municipalities. Slightly higher values where noted only in Mionica (1.7%) and Barajevo (1.6%). Diapers are represented in the overall waste composition in range from around 2% to 5%, and the exceptions are Ub and Ljig with 8.5%, and Vladimirci has the lowest amount of only 1.8%. Fine elements, i.e. soil, ash and other fractions smaller than 20mm, are the most represented fractions after organic components. For these fractions there are also variations in composition depending on the municipality: in Lajkovac fine elements were 26.8%, in Barajevo 17.9%, in Obrenovac 6.2% and in Ljig 5.1%. Comparison of fractions in the different municipalities is also shown in figure 3.

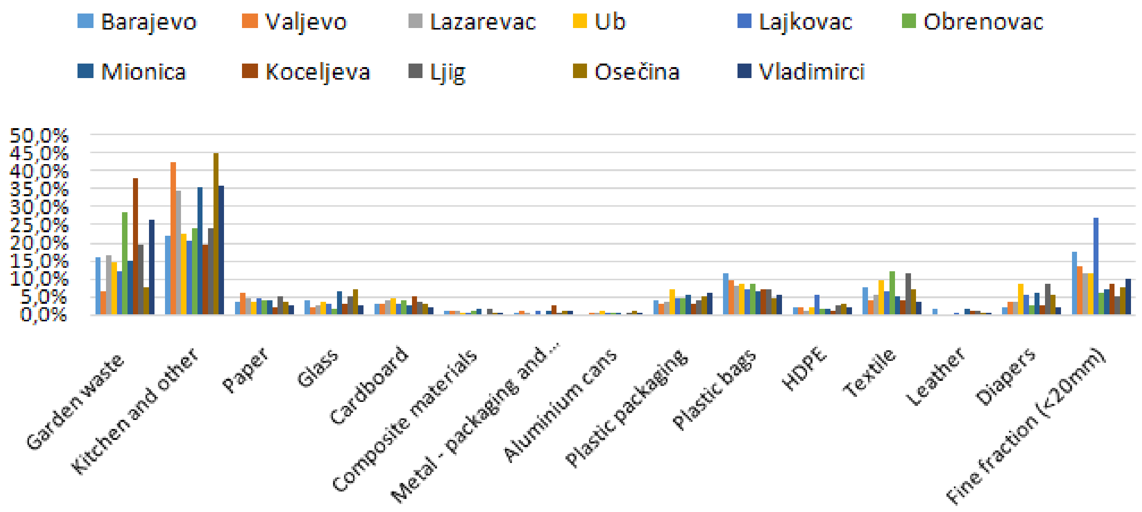

Figure 3. Comparison of waste composition for all municipalities within region

Similar to the previous results, comparison between two season sampling sections on a regional level is shown in figure 4.

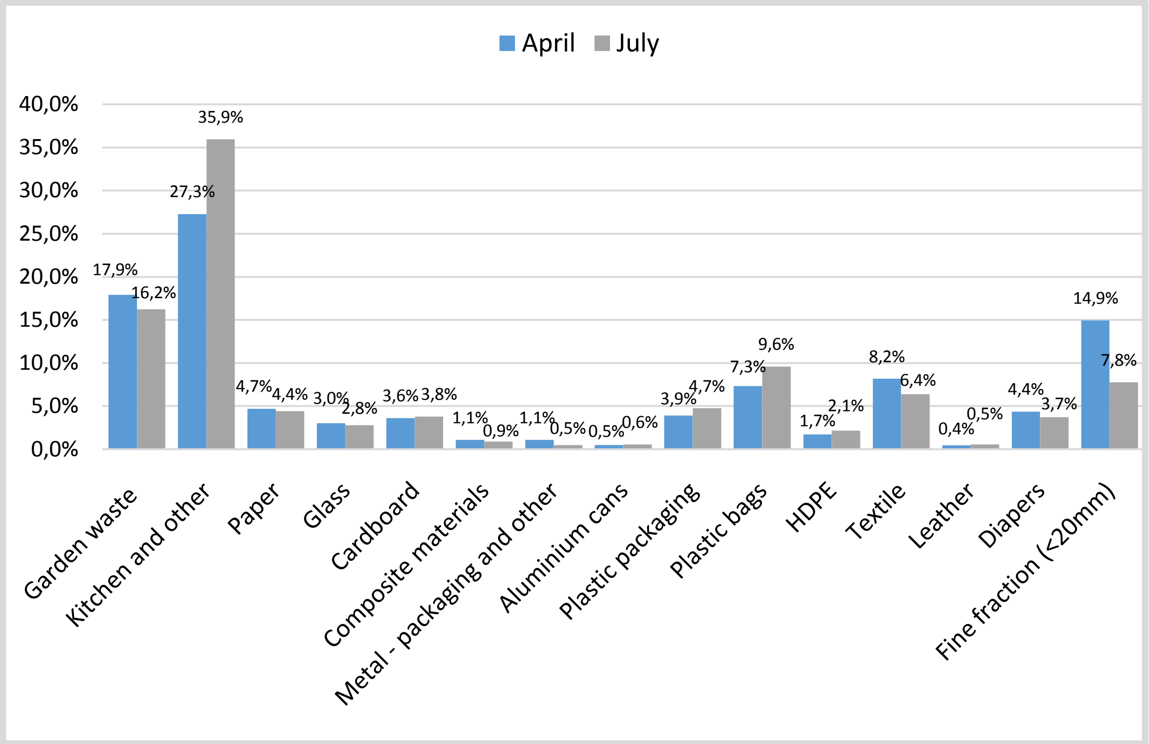

Figure 4. Comparison of waste composition according to period of analysis on regional level

Based on the population in each municipality, and their share in the region (Table 2), and the corresponding waste composition for each municipality, average composition of waste in the region can be calculated. If we compare such results for spring and summer analysis it can be seen that the biggest difference is for category of "other biodegradable waste" and "fine elements". In the first categories, which essentially represent kitchen waste, in the summer season proportion was higher by 9% over the spring analysis. Fine elements during the spring measurements were practically twice as much as during the July analysis, which is expected, given that most of these fraction makes the ash generated because of heating season. Major differences were observed in the case of plastic bags, which were more in the summer analysis, unlike the textile, which showed a greater share in the measurement in April. In the other factions, there aren't significant differences depending on the period over which the analysis was done.

Considering values for waste composition in summer and spring analysis, average waste composition for region was evaluate. Such obtained result for waste composition shows that the highest share has organic fraction with 48.7%, where garden waste has share of 17.1% and other biodegradable waste has share of 31.6%. Fraction of fine elements has share of 11% and represents great amount of waste which is a negative result, considering that this fraction can't be used in any waste treatment. Textile and diapers with share of 7.3% and 4.0% respectively also represent non favorable fractions from treatment and reuse point of view.

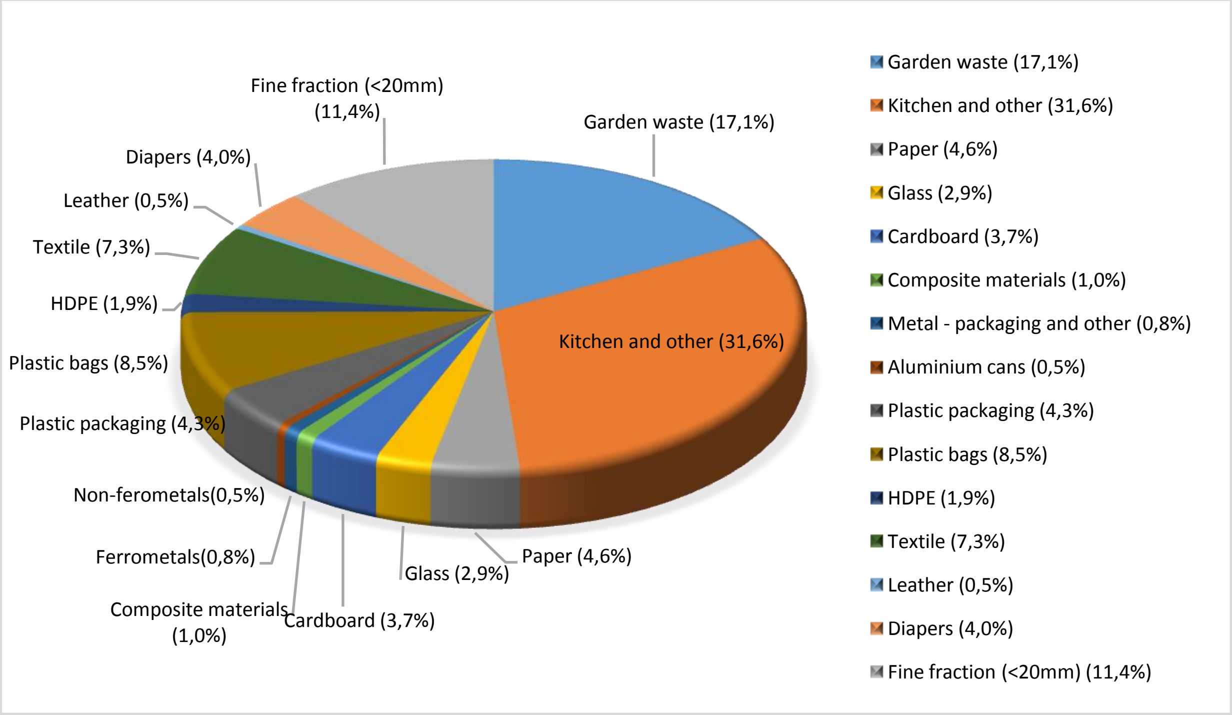

Figure 5. Average waste composition for whole region

Recyclable fractions, as paper and cardboard together have 8.3%, i.e. 4.6% and 3.7% of share respectively. Glass has share in expected boundaries and has share of 3%. Composite materials have small share (1.0%), and almost identical share is for packaging metals (0.8%). Metals fractions together takes 1.3% of share, which means that aluminum cans take only 0.5% in total waste composition. Plastic with 3 subcategories has 14.7% share in total amount, and PET with best recycling potential takes 4.3%. Plastic bags share (8.5%) is quite high, while high density plastic is 1.7%. The least represented fraction, next to aluminum cans, is leather with 0.5% share in total waste amount.

CONCLUSIONS

Specifying waste quantities and morphological composition is a key for successful municipal waste management. Such knowledge is indispensable to municipal and industrial stakeholders who are involved in urban waste management for the purpose of developing strategies and devising concepts for sustainable municipal waste management, waste recycling and waste disposal.

In addition to that, waste analysis represents an integral part of waste management and if properly conducted, it can identify waste generators at the level of households and spatial distribution thereof, the amount of waste components which can be separately collected and the quality and quantity of generated wastes. The analysis is also essential as the first step in preparing long term municipal waste management system and helps in identifying strategies to reduce waste generation, its treatment and disposal.

The situation in our country relevant to this aspect is not yet on a high level. The great majority of data regarding waste quantities and types are obtained on the basis of estimates and experiences at the terrain and not on really measured values and thus do not produce realistic qualitative and quantitative picture about waste and make it impossible to identify fractions which are compostable, recyclable, non-recyclable, and those having or not having energy values. All this may lead to a wrong choice of model for municipal waste management. Of course, we also know that waste separation before actual collection is here at a very low level although there have been educational and cultural incentives for that. Lately, the economic feature is slowly occurring and giving rise to the expansion of this type of waste collection. However, it should be highlighted that recycling of paper and metal in our country has appeared with the establishment of this type of industry. The results of the existing recycling or reprocessing of certain waste fractions must be included in the total waste quantities.

Concrete measurements of waste quantities and waste morphological composition at the territory of Kolubara region which have been explained in this paper can be used for further decisions. In other words, after full characterization of waste composition and information regarding the percentage of our waste that is recyclable, non-recyclable, compostable, and the percentage having an energy value and the percentage not having it, we can come to basic information about the model for municipal waste management which can be sustainable solutions for current conditions (economy, economics, infrastructure, credit facilities, etc.). Also, this will exactly be the incentive for the selected model to facilitate waste management and in time the method itself for specifying waste quantities and composition will become more efficient and provide better outcomes.

Based on the above stated, it is possible to conclude that the impact of characterization and municipal waste morphological structure onto the waste management model is decisive and segregating. The municipal waste profile should also include data regarding waste that is recycled (paper, metal, and plastics), differently treated and/or waste that is not found in the selected representative sample. It is also necessary to get as much as possible straightforward results which will create a realist municipal waste profile on the basis of which it will be viable to choose proper waste management model in our country.

REFERENCES

Batinić, B., Vujić, D., Ubavin, D., Stanisavljević, N. Specifying waste quantities and morphological composition in the province of Vojvodina, Proc. of PSU-UNS Inter. Conf. on Engineering Technologies, ICET 2009, Novi Sad, April 28-30, 2009 (pp 124-128), http://icet2009.ftn.ns.ac.yu.

Faculty of Technical sciences, Department of environmental engineering, Measurements of quantity and morphological composition of waste in Kolubara waste region, Novi Sad, Jul 2013.

Vujić G., Jovičić N., Redžić N., Jovičič G., Batinić B., Stanisavljević N., Abuhress O.: *A fast method for the analysis of municipal solid waste in developing countries - case study of Serbia*, Environmental Engineering and Management Journal, August 2010, Vol.9, No. 8, 1021-1029.

National waste management Strategy 2010-2019, Belgrade, June 20, 2009.

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NICKEL BASED SECONDARY RAW MATERIALS AND PROCEDURES FOR THEIR PROCESSING

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ABSTRACT

Over 30% of world nickel production is obtained from its secondary raw materials. The most important nickel secondary raw material is a steel scrap. Steel scrap is relatively easy recyclable by melting to the ferronickel, with the correction of composition. Besides ferrous metallurgy, the most important sources of nickel secondary raw materials are chemical industry (galvanization, petrochemistry, oil industry) and industry of Ni-Cd batteries. This paper presents the hydrometallurgical treatment i.e. preparation and processing of nickel based secondary raw materials, such as: nickel-graphite powder and spent nickel-based catalyst. The nickel recovery degree in both processes are high and ranges around 80% for the nickel-graphite powder and about 95% for spent nickel-based catalyst.

Key words: *nickel-graphite powder, nickel based catalysts, recycling, nickel sulphate.*

INTRODUCTION

The secondary raw materials of non-ferrous metals can originate in metal production and treatment, accompanied by their incorporation into the final product and its elimination due to amortization, and can be classified as process or amortization waste (Ilić et al., 2002). The ratio of process waste and amortization waste significantly differs for different non-ferrous metals. In the structure of nickel secondary raw materials the proportion of process waste is 42%, while the remaining 58% is amortization waste. This ratio is slowly moving towards reducing the proportion of process waste and increasing the proportion of the amortization waste.

The largest part of produced nickel is used for alloying and steel production, so the steel waste presents the most important nickel secondary raw material. It is usually directly remelted to ferro-nickel with composition correction or being used for alloying in ferrous metallurgy (Matković et al., 2006a).

Besides the ferrous metallurgy, the most important of nickel secondary raw materials are spent Ni-Cd batteries and byproducts of their production (Frenay and Feron, 1990), spent catalysts from the chemical and petrochemical industries, waste solutions from galvanization process and others.

The rapid development of industrial production influenced the increase of industrial waste quantity. Much of the industrial waste is recycled and returned to the production, while the small part of it is being minimized or stored according to the environmental standards and regulations. Environmental standards, which are becoming more rigorous day by day, are forcing many research teams to think about how to deal with waste (Đurković and Đurković, 1991; Cutchey , 2000; Lee et al., 2010; Abdel-Ala and Rashad, 2004; Sulek et al., 2004; Mulak et al., 2005). Non-hazardous waste that is degradable over time, or not degradable at all, is not a danger to the environment.

Hazardous waste, which is a byproduct of primary production, represents a major problem for the environment beginning from its proper storage, through transportation and further treatment. The best solution to the problem of hazardous waste is its processing at the site, although it rarely happens. Especially dangerous materials are those that contain heavy metals and their compounds that are soluble or insoluble in various media.

TREATMENT OF Ni-Cd BATTERIES AND BY-PRODUCTS OF THEIR PRODUCTION

Spent Ni-Cd batteries are processed to regenerate nickel and cadmium (Frenay et al., 1994; Matković et al., 2006a). It is possible to regenerate about 70% of manufactured batteries. The content of valuable metals in batteries without electrolyte is 20-25% for each metal separately, depending on the type of battery and amortization degree.

Technological treatment of Ni-Cd batteries consists of battery preparation, positive battery block treatment to ferronickel or nickel sulfate and negative block treatment to cadmium or cadmium oxide (Gulišija et al., 2006).

The process of pyrometallurgical treatment of a positive block is based on melting in electric arc furnaces. The obtained ferronickel contains about 25% of nickel.

Hydrometallurgical treatment is based on nickel powder dissolving in sulfuric acid. To release nickel powder from the positive block, crushing was done in the disintegrator, and obtained mixture of nickel powder and the steel shell is further processed on a magnetic separator. In this way the nickel powder separates from iron. Nickel powder is dissolved by sulfuric acid with the addition of nitric acid at elevated temperatures and further processed similarly to nickel-graphite powder that occurs as byproduct in the production of Ni-Cd battery (Figure 1). The obtained solution of nickel-sulphate is separated from the insoluble parts and analyzed on iron. If the iron content is higher comparing to the standard, than the solution purification is required. The purified solution of nickel sulphate crystallizes and the crystals are being filtrated and dried in the air. The degree of crystallization depends on the concentration of nickel in a solution and amounts up to 70%. The residual solution from the crystallization returns in the process so that the technological losses of nickel during the leaching and crystallization are minimized.

In the production of positive Ni-Cd battery block natural graphite is used to increase the contact surface of electrode (Sokić et al., 2003). Over the time there is contamination of graphite by nickel and creation of graphite-nickel powder that cannot be used. The nickel content in it ranges from 35-40% and as such represents a very rich secondary raw material of nickel. Its recycling significantly complicates the increased content of cadmium and iron (up to 1% for each metal respectively).

The hydrometallurgical treatment is based on two stages leaching of nickel-graphite powder with sulfuric acid solution (Figure 1). After nickel transition in the solution in the form of nickel-sulphate and its separation from the insoluble graphite, the solution is purified from iron by precipitation in the form of iron hydroxide. Purification of nickel-sulphate crystals of cadmium is done by their recrystallization. Number of stages of recrystallization depends on the content of cadmium in nickel-graphite powder. The final products of the processing are nickel-sulphate of technical quality and graphite that are used in industry. The recovery degree of nickel is around 80%.

Based on experimental laboratory investigations, the optimal technological parameters of nickel-graphite powder recycling were determined and confirmed in the semi-industrial plants. The process flowsheet is presented in Figure 1.

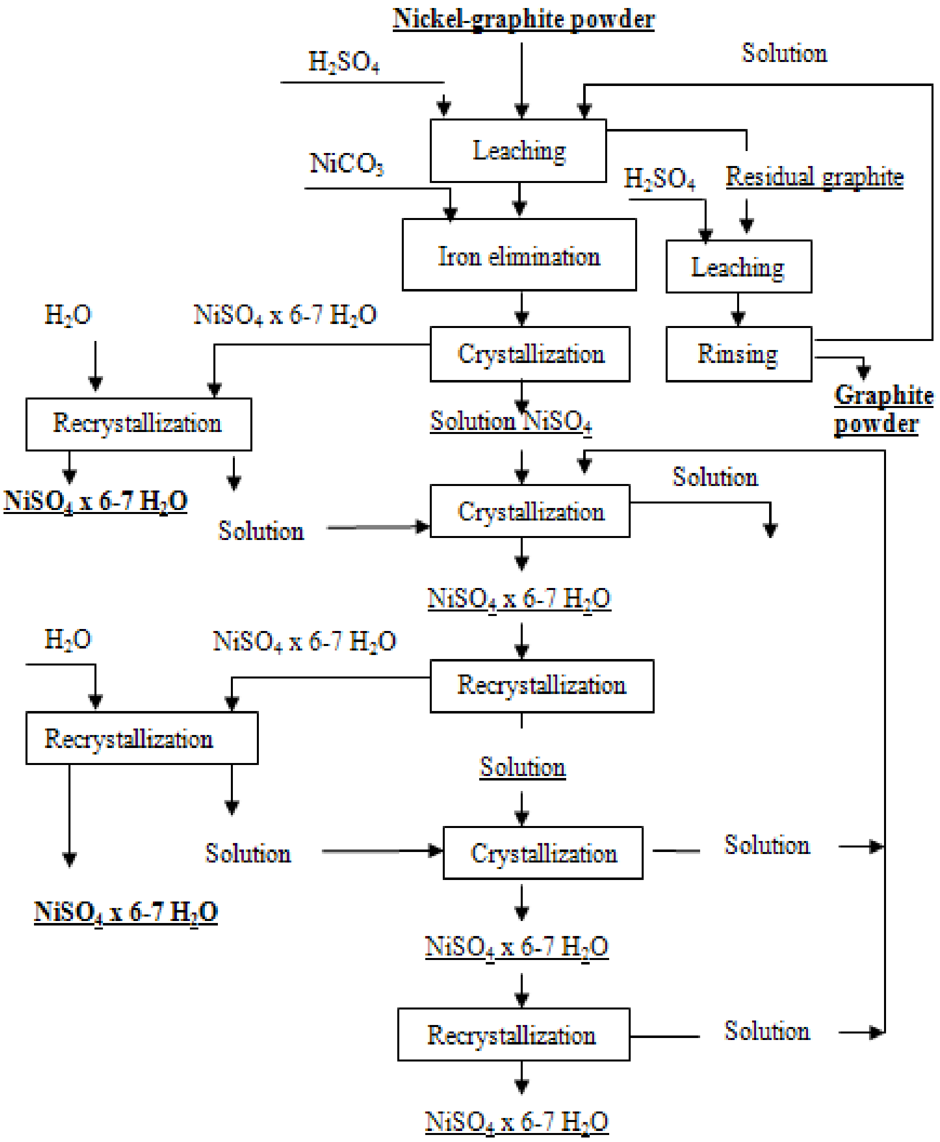

Figure 1. Flow sheet for the hydrometallurgical treatment of nickel-graphite powder

TREATMENT OF SPENT NICKEL-BASED CATALYST

During the selective hydrogenation of the highly active plants oils, the spent nickel based catalysts that are hazardous waste are produced. Catalyst activity decreases during the process and after a certain time become unusable. The used catalysts are hazardous waste with index number of 160802 and classified in the H11 category of hazardous materials. Currently they are stored at generation site, and exported with high costs. Investigations on similar materials (Matković et al., 2006b; Matković et al., 1993), conducted in ITNMS, have led researchers to attempt to get a useful component of nickel from hazardous wastes, and hazardous waste transform into non-hazardous or less hazardous.

Based on the literature, there are two types of processes for the recycling of spent nickel catalyst, such as pyroprocess and hydroprocess. Pyroprocess includes the high-temperature oxidation of spent catalyst and nickel ore, smelting the oxide mixture, then reduction and finally the separation of nickel. Hydroprocesses are based on selective dissolution of components with appropriate leaching solution and their separation from these solutions. Recently, are used a combined pyro and hydro-processes for processing of spent catalyst (Berrebi et al., 1992).

Based on laboratory investigations, the technological parameters for the hazardous waste, which has a practical value, processing in non-hazardous waste and commercial product, were defined. Spent catalyst which is a powdered form, with a highly developed surface, is suitable for hydrometallurgical processing. Table 1 shows the chemical composition of hazardous waste and the referent value.

*Table 1: Chemical composition of hazardous waste and the reference value**

	Content of metals, mg/kg														
	Pb	Cd	Zn	Cu	Cr	Hg	As	Ba	Sb	Co	Mo	V	Al	Be	Ni
U1	27,2	0,5	21,7	0,2	4,4	0,2	2,2	4,6	2,2	69,2	0,4	3,5	1134,2	0,05	195000
RV	1000	60	5000	60000	2500	7	50	100000	700	100000	9000	2000	-	30	3000

U1-The sample of hazardous waste
RV- Referent value
*- Results of the Municipal Institute of Public Health

Presented chemical composition of the investigated sample makes waste dangerous primarily because of the high content of nickel. Removing of nickel, the hazardous waste is converted into harmless or less dangerous.

First of all, the preparing of hazardous waste for the hydrometallurgical treatment was done. The preparation involves two steps: degreasing and thermal treatment to remove organic substances. Hydrometallurgical treatment includes two steps leaching by sulphuric acid, with initial concentration of 220g / l.

The influences of temperature, time and solid-liquid ratio on the degree of recovery of nickel for both single and double-step leaching were determined. The results are shown in the Figures 2, 3 and 4.

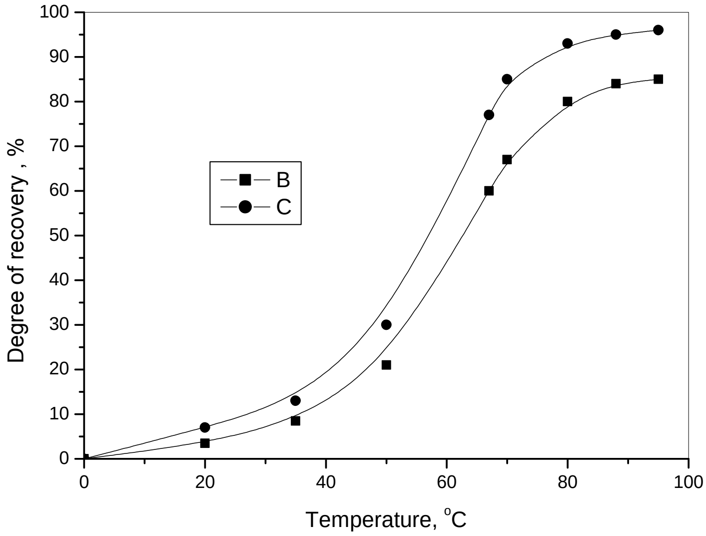

Figure 2. Influence of the temperature on the degree of recovery of nickel
B) one-step leaching, t=3h C) two-step leaching, t_1*=3h,* t_2*=2h*

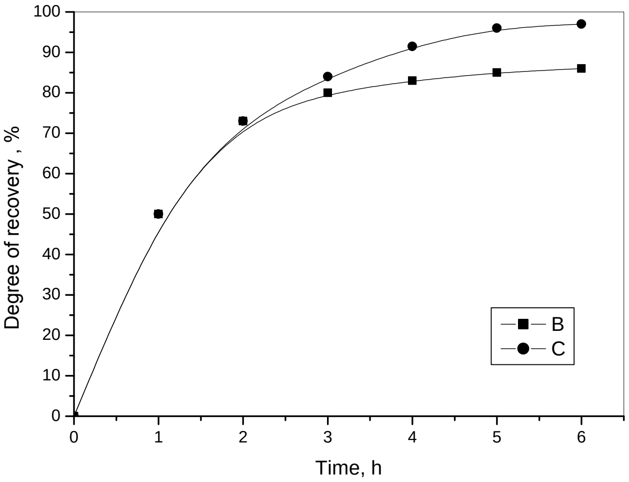

Figure 3. Influence of the time on the degree of recovery of nickel, T=90°C;
B) one-step leaching, C) two-step leaching

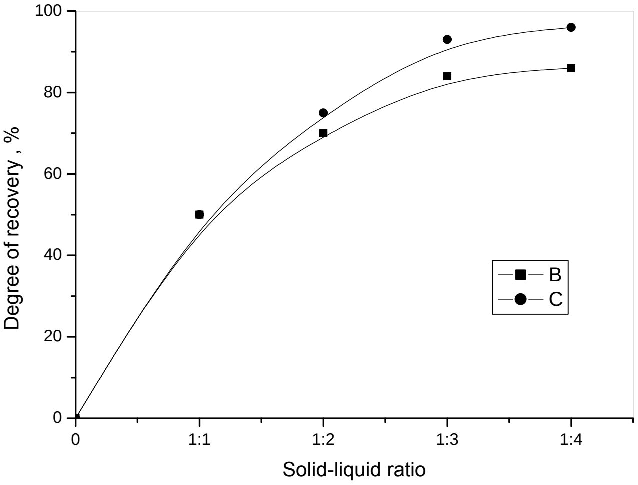

Figure 4. Influence of the solid-liquid ratio on the degree of recovery of nickel, T=90°C;
B) one-step leaching, C) two-step leaching

The nickel leaching process from the spent catalysts is exotermal. Experimental results, Figures. 2 and 3, show that the reaction is very slow in its initial stage, until temperature is below 60^{0}C. When the temperature reaches 60^{0}C the onset of reaction is observed and the solution begins to boils, what enables better contact between catalyst and solution. Optimal leaching parameters are: temperature 80-90^{0}C, time 2-5h and solid-liquid ratio 1:4. The reaction stops when sulfuric acid concentration reaches 30g/l. When the acid concentration decreases below this limit, the reaction can be reactivated with an addition of acid and oxidant.

In the first leaching stage of the double–step process, the nickel recovery degree of 80% is accomplished. In the second leaching stage, with the subsequent acid addition, the nickel recovery degree accomplishes 95%. The obtained solution is evaporated till $NiSO_4 \cdot 7H_2O$ is crystallised, while the sediment from the first leaching stage is sent to the second leaching stage. If the quality of the $NiSO_4 \cdot 7H_2O$ crystals is satisfying, they are dried and packed, and if not, they are sent to the recrystallization. The residual sediment contains Al_2O_3 (catalyst bearer) and SiO_2 from the filtration agent. In further treatment of the sediment, the remaining nickel is removed to a referent value of 3000 mg / kg. On that way, the hazardous waste is converted into non-hazardous.

Based on this investigation, the process flowsheet for reprocessing of the spent nickel catalyst is suggested, and presented in Figure 5.

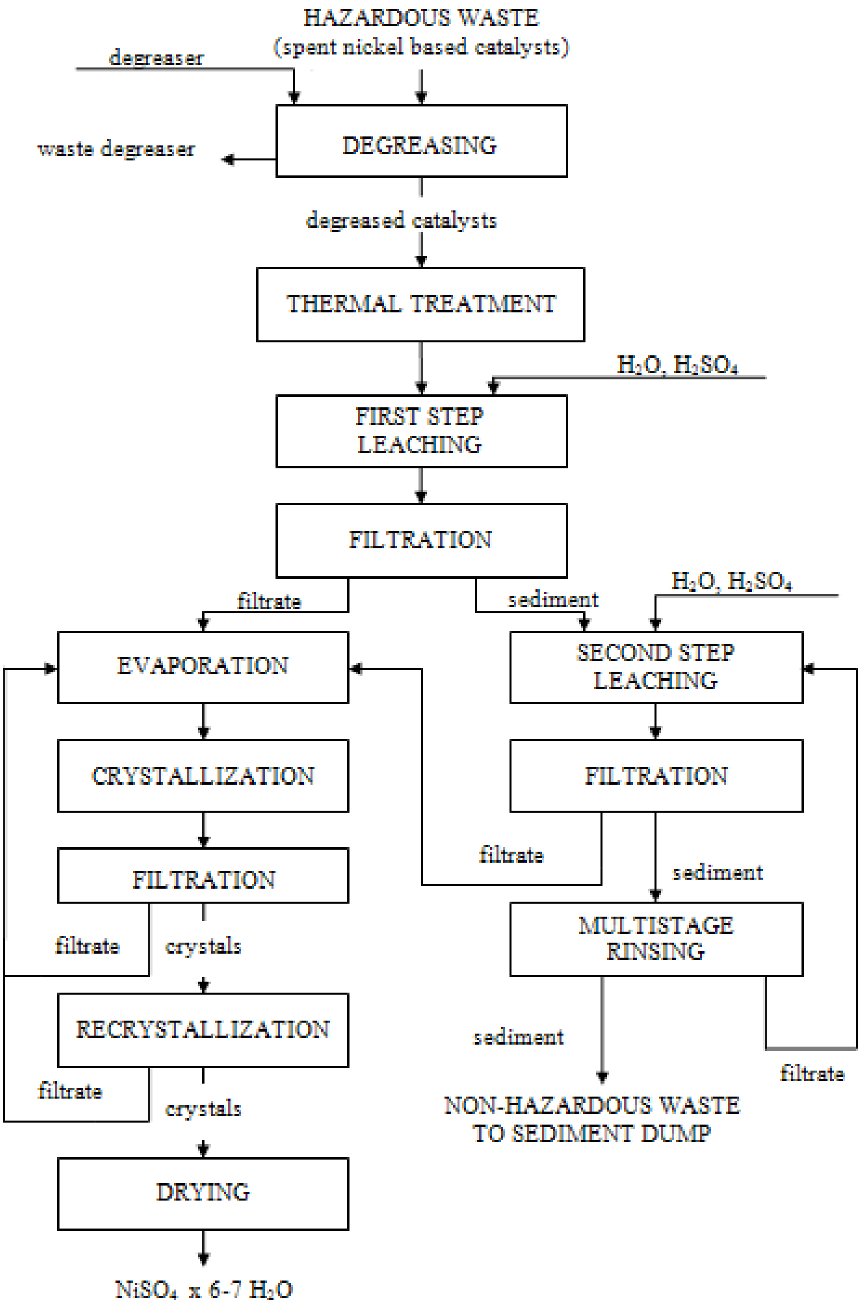

Figure 5. Flow sheet for the hydrometallurgical treatment of spent nickel-based catalysts

CONCLUSION

In the production of positive Ni-Cd battery block the nickel-graphite powder with 35-40% of nickel was obtained as a byproduct. It is being treated by hydrometallurgical two stages leaching with sulfuric acid solution. The graphite powder and solution from which nickel-sulphate crystallized are obtained after filtering. The recrystallization is necessary due to the high content of cadmium and iron, influencing the reduced recovery degree (80%). The final products of treatment, the nickel-sulphate of technical quality and graphite are further used in industry.

Hazardous waste, generated during hydrogenation of the highly active plants oils can be successfully recycled. By suggested hydrometallurgical treatment the following effects are achieved:

- hazardous waste is converted to non-hazardous, environmentally friendly according to lawful regulations,
- a commercial product is obtained.

The recovery degree of nickel is 80% for first leaching stage and 95% for second leaching stage.

Satisfying economic and environmental results are achieved after the investigations on hydrometallurgical treatment of nickel based secondary raw materials.

ACKNOWLEDGMENT

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REFERENCES

Abdel-Ala, E.A., & Rashad, M.M. (2004). Kinetic study on the leching of spent nickel oxide catalyst with sulfuric acid. *Hydrometallurgy*, 74, 189-194.

Berrebi, G., Dufresne, P., & Jacquier, Y. (1992). Recycling of Spent Catalysts. *Proseedings of the International Conference on the Recycling of Metals*, Düsseldorf, Germany, 31-36.

Cutchey, C. (2000). Catalyst Recycling-An Elegant Loop. *Malaysian Oil Science and Technology*, 11 (1), 31-33.

Đurković, B., & Đurković, D. (1991). *Metalurgija retkih metala*, Tehnološko metalurški fakultet, Beograd, 250-260.

Frenay, J., Ancia, Ph., & Preschia, M. (1994). Mineralurgical and metallurgical processes for the recycling of used domestic batteries, *Second International Conference on The Recycling of Metals*, Proceedings, Amsterdam, pp. 13-20.

Frenay, J., & Feron, S. (1990). Domestic battery recycling in Western Europe, *Second Int. Simp. Recycling of Metals and Engineered Materials*, The Minerals, Metals & materials Society, pp. 639-647.

Gulišija, Z., Sokić, M., Matković, V., & Marković, B. (2006). Postupci pripreme i prerade otpadaka nikla i legura nikla, *I Simpozijum o reciklažnim tehnologijama i održivom razvoju sa međunarodnim učešćem*, Zbornik radova, Soko Banja, 85-90.

Ilić, I., Gulišija, Z., Radovanović, N., Sokić, M., Matković, V., & Marinković, J. (2002). *Resursi i reciklaža sekundarnih sirovina obojenih metala*, Monografija, Institut za bakar, Bor, 151.

Lee, J.Y., Rao, S.V., Kumar, B.N., Kang, D.J., & Reddy, B.R. (2010). Nickel recovery from spent Raneynickel catalyst through dilute sulfuric acid leaching and soda ash precipitation, *Journal of Hazardous Materials*, 176, 1122-1125.

Matković, V., Marković, B., Sokić, M., & Vučković, N. (2006b). Recycling of Spent Nickel Based Catalysts, *Acta Metallurgica Slovaca*, Special Issue, 12 (1), 284-288.

Matković, V., Ratković, Lj., Vidojković, V., Vujić, V., Paunović, M., & Stanković, D. (1993). Prerada otpadnih katalizatora na bazi nikla, *II Simpozijum Hemija i zaštita životne sredine*, Vrnjačka Banja, 525-527.

Matković, V., Gulišija, Z., & Sokić, M. (2006a). The Secondary Nickel Application for Alloying of Wear Resistant Cast Iron, *Acta Metallurgica Slovaca*, Special Issue 12 (1), 277-283.

Mulak, W., Miazga, B., & Szymczycha, A. (2005). Kinetics of nickel from spent catalyst in sulfuric acid solution, *International Journal of Mineral Processing*, 77, 231-235.

Sokić, M., Matković, V., Gulišija, Z., Marković, B., & Vučković, N. (2003). Nickel-Sulphate Reclamation from By-Products of Ni-Cd Batteries Production, *35th IOC on Mining and metallurgy*, Proceedings, Bor Lake, Yugoslavia, 392-397.

Sulek, B., Szymczycha, A., & Mulak, W. (2004). Sulphuric acid leaching of nickel from a spent catalysts. *In: Proceedings of Global Symposium on Recycling, Waste Management and Clean Technology*, Madryt, 2081-2090.

IV International Conference
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USING RECYCABLE MATERIALS IN CONSTRUCTION – REINFORCEMENT OF CONCRETE SLABS WITH POLYMER FIBERS

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ABSTRACT

In production of concrete slabs instead of using steel armature polymer fibers are increasingly present and it’s benefits are coming out. Alongside of improving concrete characteristics, usage of this fibers makes significant economical savings. One of commercially known products is Ruredil X Fiber 54 and it’s usage costs up to 42% less compared to making concrete whit steel armature. The main drawback with this product is that it’s not made of recycled materials although it’s main components are recyclable (polypropylene and polyolefins). Producing Ruredil X Fiber 54 out of recycled polymere fibers would not only contribute to sustainable usage of raw materials but would have significant savings.

Key words: *plastic waste, polymer fibers, reinforcement of concrete, plastic recycling.*

INTRODUCTION

While producing concrete slabs it is needed to choose materials that provides wanted characteristics of concrete and makes it more resistant, if it is needed. To make concrete tougher armature is used, which binds medium and increases sthrenght and resistance. Mostly, steel armature is used. Using armature of polymer fibers can also give wanted characteristics of concrete. This armature is mostly made in fiber shape.

Mortar and concrete that are reinforced by fibers (FRM) i (FRC) are being studied for years, because materials produced this way can have better characteristics, like tensile strength, elasticity modulus,and toughness. The addition of small volume fractions of synthetic fibers (up to 2%) to the mixture can improve the toughness of mortars and concretes (*Silva et al, 2005, Wang et al, 2000*). Commonlly used polymers are polypropylene, polyethylene, nylon, aramid and polyester.

We are differentiating four types of concrete which are containing the polymers: polymer concrete (PC), polymer modified concrete (PMC), polymer micro reinforced concrete (PMRC) and polymer impregnated concrete (PIC). PC is created through the polymerization of the mixture made of monomers and aggregates. PMC is obtained through the addition of monomers or polymers into a green portland cement concrete mixture, which are subsequently vulcanized and polymerized after the concrete setting. PMRC is obtained through the addition of polymer fibers into a green portland cement mixture being set after the mixing, whereby one is obtaining a micro reinforcement of concrete. PIC is obtained through the impregnation of consolidated portland cement concrete with liquid monomer and subsequent in-situ polymerization of that monomer (*Ršumović et al, 2003*).

Plastics are considered one the most significant invention of the 20th century. From the beginning of production in 1940 it’s application is very wide. Production and consumption of plastics constantly rises from year to year. According to Central Pollution Control Board world production of plastics is 150 million tones per year (data from 2012).Considering that plastics are mostly not biodegradable, their disposal represent big environmental problem (*Al-Salem et al, 2009).*Therefore it is needed to find alternative method to solve waste production problem. Waste can be stored, incinerated or recycled. When storing there is a problem of lack of space, while incinerating makes big amount of waste gases that affects air quality and human health. (*Ferreira et al, 2012*). One of the best ways that is recommended is recycling. Recycling is a system that transforms secondary raw materials, converted to waste, into the prepared raw material for the production of the final product. Plastics are industrially produced out of oil and natural gas. By using non recyclable materials non renewable energy resources are consumed. According to Plastics Europe average percent of recycling plastic waste in Europe is 15% (*Vujić i sar, 2009*)

Different kinds of plastic materials are produced in Serbia. The most significant are su polyethylene (PE-LD i PE-HD), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET) i polystyrene (Table 1).

Table 1: Production and consumption of basic plastic materials in Serbia (t) (Bogdanović, 2009)

Polymer	2005	2006	2007
PE-LD	29 224	33 123	34 035
PE-HD	16 253	22 332	25 209
PP	11 409	22 040	24 629
PS	19 939	22 840	26 644
PVC	33 472	42 617	42 625
PVC mixture	3 233	4 209	5 740
PET	30 435	47 484	58 282
Other	47 719	51 795	70 725

In Serbia there is also export and import of plastic materials. In Table 2 is shown statistical data of production, consumption, import and export of some plastic materials in Serbia.

Table 2: Basic statistical data of plastic materials (first half 2008 and first half 2009) (Bogdanović, 2009)

		I-VI 2008. (t)	I-VI 2009. (t)
PE-LD	Production	27 513	24 900
	Import	22 562	20 371
	Export	15 038	15 959
	Consumption	22 989	20 485
PE-HD	Production	40 346	34 700
	Import	34 987	27 440
	Export	12 098	9 418
	Consumption	17 457	16 678
PP	Production	17 903	5 864
	Import	8 132	1 427
	Export	15 593	16 390
	Consumption	25 364	20 782
PVC	Production	-	-
	Import	-	-
	Export	26 132	15 930
	Consumption	26 132	15 930
PS	Production	-	-
	Import	-	-
	Export	14 126	14 209
	Consumption	14 126	14 209

PET	Production	-	-
	Import	-	-
	Export	27 110	20 861
	Consumption	27 110	20 861
Other	Production	-	-
	Import	-	-
	Export	37 003	30 421
	Consumption	37 003	30 421

USE OF RECYCLABLE MATERIALS IN CONSTRUCTION ENGINEERING - STRENGTHENING CONCRETE SLABS WITH POLYMER FIBERS

One of ways of reuse of plastics during production of concrete slabs is production of floor plates without armature. Sinthetics fibers play significant role in constriction engineering for about 25 years and it's application is more and more various and frequent. There are two types of fiber: micro fibers, used as protection from cracking and macro fibers used as reinforcement in supporting elements. Macro fibers, known as structural fiber, are produced to replace classic steel armature, steel needles or nets and compensate disadvantages that are results of their application.

Ruredil Fiber X 54 fibers are available on market, are often used during production of concrete floors. these fibers can be used during constructing of massive floor plates of prefabricated elements (wall panels, tanks for drinking water, cable channels, roof elements, etc.) supporting tunnel walls. It also found application in constructing of industrial and house floors, parking lots, storages, services, airport runways and harbor floors.

During application of these fibers some economic savings can be achieved compared to steel armature and steel needles. Structural sinthetics fibers RXF54 should be added during mixing concrete. These fibers are composed 80% structural component made of polyolefin copolymers macro fibers and microfibers 20% component against cracking, made of polypropylene fibers. This mixture after couple minutes creates three-dimensional net of fibers that are completely replacing classic armature, increasing durability and mechanical properties of concrete (resistance on tensile, banding and fraying). Taht way costs of building are reduced.

Advantages of RXF54 are incomparable during it's use as a replacement for steel fibers (1 kg of RXF54 replace 12- 15 kg steel needles that can be easy magnetized and are usually unequally distributed, that can lead to resurfacing and pulling out of the concrete and it also does not prevent cracking the concrete). Fibers are chemical inert, these are not subject to corrosion, there is no magnetization, their share of 1,5 kg/m^3 reduce thickness of concrete, they are perfectly coalesce with concrete and it increase endurance of concrete. There is no need for further mechanization and fazes during production and installation of concrete. As final treatment of concrete can be used all materials (*http://www.podovi.org/industrijski-podovi/podne-ploce-bez-armature*).

PROPERTIES OF CONCRETE REINFORCED WITH POLYMER FIBERS AND ADVANTAGES OF THEIR APPLICATION

Properties of concerte armirated with this fibers are investigated earyer (*Focacci and Mantegazza, 2004*). Non metallic fibers considered here are commercially known as Ruredil X Fiber 54.

The experimental results allow the following observations:

- It is confirmed that the presence of fibers in the concrete matrix poorly affects the concrete compressive strength;

- The presence of fibers seems to increase the splitting tensile strength of concrete, this result is not confirmed by the bending tests, in which the flexural tensile strength is not affected by the presence of fibers;
- The presence of fibers strongly modifies the postpeak behavior of concrete allowinng the presence of a “residual strength” which remains almost constant even for considerable displacements. This is due to the fibers debonding during the opening of cracks;
- Hooked steel and MCP fibers at the same volume ratio produce similar effects on the flexural results, MCP fibers present a lower dispersion of results;
- The increase of MCP fibers volume ratio produces an increase of the residual strength, whereas the pre-cracking behavior is unchanged (*Focacci and Mantegazza, 2004*).

Except of specified properties that are affected by use of these fibers it is very important to emphasize economic savings (*Table 3*).

Table 3: A comparative analysis of applied reinforcement of storage space (1000 m^2) provided for load – forklift 5,5 t/m^2 (http://www.podovi.org/industrijski-podovi/podne-ploce-bez-armature)

	reinforcement		
	steel armature 10 kg/m^2	steel needles 25 kg/m^3	Ruredil X Fiber 54 1,5 kg/m^3
quantity (kg)	10000	3750	180
price of reinforcement (€)	8500	3000	2700
thickness of the concrete slab (cm)	15	15	12
price of concrete (€)	10500	10500	8400
total price (€)	19000	13500	11100
total save (%)		29	42

For production of 1 m^3 of need 1.5 kg of Ruredil X Fiber 54 fibers, while 1 kg of these fibers replacing 12 to 15 kg steel needles. For production of 1 m^2 of floor slabs need 10 kg of steel, what results with savings of 42% compared to steel armature and 13% compared to steel needles. Naturally, with changing of floor slabs properties, properties of concrete have to be changed as well as quantity of armature.

DISCUSION

Price of Ruredil X Fiber 54 final product is 15 €/kg (*http://www.podovi.org/industrijski-podovi/podne-ploce-bez-armature*). Polymer that dominate in these fibers are polypropylene and polyolefins (*Table 4*). Prices of recyclates of polypropylene and polyethylene (HDPE, LDPE and LLDPE) are 1,37 to 1,52 €/kg and 1,48 do 1,65 €/kg, respectively (http://pieweb.plasteurope.com/).

Table 4: A comparative analysis of average prices of concerte reinforcement fibers (www.alibaba.com)

	Prices of non-recycled polymer fibers (€/kg)	Prices of recycled polymer fibers (€/kg)
polypropylene	1.69	1.54
polyolefins	3.45	1.15

Price of recycled polypropilene fibers is that are used for concerte and mortar reinforcement are between 0,77 and 2,31 €/kg, while prices of high quality recycled fibers used for roads building are between 2,19 and 2,66 €/kg. Prices of non-recycled polypropilene fibers are between 1.54 and 1.85€/kg, while prices of non-recycled polyolefin fibers are between 3.08 and 3.85 €/kg.

Disadvantage of Ruredil X Fiber 54 is that it is not made of recycled materials, so beside economic savings there is no ecological importance. However, materials that these fibers are made of are recyclable, that means there would be reduced quantity of generated waste that should be delayed. It would also have significant importance for reducing of non-renewable sources of energy (oil and gasses).

CONCLUSION

Considering that quantity of produced and used plasctic polymers increases every year in Serbia as well as in whole world, it is nessesery to find new solutions for reuse of this waste as much as posible. Economical profitability is very important and it is the biggest motivation during selection of materials that will be udes during building. The use of these fibers in stead of steel armature or steel needles bring economical savings of 42% and 13%, respectively. Use of some recycable polymers durin the production of floor slabs is great stimulus for recycling of plastic masses and it is also has econimical profitability. Price of recycled polypropilene fibers is 9% lower than non-recycled fibers. While price of recycled polyolefine fibers is 67% lower than non-recycled fibers. Beside that sources show that characterisctics of concerte reinforced this way are beter than concerte reinforced with classic armature.

REFERENCES

Rušumović M., Vukelić, N., Zec, M., Vacić, V.,(2003) Polymer materials in concrete, *Institut for roads, Beograd, Road and traffic* 4, Pages 47-51

Bogdanović, V. (2009) Status and perspectives of plastic production and processing of plastics and rubber in serbia, , *Polymeric materials and additives* Conference paper, Zagreb

Silva, D. A., Betioli, A. M., Gleize, P. J. P., Roman, H.R., Gomez L. A., Ribeiro J.L.D. (2005) Degradation of recycled PET fibers in Portland cement-based materials, *Cement and Concrete Research* 35, Pages: 1741 – 1746

Al-Salem, S.M., Lettieri, P., Baeyens, J. (2009) Recycling and recovery routes of plastic solid waste (PSW): A review, *Waste Management* 29, Pages: 2625–2643

Focacci, F., Mantegazza, G. (2004) Non-metallic (MCP) fibers reinforced concrete: mechanical characterization and slabs on grade design aspects, *6th RILEM Simposium on fibre - reinforced concretes (FRC) BEFIB*, 20-22 September 2004, Varetina, Italy

Vujić, G., Ubavin, D., Batinić, B., Vojinović Miloradov, M., Štrbac, D., Gvozdeac, B., Stanisavljević, N., Milovanović, D., Adamović, D., Bačlić, S., Dvornić, A. (2009) Waste composition establishing and quantity assessment for the purpose of defining strategy of secondary raw materials menagment as part of the sustainable development of Serbia Republic

http://pieweb.plasteurope.com/ (2014/08/30)

www.ali-baba.com (2014/09/15)

http://www.podovi.org/industrijski-podovi/podne-ploce-bez-armature (2014/08/28)

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POSSIBILITIES FOR SAFE DISPOSAL OF HISTORICAL HAZARDOUS WASTE – JAROSITE PRECIPITATE

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ABSTRACT

A major contribution to protecting the environment of the town of Šabac and globally is in finding solutions for the safe disposal of waste. For decades, the hydrometallurgical process of production of electrolytic zinc as a by-product generated hazardous waste - jarosite precipitate. The aim of this paper is to present the technological processes for the recycling and recovery of sludge by varying the process parameters through introducing a new procedure for processing sludge in the direction of the maximum valuation of zinc metal.

Key words: *jarosite sludge, hazardous waste, safe disposal.*

INTRODUCTION

The main hypothesis of the successful waste products management in zinc hydrometallurghy is decreasing the amount of pollutants in waste which pollute the environment. Around the world, a great attention is given to solving the problem of jarosite residue. By examining the kineastetic and termodynamics of the precipitation, we concluded that it is very important to maintain a certan pH value and temperature for jarosite stabilisation during hydroxide precipitation (*Arslan and Arslan, 2003*). The problem of introducing a new advanced technology which would obtain a jarosite with such characteristics that could be discarded or valorised (cement plants, steel plants); the general problem of jarosite discarding was examined by *Moors and Dijkema, 2006.* The possibility of using the jarosite as a potential raw material in construction and ceramics industry was considered by *Pappu, Saxena and Asolekar, 2006*. Everyone agrees that the solution to the problem is in previous refinement of the jarosite residue and waste liquids through new advanced technologies [5], changing of the present or valorisation of jarosite of satisfying quality. By desreasing the amount of zinc in the residue, it becomes more suitable for implementing as a raw material for pigments or cement. [9] If there is a possibility of jarosite valorisation, the company improved its economical, and solved its ecological problem connected to the residue discarding. Until the moment of valorisation, it is often required to discard the residue, and the treated residue is the safest then.

In the factory "Zorka" - "Non-Ferrous Metallurgy", Šabac,jarosite precipitate represents the historical pollution from 1976 when hydrometallurgical - jarosite process zinc ore processing was introduced.

The motive of this work is the need to define the procedure as a function of environmental care by reducing the amount of existing waste in the landfill and using of newly generated waste from the current production.

Experimental and semi-industrial tests have shown that it is possible to:

1. reduce the amount of process water, thereby decrease pollution of ecosystems, by introducing a new method of washing the precipitate,
2. introduce a new procedure for processing jarosite precipitates, and
3. combine old and new methods of processing all of the residue from hydrometallurgical zinc.

THEORY AND ANALYSIS

The theory-based treatment of the precipitated jarosite residue is basically the same as in the waste water from the electrolytic zinc production because of the present metal cations.[1,2]

The metal cations present in the waste water (i.e. jarosite residue) are drained into hard-soluble hydroxide by using hydrated lime residue prepared in the form of water suspension. The reaction for the hydroxide metal generation is:

$$M^{n+} + nOH^{-} = M(OH)_n \qquad (1)$$

After the sulphuric acid is neutralised by adding lime milk to the jarosite pulp, the pH level is increased and the conditions for metal cations hydrolyses are achieved (Pavlovic, 2002).

Hydrolysis reaction proceeding acording to the equation:

$$M^{n+}aq + 2nH_2O = M(OH)_n + H_3O^{+}aq \qquad (2)$$

By adding calcium-hydroxide, the released hydronium ions are neutralised with creating of plaster, which increases the chemical reaction from left to right quantitively. The total reaction of the precipitation of bivalent metals hydroxide is:

$$MSO_4 + H_2SO_4 + 2Ca(OH)_2 = M(OH)_2 + 2CaSO_4 + 2\mathrm{H_2O} \qquad (3)$$

The optimal pH value after the hydroxide precipitation is at app. 9,5 – 10,5. The majority of the metals hydroxide which are present in waste water of zinc electrolysis (or jarosite residue) are amphoteric, therefore hydroxides are dissolved at high pH values, while they release metal in the ion state (zinc, etc). There is an equation between pH value at which hydroxides and their soluble products are separated:

$$\mathrm{pH} = \log \mathrm{L} - \frac{\log \mathrm{M}^{n+}}{\mathrm{n} - \log \mathrm{K_W}} \qquad (4)$$

where:

L = dissolving product,

$$\mathrm{L} = [\mathrm{M}^{n+}] . [\mathrm{OH}^{-}]^{n} \qquad (5)$$

K_w – water ion products.

At optimum pH conditions of the precipitation process, the content of the unsettled metal ions in the precipitated water is extremely low (zinc ~ 5.10^{-5} g/dm^3 , while the other cations are only found in traces), which completely meets the law regulations for this type of precipitated water, and the precipitated water can be emissioned into the natural recipient (Stanojevic, 2001).

The processing of sewage sludge requires us to meet with the term cementation in zinc hydrometallurgy. Cementing involves the extraction of metals from aqueous solutions in the form of a metal pellet by means of a second metal that is more electronegative than the metal to be cemented. The process can be explained as a function of electrode potential. The metal with the positive potential passes into the solution and it is replaced with a metal which has a less positive potential (see Table 1).

Table 1: Electrode potentials

Elements	Ca/Ca^{2+}	Zn/Zn^{2+}	Fe/Fe^{2+}	Cd/Cd^{2+}	Pb/Pb^{2+}	Fe/Fe^{3+}	Cu/Cu^{2+}	Ag/Ag^{+}
Volts	+2,87	+0,763	+0,44	+0,402	+0,126	+0,036	-0,337	-1,369

The dissolution rate of metals, ie the rate of change of concentration noble metal ions is given by the equation:

$$-\frac{dc}{dt} = k\frac{S}{V}c \qquad (6)$$

Where:
k - rate constant,
S - surface touches the surface of the metal and the solution,
V - volume of the reacting solution,
c – concentration.

The process may be a chemical pack cementation and diffusion controlled. Temperature increase accelerates chemical reactions. Speed cementation depends on the used metal hardening. Deposition of lead by zinc is much faster than the iron, which *Lameck, 1956* showed in previous studies on the impact of certain elements of the deposition others. When the rate of metal deposition is very high, the deposited particles are small and forms the adhesion film. The process becomes diffusion controlled since the metal ions diffuse through the film adhesion to the metal surface enrichment.

EXPERIMENTAL

Some zinc electrolysis solved the problem of decreasing of hazardous substances from liquid and solid products of the zinc production with the construction of a plant for the refinement of waste water and jarosite residue.

PRECIPITATEWASHING

In Šabac electrolysis, a series of experiments with three-stage washing jarosite precipitate shell and tube vacuum filters was conducted, without facilities for wastewater treatment and single flush sediment on a horizontal bandsaw vacuum filter - as part of the treatment plant.[6,11] The average concentration of hazardous substances in wastewater monitored at these experiments is given in table 2.

All tests were carried out with the use of dried jarosite precipitate in order to ensure the same initial conditions for all experiments. Experimental verification process at reduced semi- industrial plant facility, confirmed the process parameters obtained in the laboratory experiments.

Prior to jarosite precipitate transport to the waste storage, the precipitate is converted to the mixing and dispersing the pulp in water. The plant for wastewater treatment is an integral part of the Leach plant facility with standard equipment that has already been used in the Leach plant and it is directly linked to the section for the treatment of jarosite precipitate so that the two plants located in the same location, under the section for acid wash jarosite. The fluid flow is combined by using pumps and gravity. The addition of reagents is done by means of pumps, transport sludge to the filter performs the pumps, and the flow of water into the stage neutralization, from neutralization to sedimentation and sedimentation of the river gravity. A series of tests (3 samplesin, 24h during the 7 days) to determine the optimum pH of the metals from the waste water and at the measuring points 1, 2, 3 and 4 shown in Figure 1.

Table 2: The average concentration of hazardous substances in waste liquids of zinc electrolysis

Hazardous substances in waste liquids of zinc electrolysis	Average quality of waste liquids (mg/l)	Precipitated water with barrel-like filters (mg/l)	MDK (mg/l)
Zinc, Zn	4,000	0,050	0,200
Cadmium, Cd	0,010	-	0,005
Copper, Cu	0,034	-	0,100
Iron, Pb	0,260	-	0,300
Lead, Pb	0,020	-	0,050
Cobalt, Co	-	-	0,200
Nickel, Ni	-	-	0,050

The processes and parameters shown in Figure 1 should satisfy the following:

- Two refining steps with the hydrated lime in the form of suspension,
- Final value at pH=10,
- Refining time from 10 to 30 min.
- Intensive mixing for the successful preparing and homogenisation of the lime milk, enabling intensive contact between water, metal ions, flocculants and polyelectrolyte.

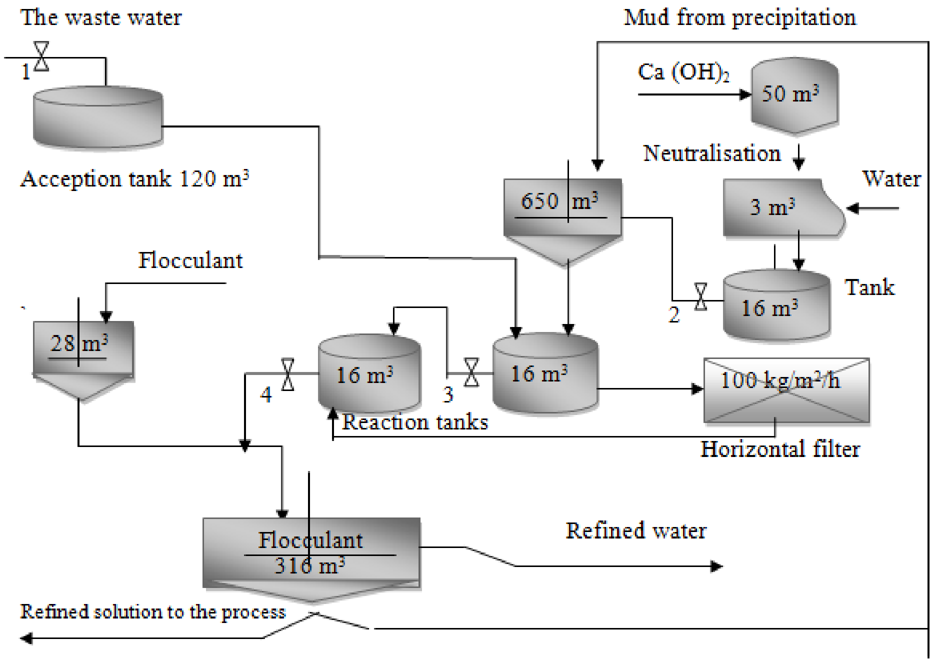

Figure 1. Block scheme for the refining waste water from the zinc electrolysis (1, 2, 3, 4 – signs for the pH control places)

PROCEDURES OF PROCESSING HYDROMETALLURGICAL SEDIMENT

Back in 1986 -1987, "Zorka" - Institute prepared the project: Production of lead and silver jarosite residue from hydrometallurgical zinc production. The project was not implemented in practice because the sanctions incurred, then because of reduced output and lack of funds for investment.

During 2012, thinking about the treatment of jarosite precipitate was again renewed, which over the years accumulated on the tailings. Jarosite complex is a compound made of $R^{+}[Fe_2(SO_4)_2(OH)_6]$ where R = K^+, Na^+, NH_4^+, Ag^+, Zn^{2+},Cu^+, Cd^{2+}, Pb^{2+}, H_3O^+,... and it is in a category of hazardous waste. The average daily production of the jarosite residue is 56t per day, with the average amount of 5, 4% of zinc in the residue.

The processing of jarosite precipitate by leaching with hydrochloric acids, was somewhat similar to the processing of jarosite precipitate with concentrated sulfuric acid, which the Institute demonstrated in the project.

The main products of refining jarosite and Pb/Ag precipitate with hydrochloric acid, HCl would be:

- Zn - is in the form of zinc hydroxide Zn $(OH)_2$,
- Cu - is obtained in the form of a metal powder which is being conditioned at the cathode,
- Pb - is obtained in the form of a metal powder which is being conditioned in the rod,
- Fe - is obtained in the form of iron trichloride $FeCl_3.6H_2O$ (used for purifying drinking water or from it aside Fe_2O_3 and hydrochloric acid), and
- gypsum ($CaSO_4$) - the leaching process it is necessary to neutralize the sulfur, which is obtained by milling limestone. There was thus obtained unroasted gypsum which is used as a filler in cement manufacturing.

The average composition of the jarosite precipitate would be processed to: 10% Zn, 23% Fe, 0.4% of Cu and 4% of Pb. Primary manufacturing equipment would consist of three reactors at 15 $m^3$and the inner layer resistant to acid, filter capacity of 2-3 t / h, evaporator 20 m^3, the extraction device capacity matching phase of 12-13 m^3/h, a furnace, and the required number of pumps, valves and fittings. The costs of production would be as follows:

1. Hydrochloric acid - about 4000t per year,
2. Limestone - 7000t per year,
3. Electricity - 6 million KWh per year,
4. Gross wages for employees - staff of 50 workers needed
5. Packaging material,
6. Costs for design and
7. The cost of the equipment.

The annual processing capacity would be at the level of 30000t solids with recovery of 85%. The project would be implemented in 10 years, since the estimated quantity of jarosite. The same processing capacity is planned for sludge using concentrated sulfuric acid and combined processing procedures.

Due to processing using HCl, which should be available, it would be more expensive to produce, and since the utilization of certain elements is not confirmed the processing of this project is for now abandoned.

Since the "Zorka" - "Non-ferrous Metallurgy" in regular production products as a byproduct of SO_2 gas, and from him sulfuric acid in contact II "Zorka" - "Mineral Fertilizers", because on the basis of previous research in 2013 made experiments refining jarosite using H_2SO_4 partially in the laboratories of zinc factory in accredited laboratories for testing of industrial waste (Anahem Ltd.) in 2013.

Laboratory studies refining jarosite precipitates were carried out with instrumental technique to ICP plasma and atomic absorber 5100 PC. A representative composite sample of jarosite is taken according to the standards for the taking of samples which are in the form of the residue with 11 wells at a depth of 3m. Selection of the sample is determined by the geological profile of depression tailings with a depth of at least 5m. Each sample is the average weight of over 10kg, out of which the composite sample is prepared. As a non-homogeneous composition of the jarosite precipitate, the mixture 6 is made (with different contents of zinc and with varying amounts of cement means - by varying the stoichiometry of the composition adding up to in excess).

In Figure 2, a method is provided for processing jarosite and Pb/Ag precipitates from "Zorka" Šabac.

Experimental work was to investigate the effect of temperature, type and quantity of cementresources, reaction time, speed of stirring, the concentration of metal that is cemented, the nature of sewage sludge that is to be valorized on the degree of cementation and the quality of the resulting cement slurry.

Leaching is performed in the following conditions:

- Temperature: t = 60^0C i 90^0C ,
- Duration: τ = 20min,
- With vigorous stirring (300-500 / min).

Cementing II was performed with the following conditions:

- Temperature: t = 25-50^oC,
- Duration: τ = 20-30 min,
- Intensely stirring for t = 25° C at 400 r / min and stirring at t slightly greater than 30° C at 100 r/min.

For the purpose of safe disposal of hazardous waste is managed by the following reasoning:

1. apply the technological process that will give the maximum utilization of zinc as the main product zinc factory,
2. make use of the entire amount of the residue whose composition is inhomogeneous, and in this sense, the most optimal to make the mixture,
3. use the existing Zn powder, also a product of zinc factory, for hardening and
4. if Zn tiles or Zn granules for hardening II are missing, replace them with Zn powder.

Since cementing performed with zinc as cementation agent, the chloride solution after cementation becomes richer in zinc which are periodically separated by neutralization. Thus the utilization of the base metal is increasing in the manufacture of zinc. In addition to zinc as products of the processing are: copper, silver, lead and $CaSO_4$.

Combined methods of processing sludge from electrolytic zinc: Waelc process and restoring zinc oxide, which occurs as a product of the prior proceedings in the regular process of production in Leach plant and zinc sulphate are still under consideration. Waelc method is basically a process of reducing roasting and evaporation of the metal created by reduction of the zinc and lead (Kamberovic et al., 2011). Zinc sludge which can be processed in this way must be accurately determined by the composition: 19-24% Zn, Pb 5-12-%, 0.3 to 1.3% Cu, 0.1-0.2% Cd , Fe 23-32%. Jarosite precipitate in this case it must be combined with some other precipitates to obtain the required quality of the batch Waelc processing.

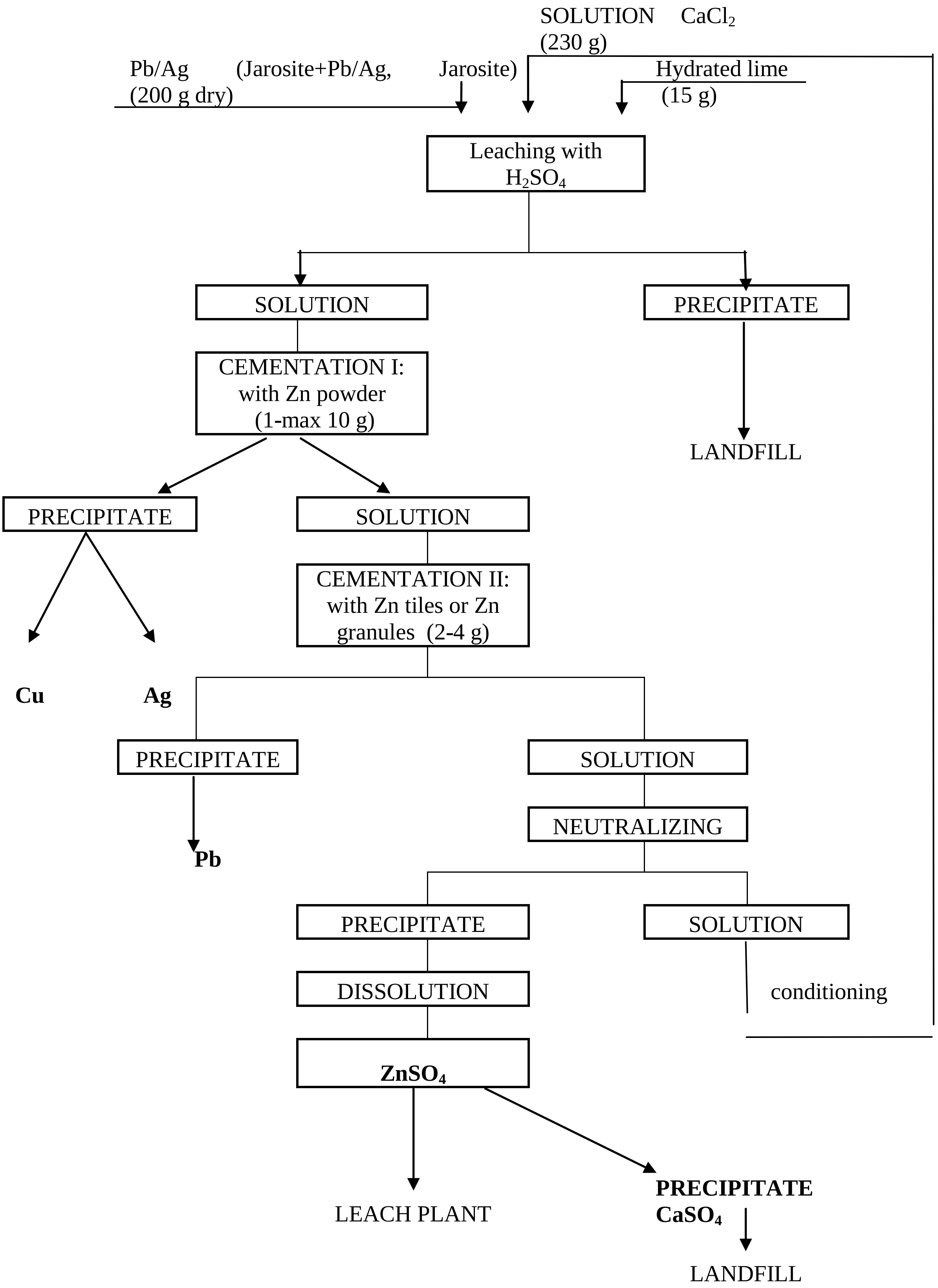

Figure 2. The processing of jarosite and Pb /Ag precipitates

RESULTS AND DISCUSSION

In this paper we discussed the results related to the increase in the amount of zinc as the main product of the factory electrolytic zinc in each of the possible solutions: recycling-returning by washing or processing residue.

The summary of the introduction of a new method of flushing sediment:

- It was established that the reaction of the precipitation is very fast, i.e. the sufficient reaction period is 10 min;
- Hydrated lime rate was established on 2 kg $Ca(OH)_2$/kg Zn solution;
- Flocculant rate is 5 g/m^3 of waste water;
- The density of the jarosite pulp does not have any important impact on the precipitation efficiency of heavy metal cations from the pulp. On these grounds, having in mind the optimal pulp density for the hydraulic transport needs, the dry jarosite residue and added water ratio was chosen - S:L=1:5;
- The zinc content in the three-fold washed residue is 0,5%, which is far better compared to the leading electrolytic plants in the world (1%), and even greater compared to the model of one-fold washing on horizontal filter: 0,1% (Figure 3). Additionally, the amount of water for the jarosite residue is three times smaller, which is a significant moment because of the problem with the consistency of the system capacity. [6]

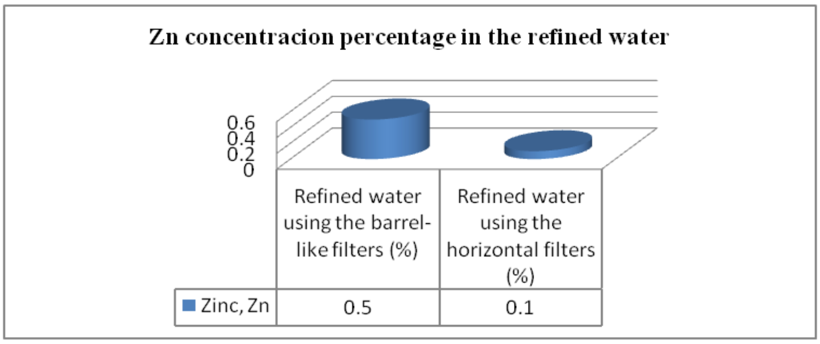

Figure 3. The eficiency of the refinement of waste liquids model

Summary of the introduction of a new procedure for processing jarosite and Pb/Ag precipitate with hydrochloric acid:

- It is assumed that the expected amount of zinc, obtained by processing 30,000 tons of dry jarosite was 2,550 t / year, or about 8% increase in efficiency, which is not confirmed in the project.

Summary of the introduction of a new procedure for processing jarosite and Pb/Ag precipitate with sulfuric acid:

- Leaching reaction takes 20 min, and the cementing phase II samples from the expected 30 minutes, the maximum duration up to 12h,
- Quantities of leach means of calcium chloride, $CaCl_2$, and hydrated lime ($Ca(OH)_2$), as well as the necessary amount of sulfuric acid (about 140g of conc. H_2SO_4) in the compositions gave results for the use of the zinc from about 9% to 75% in the depending on the content of Zn in the sludge - a higher content of Zn, showed lower utilization, if the amount of the means of leaching and cementation stoichiometry,
- Quantity of cement resources: Zn powder is varied by stoichiometric amounts of process up to 5 times larger and we came to the conclusion that the average content of Zn in the Zn sulfate, which is obtained as a product in the processing required stoichiometric amount (see Figure 2),
- The ratio of solid phase to the liquid in the pulp reaction is: S:L = 1: 5,
- It takes intensive mixing of the reaction pulp,
- Grout must be well rinsed with boiling water in order to achieve greater efficiency,

- A more optimal processing residue if Zn tiles are used for hardening II (see Tables 5 and 6),
- Processing sludge, considering the amount of 300.000t dry matter in the landfill, would last for 10 years, where it would annually be produced ~ 156 t, and which would increase production by 0.5%. Version I is considered - where Zn powder and Zn plates are used as cementation means.

Six mixtures of the following chemical composition are prepared from sample jarosite precipitate (shown in Table 3).

Table 3: Percentage of zinc Zn in the prepared mixtures of jarosite sludge processing

Mixture	1	2	3	4	5	6
Zn, %	6,83	9,77	2,65	8,0	8,59	2,39

According to the norms of materials used, the total cost and sales price profit is calculated for the mixture, Table 4.

Table 4: Profit for alternative solutions processing the mixture jarosite precipitates

Version I	Selling Price	Total cost of mixture	Profit = selling price – total cost	Version II	Selling Price	Total cost of mixture	Profit = selling price – total cost
Mixture 1	0.1010	0.0265	0.0745	Mixture 1	0.1010	0.0267	0.0743
Mixture 2	0.0310	0.0244	0.0066	Mixture 2	0.0310	0.0246	0.0064
Mixture 3	0.1019	0.0579	0.0440	Mixture 3	0.1019	0.0581	0.0438
Mixture 4	0.1010	0.0269	0.0741	Mixture 4	0.1010	0.0272	0.0738
Mixture 5	0.0310	0.0239	0.0071	Mixture 5	0.0310	0.0241	0.0069
Mixture 6	0.1019	0.0578	0.0441	Mixture 6	0.1019	0.0578	0.0441

Version I represents the processing of jarosite precipitate with the use of such cement funds: Zn powder and Zn plate, as provided in the scheme of processing (Figure 2). In Version II, Zn powder is used for both first and second cementing.

Processing of the obtained experimental results was carried out by defining the mathematical model of linear programming [3,4] and then applied software: *POM -QM for Windows, V3*. The following results were obtained shown in Tables 5 and 6.

Table 5: Optimal production of precipitates in the processing according to version I (g Zn)

	mixture 1	mixture 2	mixture 3	mixture 4	mixture 5	mixture 6		
objective	0.0745	0.0066	0.044	0.0741	0.0071	0.0441		0
jarosite	0.099718	0.144596	0.040174	0.1168	0.127132	0.036232	<	154000000
Zn powder	0.0495	0.0495	0.2475	0.0495	0.0495	0.2475	<	83053567
Zn plate	0.0396	0.0396	0.0396	0.0396	0.0396	0.0396	<	61882333
leaching solution	0.5873175	0.372141	0.43659	0.5873175	0.372141	0.43659	<	913452772
recurculate	0.223865	0.394163	0.236136	0.206783	0.411627	0.240078	<	350297312

The optimum annual production of Zn from jarosite and Pb/Ag residue in version I got in to produce a mixture of 1 in the quantity of a mixture of 153t and mixture 6 in the amount of 3t, for a total of 156t, and when the financial gain it will be 11,554,479,70 RSD. In version I the entire amount of jarosite and other resources will be spent.

Table 6: Optimal production of refining residue to variant II (g Zn)

	mixture 1	mixture 2	mixture 3	mixture 4	mixture 5	mixture 6		
objective	0.0743	0.0064	0.0438	0.0738	0.0069	0.0441		0
jarosite	0.099718	0.144596	0.040174	0.1168	0.127132	0.036232	<	154000000
Zn powder	0.0891	0.0891	0.2871	0.0891	0.0891	0.2871	<	83053592
leaching solution	0.587318	0.372141	0.43659	0.587318	0.372141	0.43659	<	547461599
recirculate	0.223865	0.394163	0.236136	0.206783	0.411627	0.240078	<	208673310

The optimum annual production of jarosite Zn and Pb/Ag for variation II of the residue is obtained if a mixture 1 is produced in an amount of 93t where 61t jarosite precipitate remains unused (the other raw materials to be consumed), and at the same time it will bring about a financial gain of 6,925.793 RSD.

The summary of anticipated results of the combined method of processing sludge:

- The anticipated results for the production of 30,000t of dry matter per year jarosite precipitates are to be expected 2.100t Zn / year if it was a mix: Waelc + hydrometallurgical processing.

Table 7 provides an overview of the obtained and anticipated results hydrometallurgical processes for the disposal of sludge.

Table 7: Results of different methods for jarosite and Pb /Ag precipitates disposal

	"Zorka" Šabac			Project phase	
	Flushing sediment	Version I	Version II	Processing with HCl	Waelc +hydrometallurgical
Zn, t/year	1280	156	93	2550	2100

CONCLUSION

If it would be possible to restore the allocated substances in the process, that would, in addition to the environmental situation, improve the economics of the production process.

According to the method of washing the jarosite precipitate by single horizontal filter, respectively merging precipitaced process on jarosite precipitate in the process and waste water, the utilization of zinc is increased to about 4%, and the amount of process water is reduced three times, so that the problem of excess water and dangerous pollutants is simultaneously solved.

Processing of jarosite and Pb/Ag precipitate with sulfuric acid, and using Zn powder and Zn plate as cement resources increases utilization of zinc by 0.5%

Processing of jarosite and Pb/Ag precipitates with sulfuric acid, and using a Zn powder as cement means increases the utilization of zinc by 0.3%.

Processing of jarosite and Pb/Ag precipitate with hydrochloric acid to increase the utilization of zinc by about 8%, which was not confirmed in semi-industrial conditions.

Combined processing of jarosite and Pb/Ag residue and other deposits from hydrometallurgical zinc old Waelc and finishing Waelc oxide by hydrometallurgical process, would give the increase in efficiency of about 7%. In doing so, the combination of this method with flushing sediment could happen within the normal production process, where the necessary working condition would be fulfilled - maintaining a constant total operating volume of the solution.

REFERENCES

Ahmet Semih Sunkar, Investigation and development of possible leaching processes for recovery of zinc and lead from cinkur leach residues, Thesis submitted to the Graduate School of Natural and Applied Sciences of Middle East Technical University, January 2005

Arslan Cuneyt , Arslan Fatma, Thermochemical Review of Jaroste and Goethitee Stability Regions at 25 and 95^{o}C, Turkish J. Eng. Env. SCI., 27 (2003), 45-52.

Backović, M., Vuleta, J., Popovic, Z. (2014), Economics and mathematical methods and models,the twelfth revised edition, Faculty of Economics, Belgrade, p. 610

Backović, M., Popovic, Z., (2012), Mathematical modeling andoptimization,(monograph), Faculty of Economics, Belgrade, p. 336

International Symposium-World Zinc ´93, Improved Jarosite Process, Hopart, 10-13 October in 1993.

Investment Program, "Waste water treatment and sludge treatment jarosite," HI "Zorka" Sabac, RO "Zorka" - "DEVELOPMENT", Sabac, 1991

Kamberović Zeljko Vucinic Aleksandra Jankovic Elena, Gavrilovski Milorad Andjic Zoran, Marija Korac, "The Stockholm Convention on Persistent Pollutants" Guidelines on best available techniques and best environmental practices relating to Article 5 and Annex C, Category : Metallurgy, ISBN 978-86-87183-21-6, Association of Metallurgical Engineers of Serbia, Belgrade 2011

Moors Ellen H., Dijkema Gerard PJ, Embeded industrial production systems Lessons from waste management in zinc production, Technological Forecasting & Social Change 73 (2006), 250-265

Pappu Asokan, Saxena Moxini, Asolekar R. Shyam, Jaroste characteristics and utilization potentials, Science of The Total Environment, Volume 359, Issues 1-3, 15 April 2006, 232-243

Pavlović Milan, "Environmental Engineering", University of Novi Sad, Technical Faculty "Mihajlo Pupin", Zrenjanin, 2002

S.6.0448 Project "Development of technologies and conceptual solutions to meet environmental targets within the metallurgical Serbia", financed 1991-1993 from the Ministry of Science and Technology, RS

Stanojevic, Dušan, Regional Reconstruction Program in the Field of Environmental Protection in South East Europe, "Protection of River Basin from contamination of heavy metal ions from electrolytic zinc factory in Sabac," Šabac, February 2001

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ELECTRONIC WASTE MANAGEMENT

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ABSTRACT

This paper defines the impact of e-waste on the environment, techniques of removing e-waste, computer recycling methods and attention is given to consumers information how to behave with electrical devices at the end-of-life. "Electronic waste" may be defined as discarded computers, office electronic equipment, entertainment device electronics, mobile phones, television sets, and refrigerators. This includes used electronics which are destined for reuse, resale, salvage, recycling, or disposal. Others are re-usables (working and repairable electronics) and secondary scrap (copper, steel, plastic, etc.) to be "commodities", and reserve the term "waste" for residue or material which is dumped by the buyer rather than recycled, including residue from reuse and recycling operations.

Key words: *e-waste, management, recycling.*

INTRODUCTION

One of the major global problems is the world's electronic waste. The specificity of electronic waste is its complexity and speed that electronic products become obsolete and replaced by new ones. In addition, e-waste is a valuable source of secondary raw materials and toxic if it is improperly treated. Rapid changes in technology, poor initial cost and even planned obsolescence of products have resulted in rapid growth of the problems in the world. Products such as TVs, mobile phones, computers and related computer equipment, cameras, printers etc. have become a major part of the waste and therefore the flow of electrical waste is identified as the one which have recorded the fastest growth in Europe today, making 4% of municipal waste. Leading continent in the annual production of this waste is North America with over 20 million tons, followed by the Europe and Asia with about 14 million tons and other continents that have about 5 million tons. The major manufacturers of electronic and electrical waste are classified into three groups: individuals and small businesses, large businesses, institutions and government agencies and manufacturers of original electronic equipment (OEMs). The rise of e-waste is now three times higher than the increase in municipal waste. The level of recycling in developing countries is growing, but doesn’t keep pace with the growth in waste production. In the last twenty years, the developed countries have established various control mechanisms for managing waste materials, where the priority is given to the strategy of preventing the waste creation. Therefore, prevention is preferred over recycling, which is better than incineration, while the landfill is at least desirable way. However, because of the existing waste collection system , almost 90% of electronic waste ends up in landfills or incineration plants. The impact of electronic waste on the environment resulting from its use, the design (amount of material and energy use) as well as the manner of its disposal at end of life.

ENVIRONMENTAL IMPACT OF ELECTRONIC WASTE

The processes of dismantling and disposing of electronic waste in the third world lead to a number of environmental impacts. Liquid and atmospheric releases end up in bodies of water, groundwater, soil, and air and therefore in land and sea animals – both domesticated and wild, in crops eaten by both animals and human, and in drinking water (Frazzoli, C. 2010). One study of environmental effects in Guiyu, China found the following:

1. Airborne dioxins – one type found at 100 times levels previously measured
2. Levels of carcinogens in duck ponds and rice paddies exceeded international standards for agricultural areas and cadmium, copper, nickel, and lead levels in rice paddies were above international standards
3. Heavy metals found in road dust – lead over 300 times that of a control village’s road dust and copper over 100 times (Sthiannopkao, S. 2012)

Table 1. Examples of e-waste components, processes used ant potential environmental hazard (Wath, et al., Dutt et al., & Chakrabarti et al., 2011)

E-Waste Component	Process Used	Potential Environmental Hazard
Cathode ray tubes (used in TVs, computer monitors, ATM, ..)	Breaking and removal of yoke, then dumping	Lead, barium and other heavy metalsleaching into the ground water and release of toxic phosphor
Printed circuit board (image behind table - a thin plate on which chips and other electronic components are placed)	De-soldering and removal of computer chips; open burning and acid baths to remove final metals after chips are removed.	Air emissions as well as discharge into rivers of glass dust, tin, lead, brominated dioxin, beryllium cadmium, and mercury
Chips and other gold plated components	Chemical stripping using nitric and hydrochloric acid and burning of chips	Hydrocarbons, heavy metals, brominated substances discharged directly into rivers acidifying fish and flora. Tin and lead contamination of surface and groundwater. Air emissions of brominated dioxins, heavy metals and hydrocarbons
Plastics from printers, keyboards, monitors, etc.	Shredding and low temp melting to be reused	Emissions of brominated dioxins, heavy metals and hydrocarbons
Computer wires	Open burning and stripping to remove copper	Hydrocarbon ashes released into air, water and soil.

RECYCLING

Today the electronic waste recycling business is in all areas of the developed world a large and rapidly consolidating business. People tend to forget that properly disposing or reusing electronics can help prevent health problems, create jobs, and reduce greenhouse-gas emissions (Fela, 2010). Part of this evolution has involved greater diversion of electronic waste from energy-intensive downcycling processes, where equipment is reverted to a raw material form. This recycling is done by sorting, dismantling, and recovery of valuable materials. This diversion is achieved through reuse and refurbishing. The environmental and social benefits of reuse include diminished demand for new products and virgin raw materials (with their own environmental issues); larger quantities of pure water and electricity for associated manufacturing; less packaging per unit; availability of technology to wider swaths of society due to greater affordability of products and diminished use of landfills. Audiovisual components, televisions, stereo equipment, mobile phones, other handheld devices, and computer components contain valuable elements and substances suitable for reclamation, including lead, copper, and gold. One of the major challenges is recycling the printed circuit boards from the electronic wastes. The circuit boards contain such precious metals as gold, silver, platinum, etc. and such base metals as copper, iron, aluminum, etc. One way e-waste is processed is by melting circuit boards, burning cable sheathing to recover copper wire and open-pit acid leaching for separating metals of value (Sthiannopkao S. 2012). Conventional method employed is mechanical shredding and separation but the recycling efficiency is low. Alternative methods such as cryogenic decomposition have been studied for printed circuit board recycling, and some other methods are still under investigation (Yuan et al., Zhang et al., McKenna et al., Korzeniewski, et al., Li et al. 2007). Recycling raw materials from end-of-life electronics is the most effective solution to the growing e-waste problem. Most electronic devices contain a variety of materials, including metals that can be recovered for future uses. By dismantling and providing reuse possibilities, intact natural resources are conserved and air and water pollution caused by hazardous disposal is avoided. Additionally, recycling reduces the amount of greenhouse gas emissions caused by the manufacturing of new products. Benefits of recycling are extended when responsible recycling methods are used.

COMPUTER RECYCLING METHODS

Consumer recycling

Consumer recycling options consists of sale, donating computers directly to organizations in need, sending devices directly back to their original manufacturers, or getting components to a convenient recycler or refurbisher.

Corporate recycling

Businesses seeking a cost-effective way to recycle large amounts of computer equipment responsibly face a more complicated process. Businesses also have the options of sale or contacting the Original Equipment Manufacturers (OEMs) and arranging recycling options. Some companies pick up unwanted equipment from businesses, wipe the data clean from the systems, and provide an estimate of the product’s remaining value. For unwanted items that still have value, these firms buy the excess IT hardware and sell refurbished products to those seeking more affordable options than buying new. Companies that specialize in data protection and green disposal processes dispose of both data and used equipment, while employing strict procedures to help improve the environment. Professional IT Asset Disposition (ITAD) firms specialize in corporate computer disposal and recycling services in compliance with local laws and regulations and also offer secure data elimination services that comply with Data remanence standards including National Institute of Standards and Technology. Corporations face risks both for incompletely destroyed data and for improperly disposed computers. In America, companies are liable for compliance with regulations even if the recycling process is outsourced under the Resource Conservation and Recovery Act. Companies can mitigate these risks by requiring waivers of liability, audit trails, certificates of data destruction, signed confidentiality agreements, and random audits of information security. The National Association of Information Destruction is an international trade association for data destruction providers (Kuhlenbeck, 2006).

Sale

Online auctions are an alternative for consumers willing to resell for cash less fees, in a complicated, self-managed, competitive environment (Perepelkin, 2008) where paid listings might not sell (Albanesius, 2008). Online classified ads can be similarly risky due to forgery scams and uncertainty (Bray, 2008).

Take back

When researching computer companies before a computer purchase, consumers can find out if they offer recycling services. Most major computer manufacturers offer some form of recycling. At the user's request they may mail in their old computers, or arrange for pickup from the manufacturer. Hewlett-Packard also offers free recycling, but only one of its "national" recycling programs is available nationally, rather than in one or two specific states. Hewlett-Packard also offers to pick up any computer product of any brand for a fee, and to offer a coupon against the purchase of future computers or components; it was the largest computer recycler in America in 2003, and it has recycled over 750,000,000 pounds (340,000,000 kg) of electronic waste globally (Morgan, 2006) since 1995

(Haffenreffer, 2003). It encourages the shared approach of collection points for consumers and recyclers to meet (Dean, 2003).

Exchange

Manufacturers often offer a free replacement service when purchasing a new PC. Dell Computers and Apple Inc. take back old products when one buys a new one. Both refurbish and resell their own computers with a one-year warranty (Bray, 2008). Many companies purchase and recycle all brands of working and broken laptops and notebook computers from individuals and corporations. Building a market for recycling of desktop computers has proven more difficult than exchange programs for laptops, smartphones and other smaller electronics (NNBW Staff, 2009). A basic business model is to provide a seller an instant online quote based on laptop characteristics, then to send a shipping label and prepaid box to the seller, to erase, reformat, and process the laptop, and to pay rapidly by cheque (Prashant, 2008). A majority of these companies are also generalized electronic waste recyclers as well; organizations that recycle computers exclusively include Cash For Laptops, a laptop refurbisher in Nevada that claims to be the first to buy laptops online, in 2001(NNBW Staff, 2009).

Scrapping/recycling

The rising price of precious metals — coupled with the high rate of unemployment during the Great Recession — has led to a larger number of amateur "for profit" electronics recyclers. Computer parts, for example, are stripped of their most valuable components and sold for scrap. Metals like copper, aluminum, lead, gold and palladium are recovered from computers, televisions and more.

Donations/nonprofits

With the constant rising costs due to inflation, many families or schools do not have the sufficient funds available for computers to be utilized along with education standards. Families also impacted by disaster suffer as well due to the financial impact of the situation they have incurred. Many nonprofit organizations can be found locally as well as around the web and give detailed descriptions as to what methods are used for dissemination and detailed instructions on how to donate. The impact can be seen locally and globally, affecting thousands of those in need.

PROCESSING TECHNIQUES

In many developed countries, electronic waste processing usually first involves dismantling the equipment into various parts (metal frames, power supplies, circuit boards, plastics), often by hand, but increasingly by automated shredding equipment. The advantages of this process are the human's ability to recognize and save working and repairable parts, including chips, transistors, ram, etc. The disadvantage is that the labor is cheapest in countries with the lowest health and safety standards. In an alternative bulk system a hopper conveys material for shredding into an unsophisticated mechanical separator, with screening and granulating machines to separate constituent metal and plastic fractions, which are sold to smelters or plastics recyclers. Such recycling machinery is enclosed and employs a dust collection system. Some of the emissions are caught by scrubbers and screens. Magnets, eddy currents, and trommel screens are employed to separate glass, plastic, and ferrous and nonferrous metals, which can then be further separated at a smelter. Leaded glass from CRTs is reused in car batteries, ammunition, and lead wheel weights (Royte, 2005) or sold to foundries as a fluxing agent in processing raw lead ore. Copper, gold, palladium, silver and tin are valuable metals sold to smelters for recycling. Hazardous smoke and gases are captured, contained and treated to mitigate environmental threat. These methods allow for safe reclamation of all valuable computer construction materials (Carroll, 2008). Hewlett-packard product recycling solutions manager Renee St. Denis describes its process as: "we move them through giant shredders about 30 feet tall and it shreds everything into pieces about the size of a quarter. Once your disk drive is shredded into pieces about this big, it's hard to get the data off" (Haffenreffer, 2003). An ideal electronic waste recycling plant combines dismantling for component recovery with increased cost-effective processing of bulk electronic waste. Reuse is an alternative option to recycling because it extends the lifespan of a device. Devices still need eventual recycling, but by allowing others to purchase used electronics, recycling can be postponed and value gained from device use.

DISPOSAL OF E-WASTE TO THE LANDFILLS

It represents the least desirable solution and it is a particular danger because there is no soil that is completely impermeable. This can lead to leaks, highlighting hazardous substances: mercury from the printed circuit board, pcb from the condenser and cadmium from specific plastics can leak into soil and groundwater. Significant amounts of lead can be dissolved from the glass CRT (cathode ray tube) with groundwater containing various acids and they are found in landfills. Another problem is the evaporation of mercury from electric waste. In addition, uncontrolled fires may increase the emission of highly toxic dioxins and furans due to the presence of a wide range of hazardous materials in landfills.

INFORMATION FOR USERS AND E-WASTE TREATMENT

Active participation of consumers and users is essential to the effectiveness of the collection system so they must be encouraged to participate in electronic waste collection schemes to facilitate the processing operations, recycling and recovery. Especially they need to have the following information about:

1. requirements for separate collection and sorting of WEEE - Waste of Electrical and Electronic Equipment systems (electrical waste is not disposed as unsorted municipal waste)
2. their role in contributing to reuse, recycling and other forms of recovery
3. WEEE potential effects on the environment and human health
4. meaning of symbols according to the annex, which manufacturers are obliged to print on the packaging or instructions for use, or guarantees

New symbol for marking electronic waste consists of a crossed-out rubbish bin. It must be clear, legible and indelible. Sign is prescribed by the European Directive and it alert the user when the product becomes waste, it may not be rejected as municipal waste. From this year, the producers of electrical and electronic products in the EU, as well as all those who want to export to the EU area must label their products that sign. In special cases, either because of the size of the product or its features, the sign must be printed on the packaging, user guide and on the warranty.

Figure 1. WEEE symbol

In order to facilitate the reuse and proper environmental disposal of electronic waste including maintenance, upgrade and recycle, EU member states should ensure that each manufacturer provide the necessary information on re-use and treatment for each new type of electrical device which is placed on the market (within one years after it is launched a new product on the market). This information will help to identify the various components and materials of electrical devices and the location of hazardous materials in it. Any manufacturer of electronic and electrical appliances that are placed on the market after 13.8.2005. must be clearly marked on the appliance.

CONCLUSIONS

Current production and consumption of the world cause the creation of an increasing amount of waste, which slowly destroys the conditions for normal life. Whether it is a non-hazardous and hazardous waste, inadequate waste management is one of the biggest problems of modern society and a permanent threat to human health and the environment. There is a long list of these products and the largest portion goes to the landfills. In contact with other waste in a landfill, hazardous waste dissolves, reacts and goes to ground water, which pollutes the sole source of drinking water and prevents normal life. The goals of long-term policy of each company must be aligned with the goals of environmental protection. Managing electronic waste is one of the most important things that companies need to address. Most preferred is to understand that prevention is better than pollution of e-waste, but if it comes to it, the best solution would be recycling and the most dangerous is to throw e-waste on landfills. If we realize at the time that technology has become our present and future, and that we must act to the electronic waste properly, we will be able to preserve our environment in a proper manner.

REFERENCES

Frazzoli, C. (2010), Diagnostic health risk assessment of electronic waste on the general population in developing countries scenarios. *Environmental Impact Assessment Review* , 388-399

Sthiannopkao, S. (2012), Handling e-waste in developed and developing countries: Inititatives, practices and consequences. *Science of the Total Environment*

Wath, S. B., Dutt, P. S., & Chakrabarti, T. (2011), E-Waste scenario in India, its management and implications. *Environmental Monitoring and Assessment* , 172, 249-262

Fela, J. (2010), Developing countries face e-waste crisis. *Frontiers in Ecology and the Environment 8* (N0.3): 117

Sthiannopkao S, Wong MH. (2012), Handling e-waste in developed and developing countries: Initiatives, practices, and consequences. *Sci Total Environ*

Yuan, C., Zhang, H. C., McKenna, G., Korzeniewski, C., and Li, J. (2007), Experimental Studies on Cryogenic Recycling of Printed Circuit Board, *International Journal of Advanced Manufacturing Technology*, Vol. 34, pp. 657–666

Kuhlenbeck, P. (2006), Law holds businesses responsible for disposal of computers. *Austin Business Journal*, Retrieved 2009-03-17

Perepelkin, P. (2008), Brisk sales of Apple's new 3G model have consumers scrambling to profit from their 'old' phones at Cashforiphones.com , *Computer Apple Digest*. pp. 16–18. Retrieved 2009-03-05.

Albanesius, C. (2008), Gazelle Will Give You Cash for Your Gadgets. *News and Analysis (PC Magazine)*, Retrieved 2009-03-05

Bray, H. (2008), Scrounge up cash with used gadgets. *Boston Globe. Globe Newspaper Company*. Retrieved 2009-03-05

Morgan, R. (2006), Tips and Tricks for Recycling Old Computers. *SmartBiz*. Retrieved 2009-03-17

Haffenreffer, D. (2003), Recycling, the Hewlett-Packard Way. *Financial Times (CNN).* Retrieved 2009-03-17

Dean, K. (2003), Bill Aims to Cut Computer Clutter. *Wired Magazine*. Retrieved 2009-03-17

NNBW Staff (2009), Cash-strapped consumers turn to laptops recycler. *Northern Nevada Business Weekly 7* (34). Retrieved 2009-04-13.

Prashant, N. (2008), Cash For Laptops Offers 'Green' Solution for Broken or Outdated Computers. *Green Technology (Norwalk, Connecticut: Technology Marketing Corporation).* Retrieved 2009-03-17.

Royte, E. (2005), E-gad! Americans discard more than 100 million computers, cellphones and other electronic devices each year. As "e-waste" piles up, so does concern about this growing threat to the environment. *Smithsonian Magazine (Smithsonian Institution).* Retrieved 2009-03-17

Carroll (2008), High-Tech Trash. *National Geographic Magazine Online.*

Haffenreffer, D. (2003), Recycling, the Hewlett-Packard Way. *Financial Times (CNN).* Retrieved 2009-03-17.

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ADVENTAGES FROM RINSING PLANT PROTECTION PRODUCTS CONTAINERS

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ABSTRACT

After use, empty pesticide containers retain some active ingredient and their disposal is a problem which can be approached from two perspectives. In the one hand there is a problem of generating a significant volume of this packaging waste, and in the other hand it is considered hazardous waste if it is not rinsed properly and further waste management is more complicated. Proper rinsing of container immediately after usage of pesticides is the most important step in the pesticide container management hierarchy. The most simple and mostly used is triple rinsing method that removes more than 99.99% of contaminating residue. Even after emptying the agrochemical into the spray tank and allowing it to drip, the container still contains on the average 2% of agrochemical. By applying the recommended rinsing methods, the quantity of the agrochemical utilised is increased by 2% that shows economical benefits of container rinsing. The main implementation problems with this important measure are lack of motivation with smaller consumers, in economical sense, and poor consumer knowledge of environmental importance of container rinsing.

***Key words**: plant protection products, pesticide containers, rinsing effectiveness, triple rinsing.*

INTRODUCTION

Along with plant protection products (PPP), on the market appears packaging that ultimately becomes waste and is often classified as hazardous waste. Only triple rinsed PPP containers can be classified as non-hazardous waste *(EPA, 2012)*. The disposal of packaging which contained pesticides is an important and difficult problem. In the past, little attention was given to the collection of this kind of waste, but today different sectors care about that in order to avoid any pollution of the environment. Rinse containers after use of plant protection products is a simple procedure and it is the basis for all further activities. The aim is to obtain a clean packaging, harmless for the environment and human health, and on the other hand economic impact is undeniable *(Huyghebaert et al., 2003).*

Packaging plays a central role in the safe and effective delivery of crop protection products to the intended target whilst at the same time protecting the public, supply chain and users from the chemicals involved. Packaging also needs to be managed to meet other environmental goals, which have become increasingly important in the context of prevailing societal concerns about environmental sustainability *(ECPA, 2007).*

European Crop Protection Association ECPA estimates that there are around 34 000 tonnes of crop protection containers placed on the European market each year. France, Italy, Spain, Germany, UK, Portugal, Poland and Turkey account for the majority of packaging placed on the market. At least 80% of crop protection containers in Europe are plastic with the majority being High Density Polyethylene (HDPE) followed by polyethylene terephthalate (PET), the remainder being mostly film and paper based *(ECPA, 2007)*. The quantity of dangerous substances that remains in the container after rinsing, either as residue after rinsing or as product migrated into the plastic, determines the classification of the empty container based on the process and limits described in the EWC *(Briassoulis et al., 2014).*

Dangerous wastes are classified according to their origin and their composition. A crop protection container, will be considered as dangerous if it contains “biocides and agrochemical products (pesticides, etc.)” in some quantities stated in %. The limits of residue container range from 1000 to 250 000 ppm depending on the dangerousness of the product in the container (very toxic, corrosive, irritating or harmful) *(Huyghebaert et al., 2003)*. Table 1 shows the limits according to the dangerousness of the product contained in the container.

Table 1: Limits in residue according to the classification of pesticides (Huyghebaert et al, 2003)

Characteristics of the product	**Classification of pesticides**	**Maximum quantity of product in mg/kg (ppm)**
Very toxic product	A	1000
Toxic product	A	30 000
Corrosive substance	A	10 000 – 50 000
Harmful product	B	250 000
Irritating product	B	100 000 – 200 000

An analysis of data from 180 rinsed primary crop protection product packs revealed that the average rinsing effectiveness achieved using either manual triple rinsing or integrated pressure rinsing was 0.008%. These findings are supported by other publications that show that crop protection product packs can be rinsed clean below 0.01%. These results clearly indicate that individual containers, even those that contained products with the most critical classification of very toxic, can be classified as nonhazardous after proper rinsing *(ECPA, 2007)*.

RINSING METHODS

The majority of one-way containers available on the market are appropriate for rinsing with water. Three standard rinsing options are triple rinsing, pressure rinsing and integrated pressure rinsing.

Triple rinsing is the method to use in the absence of *ad hoc* mechanical rinsing equipment. It is likely to be the most practical option in developing economies. It can be used to clean all sizes of containers but the technique is slightly different for small containers that can be shaken by hand, and large containers that are too big to shake *(FAO/WHO, 2008)*.

Pressure rinsing equipment uses water under pressure (typically three bar) in the form of a static or rotating spray jet and valve. The jets of water hit the internal surfaces of the container removing and dissolving the pesticide residues. Some pressure rinsing equipment includes a sharp device that penetrates the container walls for rinsing purposes, thereby offering the additional advantage of making the container unusable for storage. These devices should be used in accordance with the manufacturers’ instructions to avoid injury to the operator *(FAO/WHO, 2008)*.

Integrated rinsing technology incorporates the rinsing process directly into large scale tractor mounted spraying equipment. Wherever possible, integrated rinsing equipment should be used. Integrated rinsing is the most efficient method of rinsing containers and provides a high level of operator safety. It is also quicker than both triple rinsing and pressure rinsing. Integrated rinsing devices rinse by using water under pressure (of typically three to five bar). A static nozzle with a valve is normally built into the induction hopper of the sprayer. The water pressure cleans the container until no residues are visible (typically requiring up to 30 seconds and 15 liters of water). The rinsate is then automatically added to the spray liquid *(FAO/WHO, 2008)*.

Triple rinsing and pressure rinsing, when undertaken to the standards are able to clean containers so that the containers should be classified as nonhazardous waste *(FAO/WHO, 2008)*. Table 2 below shows the principal differences between triple rinsing and pressure rinsing.

Table 2: Comparison of triple and pressure rinsing (FAO/WHO, 2008)

Features	**Pressure Rinsing**	**Triple Rinsing**
Number of Steps	8	17
Time Spent per Container	1 – 2 min	4 – 9 min
Container Types Rinsed	All	All
Special Equipment Needed Rinse	Nozzle/high pressure water	None

Cleaning a container by triple rinsing involves twice as many steps and takes about four times as long as pressure rinsing, but it does not need any special equipment. Triple rinsing is likely to be the preferred technique where pesticide usage is low and there is limited availability of special equipment. On the other hand, in locations where there is intensive agriculture pressure rinsing is likely to be the preferred option *(FAO/WHO, 2008).*

ADVENTAGES FROM RINSIG

Rinsing containers after use of PPP has many advantages. Even after emptying the agrochemical into the spray tank and allowing it to drip, the container still contains on the average 2% of agrochemical. By rinsing and adding the rinsate to the tank, the quantity of the agrochemical utilised is increased by 2% *(FAO/WHO, 2008),* in other words, rinsing saves money because none of the pesticide is wasted.

If the container is not declassified as nonhazardous, its handling, transportation and disposal have to be performed under the hazardous waste legislation provisions. Not only the cost and the logistics of the operation is increased but also the inability to recover the packaging material through recycling is environmentally and economically unjustified *(Briassoulis et al., 2014).*

On the opposite, new options for the clean containers valorisation arise as the residual agrochemical contamination will be sufficiently low and the containers can be classified as nonhazardous waste. Environmental friendly and easy to control disposal options, mainly recycling and secondly energy recovery, apart from lowering the disposal cost, significant potentials for economic benefits and new job opportunities arise from this way of disposal, especially in the case of recycling *(Briassoulis et al., 2014).* The amount of plastic recovered from empty crop protection product containers in 2012 would have filled 238 Olympicsize swimming pools. More than 70 000 tonnes of plastic were recovered to be recycled into useful products, such as drainage pipes, fence posts and parking cones. This amount of recycling also spared energy use amounting to 130 million liters of gasoline or 24 000 fewer cars on the road per year. About 30 000 to 70 000 tonnes of empty crop protection product containers were collected each year between 2005 and 2012, accounting for 15 to 32 percent of the total amount of containers shipped to market globally, with collection rates increasing every year and nearly 400 000 tonnes of containers were recovered *(Crop Life, 2014).*

A second category of advantages from cleaning the containers is related to environmental and health issues. When the agrochemical container is rinsed the risks of contamination of soil and water are minimised. Furthermore, if the rinsing is done immediately after emptying it reduces the chances of exposure to users, the wider public and animals. Economy in natural recourses and energy saving is also achieved when the containers are directed to recycling or to industry as alternative fuel. In parallel reduction of waste is achieved *(Briassoulis et al., 2014).*

Triple rinsing method stands out as the simplest and most widely used method and removes more than 99.99% of contaminating residue *(Crop Life, 2004).* A large scale experimental research held in 1993 by member companies of ECPA proved that primary crop protection product packs could be rinsed to leave behind less than 0.01% w/w of the original formulation in the container. More specifically 180 rinsed agrochemical containers were either manually tripled rinsed or integrated pressure rinsed and then analysed. The results confirmed the effectiveness of the methods as they show that the remaining residues were less than 0.008% w/w of the original formulation *(Briassoulis et al., 2014).*

Table 3 shows Triple rinse data results from the Pesticide Registration and Control Division (PRCD) of the Department of Agriculture, Food and the Marine (DAFM).

The container sizes varied from 1L, 2L and 5L. The pesticides included insecticides, fungicides and herbicides. The active ingredient concentrations and the type of formulations varied to try to get a broad coverage of the range of pesticides available for use. The results for the four rinses are given as the % active substance remaining in the analysed rinsate *(EPA, 2012)*.

Table 3: Analytical Results from triple rinse PPP containers carried out by the PRCD, DAFM (EPA, 2012)

Triple rinse data		**Results (% of active substance in the rinsate)**		
Active Ingredient	**Pesticide Type**	**Rins 1**	**Rins 2**	**Rins 3**
Prothioconazole	Fungicide	0.0026	0.00004	0.00003
Deltamethrin	Insecticide	0.0121	0.0003	0.0002
Cypermethrin	Insecticide	0.038	0.0002	0.0001
Chlorothalonil	Fungicide	0.0079	0.009	0.0018
Epoxiconazole	Fungicide	0.0772	0.0004	0.0003
Chlorpyrifos	Insecticide	0.104	0.0074	0.0011
Tebuconazole	Fungicide	0.0141	0.0005	0.0005
Cypermethrin	Insecticide	0.03	0.004	0.003
Dimethoate	Insecticide	0.198	0.004	0.004
Azoxytrobin	Fungicide	0.012	0.001	0.0001
Propiconazole	Fungicide	0.26	0.004	0.002
Napropamide	Herbicide	0.017	0.004	0.0005
Clopyralid	Herbicide	0.025	0.0005	0.0004
Propyzamide	Herbicide	N/A*	0.003	0.0004
Quinoxyfen	Fungicide	N/A*	0.03	0.003
Triclopyr	Herbicide	0.07	0.001	0.0003
Chlorpyrifos	Insecticide	0.008	0.0003	0.00001
Cypermethrin	Insecticide	0.016	0.001	0.0005
Fenpropimorph	Fungicide	0.14	0.003	0.002
* sample formed an emulsion and could not be analysed				

Cleaning should be undertaken immediately following emptying the container such that all of the product may be used for its intended purpose and any residual contamination is not allowed to adhere to the internal surfaces of the container. Pesticide residues that are allowed to harden and congeal on the surfaces of the container or its cap are much more difficult to remove. They often require physical abrasion and much more rinsing liquid. Rinsing immediately when the pesticides are still liquid is quick and easy. *(FAO/WHO, 2008)*.

DISCUSSION

In spite of its definite economic impact, the main objective of the rinsing of containers is not to use the last drop of product. The aim is to obtain a “clean” packaging, harmless for the environment and human health *(Huyghebaert et al., 2003)*. Despite of that, the main motivator for consumers to do needed measures after using pesticides is economical profitability. Savings that are made by rinsing used pesticide containers is indisputable. As early mentioned, when pesticide container is used and drained, it still has about 2% of original volume of pesticide, and rinsing makes significant savings.

Economical benefit is motivating only large pesticide consumers, that 2% of used agricultural product represents a significant quantity and makes large savings, what is not the case with small consumers.

Consumption of pesticides in urban areas is considerably lower than in locations where there is intensive agriculture, and is mostly used for maintenance of city green. Table 4 shows annually savings for three cities by rinsing containers after using an agrochemical for maintenance of city green.

Table 4: Comparison of PPP costs and annually savings by rinsing for different areas of urban green

City surface (km^2)	City green (km^2)	PPP costs per year (€)	Savings by rinsing per year (€)
1326	0.7	1700	34
3222	30	16500	330
702	33	18000	360

The city that is 1326 km^2 big *(www.zrenjanin.rs)* and has 0.7 km^2 in city green, spends about 1700 € per year for pesticides that are used for plant protection *(JKP "Čistoća i zelenilo" Zrenjanin, 2014)*. On the bases of known data that there is 2% of pesticides left in the container after usage, it is recognized that by rinsing containers there would be a 34 € savings per year. Much larger city that is about 3222 km^2 big *(www.beograd.rs)* and has 30 km^2 in city green, spends approximately 16500 € per year for pesticides *(JKP "Zelenilo-Beograd", 2014)*. By properly rinsing there would be a 330 € savings per year. The city that is about 702 km^2 big *(www.novisad.rs)* and has 33 km^2 in city green, spends about 18000 € per year *(JKP "Gradsko zelenilo" Novi Sad, 2014)* and saving is 360 €. It's clear that it is not enough to motivate consumers to implement the basic rule in pesticide container waste management.

CONCLUSIONS

Proper way of handling packaging waste, before and after the usage of the product, is crucial to reducing risks while using pesticides. As the most important step in this process is the rinsing of empty containers right after usage, because all of the empty pesticide containers are considered hazardous unless they are properly rinsed three times and than are treated as nonhazardous. Advantage of environmental friendly and easy to control disposal options is nonhazardous classification of PPP packaging waste. That means lower disposal cost and significant potentials for economic benefits and new job opportunities, but the most important are advantages related to environmental and health issues.

Although, there are many benefits of rinsing empty containers, many consumers are not motivated enough to implement the recommendations of handling PPP packaging waste. That is mostly the case whit small volume consumers and in urban areas where there is less agriculture, and where the economical saving by rinsing, as shown in example of a different areas of urban green, is not significant. One more of the reasons that the consumers are not handling packaging waste in accordance with recommendations is that they are not well informed and it is necessary to educate them about the benefits of rinsing as the main step in management of empty pesticide containers.

REFERENCES

Briassoulis, D., Hiskakis, M., Karasali, H., Briassoulis, C., 2014. *Design of a European agrochemical plastic packaging wastemanagement scheme - Pilot implementation in Greece*. Resources, Conservation and Recycling, 01/2014, 87:72–88.

CropLife International, 2014. *Recycling Benefits from Container Management.*

CropLife International, 2004. *Container Management: Safe and effective disposal of emptycrop protection product containers*. Brussels, Belgium: CropLife International.

EPA (Environmental Protection Agency), 2012. *Good practice guide for empty pesticide containers.*

EPA, 2012. *Technical background paper: Empty pesticide containers (PPP).*

ECPA (European Crop Protection Association), 2007. *Crop Protection Plastic Containers. The case for a nonhazardous waste classification*.

FAO/WHO, 2008. *Guidelines on Management Options for Empty Pesticide Containers*. In: International Code of Conduct on the Distribution and Use of Pesticides, Food and Agriculture Organization of the United Nations. Rome: World Health Organization.

Huyghebaert, B., Mostade, O., Sawa, J., 2003. *Management of empty pesticide containers.* Polish Academy of Sciences Branch in Lublin, Commission of Motorization and Power Industry in Agriculture.

JKP “Čistoća i zelenilo” Zrenjanin, 2014. *Procurement.*
JKP “Zelenilo-Beograd”, 2014. *Procurement.*
JKP “Gradsko zelenilo” Novi Sad, 2014. *Procurement.*
Official presentation of City of Zrenjanin, www.zrenjanin.rs (2014/8/27)
Official presentation of City of Belgrade www.beograd.rs (2014/8/27)
Official website of city of Novi Sad, www.novisad.rs (2014/8/27)

WATER QUALITY IN URBAN AREAS (GROUND WATER, DRINKING WATER, WASTE WATER AND FACILITIES)

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BIOAVAILABILITY OF HEAVY METALS IN SOIL AMENDED WITH WASTEWATER SLUDGE

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ABSTRACT

The wastewater sludge application to agricultural land could affect potential availability of heavy metals. The solubility and mobility of metals throughout sludge application is controlled by organic matter and oxides that can prevent excessive heavy metals mobilisation. A pot trial was carried out to illustrate the bioavailability of Cd, Cu, Ni, Pb and Zn on sunflowers grown on soils (sandy loam Kovárvány Brown Forest and clay loam chernozem meadow) amended with urban anaerobically stabilized municipal wastewater sludge (MWS). Sunflower plants were grown in the soils following amendment with the sludge. The addition of sludge significantly increased the average dry plant biomass. The heavy metals uptake by sunflowers generally followed the differences in metal inputs, but quantitative differences were found between heavy metals, Bioaccumulation factor and amount of metal extracted (mg/kg plant) were determined. The bioavailability and phytotoxicity of investigated heavy metals was influenced by soil properties and organic matter content and metal content in the wastewater sludge as well. The impact of soil type on the metal concentration in plant was greater that the effect of the dose, Furthermore, with repeated sludge applications as soil conditioner, these heavy metals may accumulate in the soil to phytotoxic concentrations for crops, although at certain concentrations the metals may be deficient for crop growth.

Key words: *bioavailability, bioaccumulation, heavy metals, soil types, sunflower.*

INTRODUCTION

Soils are the major sink for heavy metals released into the environment due to anthropogenic activities and unlike organic contaminants which are oxidized to carbon dioxide by microbial action. Most metals do not undergo microbial or chemical degradation, and their total concentration in soils persists for a long time after their introduction. During the past 40 years a large amount of researches have been done on heavy metals-soil interaction and plant uptake. Today, the most serious problem in global agriculture is the rapid degradation of agricultural soils through erosion and nutrient depletion through incorrect agricultural practices and the gradual decrease in the organic matter content of cultivated soils. The addition of MWS could maintain the organic status of soil and decrease the danger of runoff and erosion. Wastewater sludge contains a mixture of organic and inorganic solids, suspended and dissolved in water. Wastewater sludge can be a valuable resource if used as an organic fertilizer and soil conditioner to facilitate nutrient transport, increase water retention and improve soil tilth. The major benefits of MWS application are to increase the major plant nutrients; provision of some essential micronutrients and improve the soil physical properties, i.e., soil structure, increased water holding capacity and improved soil water transmission characteristics.

Plants take up heavy metals from soil through different reactions such as: absorption, ionic exchange, redox reactions, precipitation – dissolution, etc. It can be said that the solubility of trace elements depends on minerals in soil, soil organic matter, pH, redox potential, soil temperature and humidity.
Recent literature is harnessed to critically review the possible sources, chemistry, potential biohazards and best available remedial strategies for a number of heavy metals such as cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), chromium (Cr), arsenic (As) and mercury (Hg) commonly

found in contaminated soils. Remediation of heavy metal contaminated soils is necessary to reduce the associated risks, make the land resource available for agricultural production, enhance food security and scale down land tenure problems arising from changes in the land use pattern (Wuana and Okieimen, 2011). Distributions of total and bioavailable amounts of heavy metals were studied in brown forest soil profiles developed on different types of bedrock. Among the studied metals the bioavailability sequence was observed as: Pb (25% of total Pb) > Cu (20% of total Cu) > Ni (10% of total Ni) > Zn (2.5% of total Zn). Several factors influence the bioavailability of heavy metals to crop plants e.g., soil pH, cation exchange capacity and metal speciation. Soil pH value has been identified as the most important soil factor controlling the availability of heavy metals in wastewater sludge treated soil (Smith, 1994). However, in some cases, raising soil pH to 6.0 was not sufficient to decrease Cd concentration in grain. Raising the soil pH above this value would not be considered economically viable in many areas (Oliver et al., 1996). Therefore, increasing the soil pH reduces the heavy metals uptake up to a certain pH level, after which further increase in pH levels would not cause significant decrease in metal uptake (Smith, 1994). The binding of heavy metals in soil by native and sludge organic matter and the changes in metal speciation that occur over time, particularly once sludge application has ceased, are intimately linked. These are critical factors in assessing the potential long-term environmental effects of spreading sewage sludge on land (Smith, 1994). Increasing the complexation capacity of soil and the formation of stable organometallic complexes by applying sludge organic matter reduces the mobility of heavy metals in soil and thus lowers their availability to plants (Alloway, 1995). The decreasing stability of organometallic complexes in sludge applied soil at pH 5.6 was Cu > Cd > Zn = Pb indicating the stronger binding of Cu with organic matter compared with Cd or Zn (Smith, 1994). The uptake of sludge-borne metals into crop plant parts plays a major role in the unrestricted use of sludge on agricultural land. Concentrations of toxic metals (e.g., Cd and Pb) need to be monitored in the edible parts of crops. Furthermore, the possibility of phytotoxicity of the heavy metals (e.g., Cd, Zn, Cu, etc.) to crops might reduce yield and growth of crops if taken up in excess. Toxic effect of heavy metals could compromise the beneficial use of MWS. It is therefore critical to establish the safe application rate of MWS in different environmental conditions. Furthermore, with repeated sludge applications as soil conditioner, these heavy metals may accumulate in the soil to phytotoxic levels for plant crops, although at certain concentrations these metals may be deficient for plant growth and crop production.

The long-term benefits of application of MWS to agricultural soil are frequently limited by potentially toxic elements. The behaviour of MWS applied to agricultural land has not been extensively researched under different climate or agroecosystem conditions. The quantification of the risk associated with the use of MWS in agricultural practices will necessitate a long-term study under several field conditions. The objective of the present research work is to understand the behavioural effects of heavy metals from using the MWS on dry biomass production, their bioavailability and bioaccumulation when the transplant sunflower seedlings grown in two different soil types amended with MWS of high Cd, Cu, Ni, Pb and Zn.

MATERIALS AND METHODS

A greenhouse pot experiment was conducted to determine the bioavailability, bioaccumulation and the impacts of different application rates (0, 30 45 and 60%, w/w) of urban anaerobically stabilized MWS (obtained from Hódmezovásárhely’s sewage water purification plant, Hungary) of high Cd, Cu, Ni, Pb and Zn content on the sunflower (*Helianthus annuus* L.) transplants grown in 3 kg plastic pot of two different Hungarian soil types (sandy loam Kovárvány Brown Forest and clay loam chernozem meadow shown in Table 1) for 21, 65 and 105 days under natural day/night duration and at average temperatures of 27 ± 3°C and 18 ± 3°C, day and night regime, respectively. Table 1 illustrates some physico-chemical properties of the used soils and MWS sample. The soil samples were collected from the top 20 cm layer from arable plots after removing the top 2 cm. The soil sample was air dried and sieved to pass the < 2 mm sieve before use in the experiment and chemical analysis. Distilled water was added to each soil mixture to bring it to 60% of water holding capacity. A soil without addition of MWS was incubated as the control. Soil samples were mixed with MWS and homogenized. The

MWS-soil mixtures of different application rates were distributed in 3 kg/pots. Five sunflower seeds were planted in each pot. Upon emergence, plants were thinned to three per pot.

Table 1: Summary of some physicochemical properties of investigated soils and used municipal wastewater sludge (MWS)

Parameters	Soil samples		MWS
	Soil 1 (Kovárvány Brown Forest)	Soil 2 (Meadow Chernozem)	Hódmezővásárhely
Origin	Nyíregyháza	Szeged	Hódmezővásárhely
Topsoil profile	Sandy loam	Clay loam	
$pH_{(KCl)}$	5.78	6.20	7.8
Humus/Organic content (%)	2.54	3.55	20.4
Total N, mg/kg	8.411	334.7	43311
NO_3-N (mg/kg)	2.30	3.90	ND
NH_4-N (mg/kg)	5.60	4.50	ND
Ca (mg/kg)	893	1136	26099
Mg (mg/kg)	214	257	7860
Na (mg/kg)	64	53	1441
P_2O_5 (mg/kg)	318	378	9104
K_2O (mg/kg)	412	428	1908
Cd (mg/kg)	1.70	1.02	4.168
Cu (mg/kg)	1.40	2.4	182.3
Ni (mg/kg)	0.054	0.037	14.02
Pb (mg/kg)	1.30	0.96	540.7
Zn (mg/kg)	1.70	1.10	1068
Mn (mg/kg)	55	61	351.2
Fe (mg/kg)	945	1094	9610

At harvest, roots and shoots were collected separately, washed with water to remove any attached soil particles, rinsed with deionized water, blotted between paper towels, weighed (fresh weight), dried at 70°C for at least 24 h till constant weight (dry weight), fine ground to pass through a 1 mm sieve, and used for analyses of metal contents. The experiment was done in three replicates. Plant Cd, Cu, Ni, Pb and Zn concentrations were determined on homogenised samples of each plant part in each pot by digestion. Plant samples were digested in concentrated HNO_3 and analysed for Cd, Cu, Ni, Pb and Zn by flame atomic absorption spectrophotometry (FAAS), Soil samples were digested using aqua regia (75% conc. HCl and 25% conc. HNO_3) microwave digestion with digestion time 30 min and then centrifuged and analysed using FAAS. The available metal contents were determined by extraction of the soils with 0.005 M diethylen-triamine pent acetic acid (DTPA) at pH = 7.3, where 20 ml of DTPA solution were added to the 10 g of soil sample placed in polypropylene bottles. The bottles were shaken on a rotating shaker for 2 h and then were centrifuged (Lindsay and Norvell, 1978). The total concentrations and Cd, Cu, Pb, and Zn availability in the supernatant liquid were measured with a FAAS. Translocation factor (TF) was described as ratio of heavy metals in plant shoot to that in plant root given in equation 1. Bioaccumulation coefficient (BAC) was calculated as ratio of heavy metal in shoots to that in soil given in equation 2. Bioconcentration factor (BCF) was calculated as metal concentration ratio of plant roots to soil given in equation 3 and TnF is the Transfer coefficient of metals from soil to plant (4).

$$TF = MC_{shoot}/MC_{root} \quad (1)$$

$$BAC = MC_{shoot}/MC_{soil} \quad (2)$$

$$BCF = MC_{root}/MC_{soil} \quad (3)$$

$$TnF = MC_{plant}/MC_{soil} \quad (4)$$

Where, MC_{shoot}, MC_{root}, MC_{soil} and MC_{plant} are metals concentration in the shoot (mg/kg), root of plant (mg/kg), in soil (mg/kg) and in plant, respectively. TF > 1 represent that translocation of metals effectively was made to the shoot from root (Fayiga and Ma, 2006). BCF was categorized further as hyperaccumulators, accumulator and excluder to those samples which accumulated metals > 1 mg/kg, and < 1, respectively (Cluis, 2004). Soil organic carbon (OC) was determined by reduction of potassium dichromate ($K_2Cr_2O_7$) by OC and subsequent determination of the unreduced dichromate by oxidation-reduction titration with 0.5 M ferrous ammonium sulfate according to Walkley and Black (1934) method. The amount of oxidized OC is multiplied by 1.334 to give the final amount of soil organic matter. The results were statistically analysed carried out to determine significant differences between the measured parameters.

RESULTS AND DISCUSSION

The addition of MWS markedly increased the average fresh and dry biomass of the sunflower plants in the both soils that had lower yields without MWS amendment. The addition of MWS significantly increased the DTPA extractable Cd, Cu, Ni, Pb and Zn concentration compared to control due to higher metal contents. One aspect which should be taken into account is that the addition of MWS not only results in an increase in the total concentrations of metals, but also in the quantity of organic matter, which may have a direct effect on the heavy metals solubility and bioavailability. A number of authors have agreed that the presence of organic matter increases the DTPA-extractability of the metals. It is probable that the organic matter existing in the MWS was the main reason why higher dosages of sludge were accompanied by a greater DTPA-extractability of practically all the metals studied (Ortiz and Alcaniz, 2006). The increase in Zn availability could be explained by the fact that this element in organic substrates is associated with the more soluble fractions of organic matter, such as non humic fractions of MSW compost. Also Bell et al. (1991) found that DTPA-extractable metal content in fertilizer treated soil was higher than values in control treatment, which might be due to the presence of impurities usually found in fertilizer samples.

The experimental observations showed that there are variations in shoot and root dry weight patterns of the sunflower plants grown in different soil systems as shown in Figures 1a and 1b, respectively. The results indicated that the shoot and root dry weights of sunflower plants grown in sandy loam Kovárvány brown forest originated from Nyíregyháza, Hungary were lower than those grown in clay loam chernozem meadow originated from Szeged, Hungary. The highest weights were obtained in both soil types when amended with 45% application rate of MWS as compared to the plants grown in control soils as well as by increasing the time of cultivation.

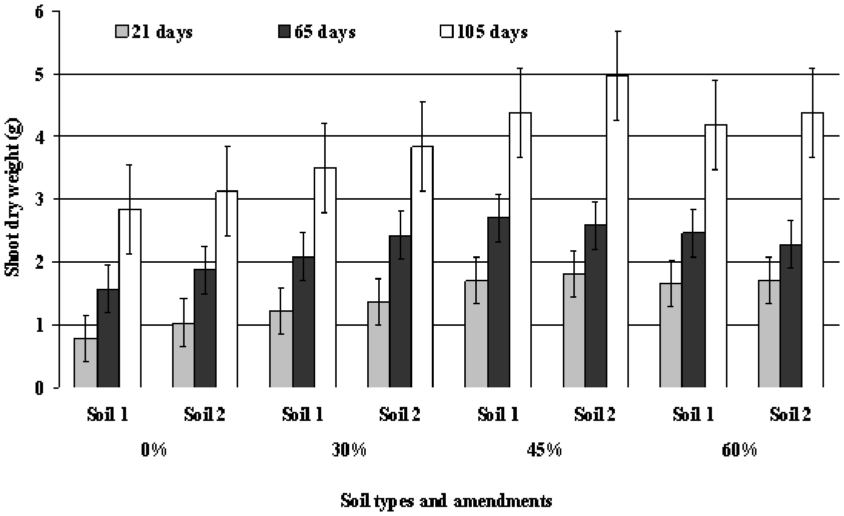

Figure 1a. Shoot dry weights pattern of sunflowers grown in different soil systems

Figure 2 indicates the increases in soil organic matter content of both soil types by increasing the application rates of MWS. Clay loam chernozem meadow (Soil 2) had higher SOM content than the sandy loam Kovárvány brown forest (Soil 1) has. Also, our results demonstrated that the lower in pH of soil 1 system is more favourable to increase the bioavailability of investigated heavy metals from

MWS. Bioavailability of Cd, Cu, Ni, Pb and Zn was greater in the soil 1 systems than in the soil 2 systems, which can be attributed to the high content of soil organic matter in the soil 2 system which may form organometallic complexes and impairs its uptake by the plants. The concentration of metals in the plants increased with the increasing the MWS applied dose. The effect of the soil type on the metal concentration in plants was greater that the effect of the dose.

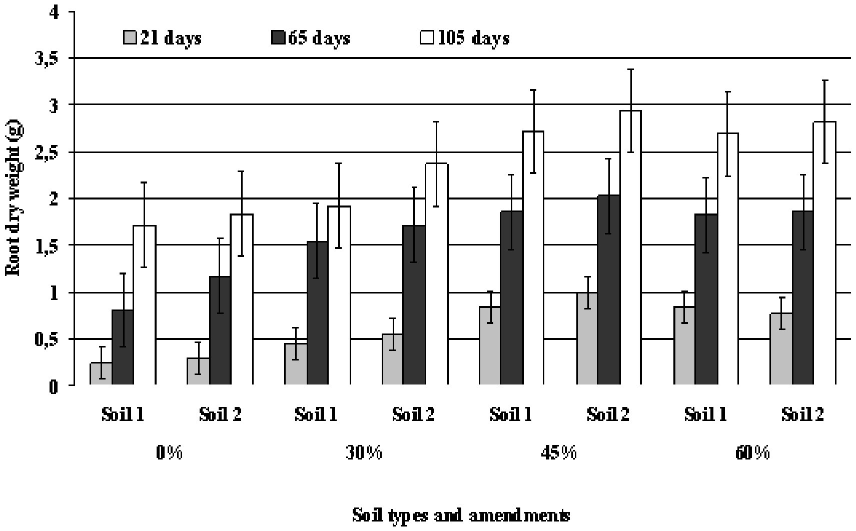

Figure 1b. Shoot dry weights pattern of sunflowers grown in different soil systems

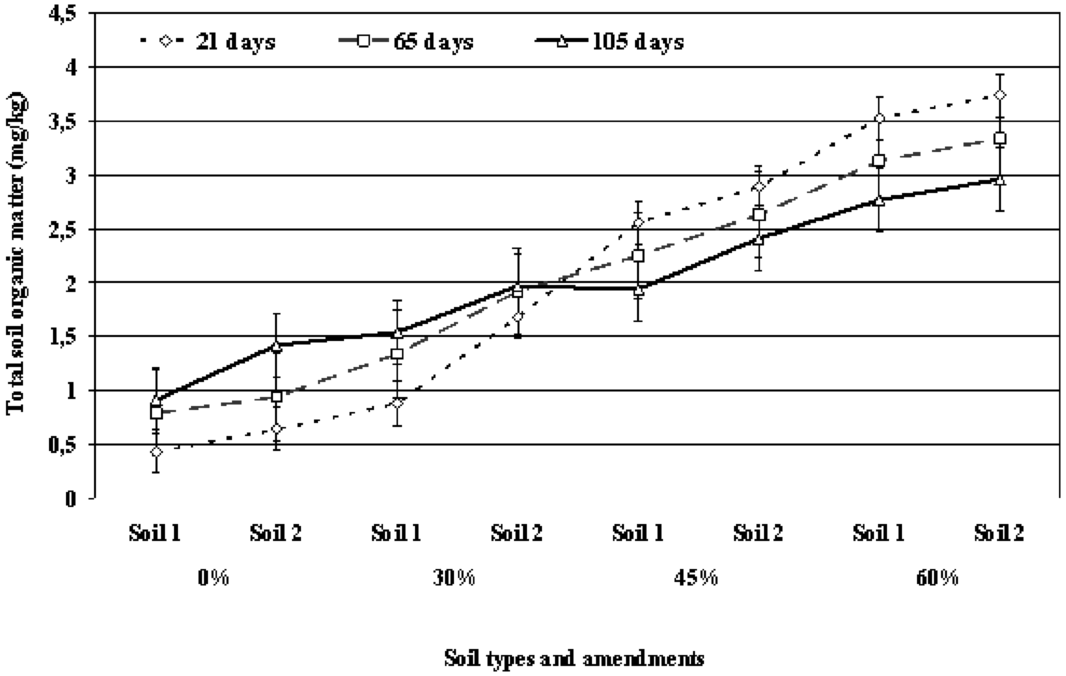

Figure 2. Soil organic matter pattern in different soil systems amended with MWS

It was found that the MWS has a potential as an organic fertilizer for agricultural practices, considering the possible improvement of the nutrient status and organic content of soils, as well as the soil properties. The transfer of heavy metals from soil to crop appears to be the greatest potential threat. In all pot experimental observations indicated that the total Cd concentration that was determined in the soil after MWS amendment and in plant tissues during the cultivation time intervals increased. The analysis did not show an increase dramatically compared to the control treatments (Table 2). The Cd concentrations in the root and shoot dry plant material exhibited almost the same trend as the Cd concentration in the soil systems in that MWS amendments led to higher concentrations in the plant roots than the control treatments.

Table 3 shows the relationship between the mobility of the Cd in soil and plant tissues in regards to TF, BAC, BAF and TnF. The Cd levels remained very similar throughout experiments, indicating almost no risk from a once off MWS application and Cd concentration remained under the guideline levels in the sunflower trials and the levels are considered too low to come to a meaningful conclusion other than that it poses no risk after a once off application.

Table 2: The total Cd concentrations (mg/kg) in sunflower plants grown in two soil types amended with municipal wastewater sludge used in the pot experiment

Soil types	Soil systems	Dry Plant parts	Cd concentrations (mg/kg) at different cultivation time intervals (Days)					
			21		65		105	
			Plant	Soil	Plant	Soil	Plant	Soil
Soil 1	Controls	Root	0.66	1.3	0.67	1.02	0.67	0.84
		Shoot	0.29		0.31		0.29	
Soil 2		Root	0.52	0.92	0.49	0.74	0.45	0.61
		Shoot	0.21		0.20		0.20	
Soil 1	Soil + 30% (MWS)	Root	0.74	1.96	0.76	1.49	0.81	1.11
		Shoot	0.32		0.33		0.37	
Soil 2		Root	0.62	1.47	0.63	1.25	0.66	1.07
		Shoot	0.39		0.40		0.44	
Soil 1	Soil + 45% (MWS)	Root	0.82	2.63	0.91	2.31	0.97	2.01
		Shoot	0.44		0.43		0.44	
Soil 2		Root	0.79	2.25	0.82	1.12	0.82	0.94
		Shoot	0.38		0.40		0.40	
Soil 1	Soil + 60% (MWS)	Root	1.12	3.06	1.15	2.25	1.3	1.89
		Shoot	0.92		0.95		0.96	
Soil 2		Root	1.08	2.41	1.10	2.09	1.14	1.12
		Shoot	0.87		0.91		0.99	

Values are presented in arithmetic mean of three replicates.

Table 3: Translocation factor (TF), Bioaccumulation coefficient (BAC), Bioconcentration factor (BCF) and Transfer factor (TnF) of Cd in sunflower plant tissues grown in sandy (soil 1) and clay loam (soil 2) amended with four MWS application rates (0, 30, 45 and 60%) for 21, 65 and 105 days

Soil systems	The relationship between the Cd-soil and the uptake by plant during different growth intervals (days)											
Soil 1	21				65				105			
	TF	BAC	BCF	TnF	TF	BAC	BCF	TnF	TF	BAC	BCF	TnF
0	0.439	0.223	0.508	0.731	0.463	0.304	0.657	0.961	0.433	0.345	0.798	**1.143**
30	0.432	0.163	0.378	0.541	0.434	0.221	0.51	0.732	0.457	0.333	0.730	**1.063**
45	0.537	0.167	0.312	0.479	0.473	0.186	0.394	0.580	0.454	0.219	0.483	0.701
60	0.821	0.301	0.366	0.667	0.826	0.422	0.511	0.933	0.738	0.508	0.688	**1.196**
Soil 2												
0	0.404	0.228	0.565	0.793	0.408	0.270	0.662	0.932	0.444	0.328	0.738	**1.066**
30	0.629	0.265	0.422	0.687	0.635	0.320	0.504	0.824	0.667	0.411	0.617	**1.028**
45	0.481	0.169	0.351	0.520	0.488	0.357	0.732	**1.089**	0.488	0.426	0.872	**1.298**
60	0.806	0.361	0.448	0.809	0.827	0.435	0.526	0.962	0.868	0.884	**1.018**	**1.902**

Values are presented in arithmetic mean of three replicates. Values >1 are in bold font.

The Cu concentrations in the soil were differed markedly between treatments for the both soils although there was an increase in clay loam soil 2 with MWS treatments (Table 4). The levels were generally lower in the shoots and the sandy soil pots. The concentrations in the plants increased throughout most of the pots with the MWS treatments although the levels were in most cases higher than in control soils (Table 4).

The Cu concentrations had a narrow variation throughout the experiments, indicating almost no risk from a once-off MWS application. The same trends as mentioned above were found in the Cd. The TF, BAC, BAF and TnF for Cu did not differ substantially between the different treatments except for the sandy soil where a slight increase was found for the sludge treatments at 60% for all the crops (Table 5). The Ni concentrations in the two soils and the rhizospheres of the sunflower plants do not reflect the expected increase whereas the soil of the sunflower plants had an increased Ni concentration with the sandy loam of soil 1 with different application rates (Table 6) of MWS.

The TF, BAC, BAF and TnF for Ni had slightly differ between the different treatments except for the sandy soil where a slight increase was found for the MWS treatments at 60% over the control for all the crops (Table 7).

Table 4: The total Cu concentrations (mg/kg) in sunflower plants grown in two soil types amended with municipal wastewater sludge used in the pot experiment

Soil types	Soil systems	Dry Plant parts	Cu concentrations (mg/kg) at different cultivation time intervals (Days)					
			21		65		105	
			Plant	Soil	Plant	Soil	Plant	Soil
Soil 1	Controls	Root	0.73	1.3	0.77	1.1	0.65	0.89
		Shoot	0.42		0.41		0.34	
Soil 2		Root	0.81	2.2	0.89	1.87	0.76	1.34
		Shoot	0.47		0.43		0.33	
Soil 1	Soil + 30% (MWS)	Root	1.31	14.9	2.02	13.7	1.47	11.3
		Shoot	0.72		0.91		0.74	
Soil 2		Root	2.04	17.4	3.33	16.2	2.21	12.1
		Shoot	1.7		1.03		0.93	
Soil 1	Soil + 45% (MWS)	Root	3.7	19.7	3.66	17.8	2.54	15.4
		Shoot	2.1		1.87		1.12	
Soil 2		Root	5.9	26.8	4.02	25.1	2.94	20.2
		Shoot	4.2		1.95		1.305	
Soil 1	Soil + 60% (MWS)	Root	7.3	25.3	5.3	23.1	3.11	18.6
		Shoot	4.9		2.4		1.45	
Soil 2		Root	9.2	39.1	6.22	32.2	3.456	24.4
		Shoot	5.2		3.01		1.67	

Values are presented in arithmetic mean of three replicates.

Table 5: Translocation factor (TF), Bioaccumulation coefficient (BAC), Bioconcentration Factor (BCF) and Transfer Factor (TnF) of Cu in sunflower plant grown in sandy (soil 1) and clay loam (soil 2) amended with four application rates (0, 30, 45 and 60%) of MWS for 21, 65 and 105 days

Soil systems	The relationship between the Cu-soil and the uptake by plant during different growth intervals (days)											
Soil 1	21				65				105			
	TF	BAC	BCF	TnF	TF	BAC	BCF	TnF	TF	BAC	BCF	TnF
0	0.575	0.323	0.562	0.885	0.532	0.373	0.700	1.073	0.523	0.382	0.730	1.112
30	0.550	0.048	0.088	0.136	0.450	0.066	0.147	0.214	0.503	0.065	0.130	0.196
45	0.568	0.107	0.188	0.294	0.511	0.105	0.206	0.311	0.441	0.073	0.165	0.238
60	0.671	0.194	0.289	0.482	0.453	0.104	0.229	0.333	0.466	0.078	0.167	0.245
Soil 2												
0	0.580	0.214	0.368	0.582	0.483	0.230	0.476	0.706	0.434	0.246	0.567	0.813
30	0.833	0.098	0.117	0.215	0.309	0.064	0.206	0.269	0.421	0.077	0.183	0.260
45	0.712	0.157	0.220	0.377	0.485	0.078	0.160	0.238	0.444	0.065	0.146	0.210
60	0.565	0.133	0.235	0.368	0.484	0.093	0.193	0.287	0.483	0.068	0.142	0.210

Values are presented in arithmetic mean of three replicates.

The Pb levels in the soils of the sunflower seedlings and plants did not reflect the expected increase whereas the soil of the sunflower plants had an increased Pb concentration with the soil 1 with different application rates (Table 8).

The sunflower seedlings and plants grown on the sandy soil exhibited a significant increase in Pb content with the MWS treatments (especially with 60%). The increased Pb uptake is also reflected in TF, BAC and BAF for the sunflowers treated with various MWS rates (Table 9). Of the five metals tested, Zn is the only one with a distinct increase in most of the treatments and plant crops for the MWS amendments (Table 10).

Levels in the clay soil were lower than in the sandy soil experiment. This could be ascribed to a possible higher natural background concentration in this soil compared to the sandy and loam soils. Plant-uptake of Zn followed the trend of increased concentration in the sandy and the clay soil (Table 10).

Table 6: The total Ni concentrations (mg/kg) in sunflower plants grown in two soil types amended with municipal wastewater sludge used in the pot experiment

Soil types	Soil systems	Dry Plant parts	Ni concentrations (mg/kg) at different cultivation time intervals (Days)					
			21		65		105	
			Plant	Soil	Plant	Soil	Plant	Soil
Soil 1	Controls	Root	0.031	0.041	0.033	0.040	0.038	0.038
		Shoot	0.012		0.021		0.025	
Soil 2		Root	0.027	0.035	0.029	0.033	0.033	0.031
		Shoot	0.019		0.02		0.022	
Soil 1	Soil + 30% (MWS)	Root	0.237	0.561	0.242	0.541	0.0311	0.511
		Shoot	0.205		0.211		0.231	
Soil 2		Root	0.201	0.412	0.232	0.402	0.241	0.396
		Shoot	0.187		0.193		0.212	
Soil 1	Soil + 45% (MWS)	Root	0.256	0.732	0.264	0.712	0.278	0.701
		Shoot	0.226		0.279		0.233	
Soil 2		Root	0.238	0.646	0.249	0.633	0.253	0.626
		Shoot	0.211		0.219		0.234	
Soil 1	Soil + 60% (MWS)	Root	0.441	0.911	0.476	0.89	0.503	0.874
		Shoot	0.291		0.307		0.355	
Soil 2		Root	0.371	0.704	0.376	0.689	0.39	0.667
		Shoot	0.311		0.324		0.332	

Values are presented in arithmetic mean of three replicates.

Table 7: Translocation factor (TF), Bioaccumulation coefficient (BAC), Bioconcentration Factor (BCF) and Transfer Factor (TnF) of Ni in sunflower plant grown in sandy (soil 1) and clay loam (soil 2) amended with four application rates (0, 30, 45 and 60%) of MWS for 21, 65 and 105 days

Soil systems	The relationship between the Ni-soil and the uptake by plant during different growth intervals (days)											
Soil 1	21				65				105			
	TF	BAC	BCF	TnF	TF	BAC	BCF	TnF	TF	BAC	BCF	TnF
0	0.387	0.293	0.756	**1.049**	0.636	0.525	0.825	**1.350**	0.658	0.658	**1.000**	**1.658**
30	0.865	0.365	0.422	0.788	0.872	0.390	0.447	0.837	**7.428**	0.452	0.061	0.513
45	0.883	0.309	0.350	0.658	**1.057**	0.392	0.371	0.763	0.838	0.332	0.397	0.729
60	0.660	0.319	0.484	0.804	0.645	0.345	0.535	0.880	0.706	0.406	0.576	0.982
Soil 2												
0	0.704	0.543	0.771	**1.314**	0.690	0.606	0.879	**1.485**	0.667	0.710	**1.065**	**1.774**
30	0.930	0.454	0.488	0.942	0.832	0.480	0.577	**1.057**	0.880	0.535	0.609	**1.144**
45	0.887	0.327	0.368	0.695	0.808	0.346	0.393	0.739	0.925	0.374	0.404	0.778
60	0.838	0.442	0.527	0.969	0.862	0.470	0.546	**1.016**	0.851	0.498	0.585	**1.082**

Values are presented in arithmetic mean of three replicates. Values >1 are in bold font.

Table 8: The total Pb concentrations (mg/kg) in sunflower plants grown in two soil types amended with municipal wastewater sludge used in the pot experiment

Soil types	Soil systems	Dry Plant parts	Pb concentrations (mg/kg) at different cultivation time (Days)					
			21		65		105	
			Plant	Soil	Plant	Soil	Plant	Soil
Soil 1	Controls	Root	0.961	1.022	0.966	1.417	0.985	1.44
		Shoot	0.633		0.652		0.667	
Soil 2		Root	0.663	0.773	0.669	0.732	0.672	0.711
		Shoot	0.344		0.365		0.367	
Soil 1	Soil + 30% (MWS)	Root	12.65	23.41	12.79	23.41	13.41	22.56
		Shoot	10.44		11.44		11.62	
Soil 2		Root	10.34	21.56	10.65	20.87	10.99	20.34
		Shoot	8.75		8.92		9.51	
Soil 1	Soil + 45% (MWS)	Root	16.38	26.41	16.74	25.805	17.54	24.412
		Shoot	12.69		12.87		13.58	
Soil 2		Root	14.67	24.454	14.87	24.044	15.41	23.488
		Shoot	11.43		11.55		11.93	
Soil 1	Soil + 60% (MWS)	Root	20.42	30.377	20.78	29.13	21.41	28.676
		Shoot	14.211		14.55		14.79	
Soil 2		Root	18.59	28.42	18.93	27.236	19.41	27.055
		Shoot	15.201		15.42		15.91	

Values are presented in arithmetic mean of three replicates.

Table 9: Translocation factor (TF), Bioaccumulation coefficient (BAC), Bioconcentration Factor (BCF) and Transfer Factor (TnF) of Pb in sunflower plant grown in sandy (soil 1) and clay loam (soil 2) amended with four application rates (0, 30, 45 and 60%) of MWS for 21, 65 and 105 days

Soil systems	The relationship between the Ni-soil and the uptake by plant during different growth intervals (days)											
Soil 1	21				65				105			
	TF	BAC	BCF	TnF	TF	BAC	BCF	TnF	TF	BAC	BCF	TnF
0	0.659	0.619	0.940	**1.560**	0.675	0.460	0.682	**1.142**	0.677	0.463	0.684	**1.147**
30	0.825	0.446	0.540	0.986	0.894	0.489	0.546	**1.035**	0.867	0.515	0.594	**1.109**
45	0.775	0.480	0.620	**1.101**	0.769	0.499	0.649	**1.147**	0.774	0.556	0.718	**1.275**
60	0.696	0.468	0.672	**1.140**	0.700	0.499	0.713	**1.213**	0.691	0.516	0.747	**1.262**
Soil 2												
0	0.519	0.445	0.858	**1.303**	0.546	0.499	0.914	**1.413**	0.546	0.516	0.945	**1.461**
30	0.846	0.406	0.480	0.885	0.838	0.427	0.510	0.938	0.865	0.468	0.540	**1.008**
45	0.779	0.467	0.600	**1.067**	0.777	0.480	0.618	**1.099**	0.774	0.508	0.656	**1.164**
60	0.818	0.535	0.654	**1.189**	0.815	0.566	0.695	**1.261**	0.820	0.588	0.717	**1.305**

Values are presented in arithmetic mean of three replicates. Values >1 are in bold font.

Table 10: The total Zn concentrations (mg/kg) in sunflower plants grown in two soil types amended with municipal wastewater sludge used in the pot experiment

Soil types	Soil systems	Dry Plant parts	Zn concentrations (mg/kg) at different cultivation time (Days)					
			21		65		105	
			Plant	Soil	Plant	Soil	Plant	Soil
Soil 1	Controls	Root	1.43	1.565	1.52	1.329	1.602	1.298
		Shoot	0.97		1.044		1.244	
Soil 2		Root	1.023	0.993	1.101	0.906	1.512	0.853
		Shoot	0.91		1.005		1.008	
Soil 1	Soil + 30% (MWS)	Root	83.41	50.45	84.012	48.411	87.92	47.203
		Shoot	62.52		68.41		73.005	
Soil 2		Root	71.62	47.442	72.21	46.511	74.61	45.005
		Shoot	50.011		51.008		54.901	
Soil 1	Soil + 45% (MWS)	Root	113.03	73.478	117.49	71.45	120.25	70.342
		Shoot	78.14		80.012		84.39	
Soil 2		Root	86.22	64.002	88.91	63.66	91.012	64.433

		Shoot	63.011		67.101		70.105	
Soil 1	Soil + 60% (MWS)	Root	144.08	85.341	146.72	83.55	149.129	80.211
		Shoot	84.21		87.106		89.011	
Soil 2		Root	95.104	70.016	97.33	68.012	97.007	65.411
		Shoot	76.106		78.21		79.202	

Values are presented in arithmetic mean of three replicates.

The concentration in the sunflowers also exhibited an increase in the MWS treatments in the sandy and clay soils. This same trend was found in the TF, BAC and BAF (Table 11). The percentages of the total Cu, Zn, Pb and Cr extracted with DTPA could be a good indicator of the quantity of metal available for plants and could reflect their comparative mobility. Organic matter plays a significant role in the availability and mobility of the heavy metals in soils. The organic matter is involved in the formation of soluble complexes especially with Cu and Zn.

Table 11: Zn Translocation factor (TF), Bioaccumulation coefficient (BAC), Bioconcentration Factor (BCF) and Transfer Factor (TnF) of sunflower plant grown in sandy (soil 1) and clay loam (soil 2) amended with four application rates (0, 30, 45 and 60%) of MWS for 21, 65 and 105 days

Soil systems	The relationship between the Zn-soil and the uptake by plant during different growth intervals (days)											
Soil 1	21				65				105			
	TF	BAC	BCF	TnF	TF	BAC	BCF	TnF	TF	BAC	BCF	TnF
0	0.678	0.620	0.914	**1.534**	0.687	0.786	**1.144**	**1.929**	0.777	0.958	**1.234**	**2.193**
30	0.750	**1.239**	**1.653**	**2.893**	0.814	**1.413**	**1.735**	**3.148**	0.830	**1.547**	**1.863**	**3.409**
45	0.691	**1.063**	**1.538**	**2.602**	0.681	**1.120**	**1.644**	**2.764**	0.702	**1.200**	**1.710**	**2.909**
60	0.584	0.987	**1.688**	**2.675**	0.594	**1.043**	**1.756**	**2.799**	0.597	**1.110**	**1.859**	**2.969**
Soil 2												
0	0.890	0.916	**1.030**	**1.947**	0.913	**1.109**	**1.215**	**2.325**	0.667	**1.182**	**1.773**	**2.954**
30	0.698	**1.054**	**1.510**	**2.564**	0.706	**1.097**	**1.553**	**2.649**	0.736	**1.220**	**1.658**	**2.878**
45	0.731	0.985	**1.347**	**2.332**	0.755	**1.054**	**1.397**	**2.451**	0.770	**1.088**	**1.413**	**2.501**
60	0.800	**1.087**	**1.358**	**2.445**	0.804	**1.150**	**1.431**	**2.581**	0.816	**1.211**	**1.483**	**2.694**

Values are presented in arithmetic mean of three replicates. Values >1 are in bold font.

Malik et al, (2010) evaluated the concentration, transfer and accumulation of metals from soil to roots and shoots in terms of BCF, TF and BAC. Overall the TF did not vary widely (except for Cd as explained above) and a clear trend in metal uptake and metal addition through MWS is absent except for Zn (to a limited extent). This indicates that experimental conditions, that the sludge treatments did not lead to detrimental conditions in terms of the investigated heavy metal uptake. Furthermore, the experiment was conducted soon after the application of the MWS and this left very little time for the metals to equilibrate with soil constituents upon its release from the MWS. The conclusion therefore is that at current application rates of use there is almost no risk of metal contamination of the food chain. This situation is bound to change if long-term continuous applications and possible changes in soil-use after a number of years are considered. Further research should be focused on continuous applications and soil-use scenarios. The availabilities of heavy metals were redistributed to other forms by incubation and addition of MWS at amendment rates 30, 45 and 60% as well as the sunflower growth for 21, 65 and 105 days. For all the amendments, the extraction of Cd and Ni concentrations decreased significantly during the first 21 days of incubation and cultivation as in Table 2 and 6, respectively. In the control soil, extraction of Cd decreased and Ni decreased after 21, 63 and 105 days of incubation and cultivation. The reduction in availability of Cd and Ni concentrations can be explained by their retention by soil organic matter (McBride et al., 2000). Gray et al. (1998) reported that soil organic matter was important in controlling Cd sorption and desorption. It was observed that the rate of decrease in availability of Cd tended to decline as incubation progressed, but the reduction in extraction of Ni fluctuated over the incubation time. In contrast, availability of Cu in the untreated soil increased and changed little with time. The results showed that extraction of Cu increased of initial content after 21, 63 and 105 days. Extraction of Zn increased by increasing the incubation time intervals to 105 days as compared with initial soil, so it changed little with time. The increases in extraction of Zn (at 105 days) and Cu (at all sampling dates) may be explained by dissolved organic matter, which promoted the dissolution of Cu and Zn by building organic complexes. Almas et al. (2000) found that the addition of organic matter increased the solubility of Zn by the formation of organometallic complexes. In this study, it was observed that the increase the extraction of Cu tended to decrease at the end of the incubation and cultivation period. This result is attributed to the tendency of soluble Cu to bind with organic matter or solid-phase materials. Organic matter in soluble and insoluble forms plays contrasting roles in controlling total soluble Cu and other metals as well. In sequential extractions of sludge-treated soils, Cu was found to predominate in the organic fraction (Sposito et al., 1982), Tyler and McBride (1982) found that Cu and Ni were less extractable from the organic soil than Zn and Cd. In all the treatments, incubation of soil derived from MWS caused a decline in exchangeable form of all heavy metals tested (Tables 2, 4, 6, 8 and 10). The results showed that the strongest reduction in the exchangeable form of all five heavy metals occurred during the first 21 days of incubation. After that, the reduction in exchangeable Ni, Pb and Zn increased very little up to the end of the experiment. However, the rate of decrease in exchangeable Cd tended to decline slowly, as incubation progressed (Table 2). Neal and Sposito (1986) found that soil sorption of Cd was reduced by the formation of soluble–organic associations in the aqueous solution. In our soil, the reduction in extractability of heavy metals is attributed, in part, to the nearly neutral pH, the presence of low sludge application rate (30%) and, in part, the high organic matter content at high sludge application rate (60%). This result concurs with that of McBride et al. (2000), who found that heavy metals were strongly retained in sewage sludge soil, which has a high organic matter and lime content. Ong and Bisque (1968) explained the phenomena of metal reduction by the fact that humic substances behave as negatively charged colloids, which may be coagulated by the electrolytes. Another phenomenon is that after the release of heavy metals from the MWS, they react chemically with the soil so that metal toxicity declines with time (Lewin and Beckett, 1980). The decrease in extraction forms of heavy metals in the soil treated with MWS was greater than in an untreated soil. This effect was especially pronounced for the treatments with low and high heavy metal bone MWS addition.

The properties of the MWS change rapidly as soon as it is amended to soil. This is particularly true where MWS is to be used in agriculture is high in organic matter, mineralisation rates prevail due to rapid microbial decomposition (Korentajer, 1991). The organic material in the “fresh” sludge is unstable in soil and will therefore undergo extensive alteration before it becomes material resistant to mineralisation (humus). In this process a large fraction of the total C is lost mainly to the atmosphere (Stevenson, 1986).

A combination of environmental factors influences the rate at which the microbially mediated processes lead to the decomposition of organic material in soil. As general rule soil organic matter decomposition is curvilinear related to soil moisture and is slow at very wet and very dry conditions (Sikora & Szmidt, 2001). Temperature affects mineralisation where increases in temperature from 10°C to 35°C also increase the breakdown rate (Sikora & Szmidt, 2001). Below and above these temperatures the rates decrease drastically. Similarly, once accumulated, heavy metals are highly persistent in the topsoil (Alloway and Jackson 1991) and can cause potential problems such as phytotoxicity (Berti and Jacobs 1996). The phytoavailability of heavy metals present in the sewage sludge depends on many factors such as the nature and amount of metal, degree of metal association in the sludge, soil, plant characteristics and weather conditions (Jin et al, 1996).

Availability of metals differed between sludge application rates. The heavy metals were less available in the high metal industrial sludge compared to the low metal domestic sludge. The accumulation of sludge-borne metals in soil could not be proven to be in excess, even at a higher application rate (60%). Furthermore, accumulation of heavy metals in sunflower seedlings and plants did not reach phytotoxic levels. A significant increase in certain yield aspects was seen after MWS amendment to the different soil types, especially in the low metal sludge treatment. The application of MWS to agricultural soils could provide an economical way to dispose of the increasing amounts of sludge generation.

The improvement of the soil properties through the increase in organic matter could play an important role in promoting the agricultural application of MWS in the future and rapid decomposition by

microorganisms and the use of mineral fertilizers. Large number of factors control metal accumulation and bioavailability associated with soil and climatic conditions, plant genotype and agronomic management, including: active/passive transfer processes, sequestration and speciation, redox states, the type of plant root system and the response of plants to elements in relation to seasonal cycles.
The effect of MWS on the growth and yield of sunflower under greenhouse conditions was studied by Lavado (2006) and López-Valdez et al. (2011) and the results indicated that sludge modified some soil characteristics during the first two months but not thereafter. Also, some plant characteristics were improved by sludge and the sludge treatments increased the yield and this implies that MWS increased the biomass and/or the yield. Our results are agreed with their conclusion as it is mentioned in Figures 1a and 1b.

The scientific evidence of both the risks and benefits associated with the application of sewage sludge to agricultural land has been well documented (Korentajer, 1991). There are probably few scientists who would argue that sewage sludge should be viewed as an unwanted by-product of sewage treatment. The literature pertaining to sewage sludge reveals that an enormous amount of research has gone into understanding and exploiting the benefits of reusing sludge and into better understanding any threat of its reuse on land. The reuse of sewage sludge on land is recognised by both government and the regulators to be the best practical environmental option (Tyson, 2002).

CONCLUSIONS AND IMPLICATIONS

Previous research work has shown that crop cultivation on MWS amended soils can be done without contamination risk to soils or phytotoxic uptake by the crop plants. These observations were based on short-term experiments. The possible long-term heavy metal accumulation in soils and subsequent uptake by crops does pose a threat to the sustainability of MWS on agricultural soils. Therefore, strict monitoring procedures are necessary and the correct management practices (e.g., controlling soil pH above 6.5 through liming). The value of sludge as a soil conditioner and fertilizer was seen in the experiments although long-term experiments under field conditions still need to be done to assess possible accumulation of heavy metals in agricultural soils. This research work forms part of a broader research programme where the following aspects are being investigated:

1. The short term impact of using MWS in agricultural practices;
2. Establishing the impact of long term application of MWS under non-beneficial conditions;
3. Establishing the status quo of MWS qualities (metals, nutrients and organic pollutants)
4. Documenting the technologies and their financial implications for MWS treatment,

This specific study has identified one major research need. The long term effects of the agricultural use of MWS needs to be assessed. The parameters of concern would be:

- Recommended dosage for different crops and different soils to obtain maximum benefit from the MWS.
- Protecting the environment against pollution.

Soil organic matter showed a strong relationship with this order due to the formation of soluble and insoluble complexes with the metals.

REFERENCES

Almas, A., R., McBride, M. B. & Singh, B. R. (2000). Solubility and liability of cadmium and zinc in two soils treated with organic matter. *Soil Science*, 165, 250-259.

Alloway, B. J. (1995). Heavy Metals in Soils. Blackie Academic and Professional, Glasgow, pp 368.

Alloway, B. J. & Jackson, A. P. (1991). The behaviour of heavy metals in sewage sludge-amended soils. *Sci. Total Environ*, 100, 151-176.

Bell, P., James, B. R. & Chaney, R. L. (1991). Heavy metal extractability in long-term sewage sludge and metal salt amended soils. *J. Environ. Qual.*, 20, 481-486.

Berti, W. R. & Jacobs, L.W. (1996). Chemistry and phytotoxicity of soil trace elements from repeated sewage sludge applications. *J. Environ. Qual*., 25, 1025-1032.

Cluis, C. (2004). Junk-greedy greens: phytoremediation as a new option for soil decontamination. *Biotech. J.*, 2, 60-67.

Fayiga, A. Q. & Ma L. Q. (2006). Using phosphate rock to immobilize metals in soils and increase arsenic uptake in Pteris vittata. *Sci. Total Environ.,* 359, 17-25.

Gray, C. W., McLaren, R. G., Roberts, A. H. C. & Condorn, L. M. (1998). Sorption and desorption of cadmium from some New Zealand soils: Effect of pH and contact time. *Austr. J. Soil Res*., 36, 199-216.

Jin, Q., Zi-jian, W., Xiao-quann, S., Qiang, T., Bei, W. & Bin C. (1996). Evaluation of plant availability of soil trace metals by chemical fractionation and multiple regression analysis. *Environ. Pollut*., 91, 309-315.

Korentajer, L. (1991). A review of the agricultural use of sewage sludge: Benefits and potential hazards, *Water S. A.,* 17 (3), 189-196.

Lavado R. S. (2006). Effects of sewage-sludge application on soils and sunflower yield: quality and toxic element accumulation. *J. Plant Nutr*., 29 (6), 975-84.

Lewin, V. H. & Beckett, P. H. T. (1980). Monitoring heavy metal accumulation in agricultural soils treated with sewage sludge. *Effluent and Water Treatment J*., 20, 217-221.

Lindsay, W. L. & Norvell, W. A. (1978). Development of a DTPA test for zinc, iron, manganese, and copper. *Soil Sci. Soc. Am. J.*, 42, 421-428.

López-Valdez, F., Fernández-Luqueńo, F., Luna-Suárez, S. & Dendooven L. (2011). Greenhouse gas emissions and plant characteristics from soil cultivated with sunflower (*Helianthus annuus* L.) and amended with organic or inorganic fertilizers. *Sci. Total Environ*., 412-413, 257-264.

Malik, N. R., Husain, Z. S. & Nazir, I. (2010). Heavy metal contamination and accumulation in soil and wild plant species from industrial area of Islamabad, Pakistan. Pak. J. Bot., 42 (1), 291-301.

McBride, M., Martinetz, C. E., Topp, E. & Evans, L. (2000). Trace metal solubility and speciation in a calcareous soil 18 years after no-till sludge application. *Soil Sci*., 165, 646-656.

Neal, R. H. & Sposito, G. (1986). Effects of soluble organic matter and sewage sludge amendments on cd sorption by soils at low cadmium concentrations. *Soil Sci*., 142, 164-172.

Oliver, D. P., Tiller, K. G., Conyers, M. K., Slattery, W. J., Alston, A. M. & Merry, R. H. (1996). Effectiveness of liming to minimize uptake of cadmium by wheat and barley grain grown in the field. *Aust. J. Agric. Res.*, 47, 1181-1193.

Ong, H. & Bisque, R. E. (1968). Coagulation of humic colloids by metal ions, *Soil Sci*., 106, 220-224.

Ortiz, O., & Alcaniz, J. M. (2006). Bioaccumulation of heavy metals in *Dactylis glomerata* L, growing in a calcareous soil amended with sewage sludge. *J. Bioresour. Technol*., 97, 545-552.

Sikora, L. J. & Szmidt, R. A. K. (2001). Nitrogen sources, mineralization rates, and nitrogen nutrition benefits to plants from composts, In: Compost Utilization in Horticultural Cropping Systems. Stoffella, P. J., & Kahn, B. A. (Eds), Lewis Publishers, Boca Raton, Florida, pp 287-305.

Smith, S. R. (1994). Effect of soil pH on availability of metals in sewage sludge-treated soils. II. Cadmium uptake by crops and implications for human dietary intake. *Environ. Poll*., 86, 5-13.

Sposito, G., Lund, L. J. & Chang, A. C. (1982). Trace metal chemistry in arid-zone field soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. Soil Sci. Soc. Am. J., 46, 260-264.

Stevenson, F. J. (1986). Cycles of Soil, Carbon, Nitrogen, Phosphorus, Sulphur, Micronutrients, John Wiley and Sons, New York, pp 380.

Tyler, L. D. & McBride, M. B. (1982). Mobility and extractability of cadmium, copper, nickel, and zinc in organic and mineral soil columns. *Soil Sci*., 134, 198-205.

Tyson, J. M. (2002). Perceptions of sewage sludge. *Water Sci. Technol*., 46, 373-380.

Walkley, A. & Black, I. A. (1934). An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Sci., 37, 29-38.

Wuana, A. R. & Okieimen, E. F. (2011). Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. International Scholarly Research Network (ISRN) Ecology, Volume 2011, Article ID 402647, 20 pages, doi:10,5402/2011/402647.

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DISTRIBUTION OF ORGANIC POLLUTANTS' CONTAMINATION LEVELS IN THE MOSCOW RIVER, RUSSIA

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ABSTRACT

The Moscow River is a river of western Russia flowing through Moscow city. The environmental stress on the Moscow River is high due to the fact that Moscow city is a big centre of industrial activity concentrated on the river bank area. So the Moscow River water contamination is a question of great interest. In our research levels of polychlorinated biphenyl (PCB), phthalic acid esters (PAE), polycyclic aromatic hydrocarbons (PAH) and organochlorine substances (OCP) were determined in the Moscow River water samples with the use of GC-MS system. Obtained results are correlated to the Moscow River bank area land use. Not all target substances, analysed in this study, were found in the water samples of the Moscow River. Acenaphtene, fluorene, phenantrene, fluoranthene, pyrene, benzo(a)anthracene, crysene, triclosan were determined in different parts of the Moscow River. Determined PAEs contamination level in the Moscow River is significantly lower, than this in world's rivers. European indicative PCB congeners (IUPAC № 28, 52, 101, 138, 153 and 180) were not detected in analyzed water samples. Nevertheless high concentrations of less toxic and low-chlorinated PCBs were found. This study indicates that more attention should be paid to further assessment in understanding the contamination sources and the Moscow River water quality monitoring.

Key words: *persistent organic pollutants, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, water contamination, contamination sources.*

INTRODUCTION

The Moscow River is a river of western Russia, having it source in Smolensk–Moscow Upland, passing through the city of Moscow and then flowing into the Oka River in the city of Kolomna. The total length of the river is 503 km, while its length within the city of Moscow is about 80 km. The environmental stress on the Moscow River is high due to the fact that the city of Moscow is the city of industrial activity. Practically all types of industrial enterprises are presented in Moscow, except mining industry. Primary industries, located in the city of Moscow, include the chemical, petroleum, metallurgy, textile, food, energy and machinery industries. Most of the factories and enterprises are located on the Moscow River bank area and could be contamination sources of the Moscow River with such substances, as polychlorinated biphenyls (PCBs), organochlorine substances (OCP), polycyclic aromatic hydrocarbons (PAHs) and phthalic acid esters (PAEs). A few studies on PAH and PCB determination in the Moscow region were conducted and showed the presence of this substances in the soil [1, 2, 3]. But no regular monitoring of these contaminants in the Moscow River water has been done over the last decades. Nevertheless this information is necessary, from the point of view that the presence of hydrophobic substances in water reflects the current level of contamination in contrast to those in sediment, which reveal the history of contamination of the river system.

PCBs, OCPs, PAHs and PAEs are of particular interest due to their endocrine disrupting properties [4, 5]. PCBs were restricted since 1970s in the USA and Europe and since 1993 in Russia, but these substances are still persistent in environment. PCBs are hydrophobic substances, which primarily adsorb on soil and sediments [6-9]. If released to water high chlorinated PCBs are primarily adsorb on sediment and suspended matter and water is enriched with lower chlorinated PCBs, due to their greater water solubility. The process of PCBs desorption from sediments in water plays the key role in the fate of these substances and can be the path of water source cross contamination with further contamination of air [10] or accumulation in aquatic organisms such as plankton, algae, and fish [11, 12]. PCBs were found world-wide in water sources [13-16]. Many OCPs have been also included in the list of Persistent Organic Pollutants (POPs) developed at the Stockholm Convention. Their uses and manufacture have been banned or restricted in the 1980s in most countries.

Many of PAHs are known to have carcinogenic and mutagenic properties. Due to their world-wide occurrence in environment 16 PAHs are included in priority substances pollutants by the US EPA and 7 of them in European Union. The sources of PAHs in environment can be different, including combustion of fossil fuel, oil recycling, coke and asphalt productions, oil refining and other industrial activities [17]. Due to high hydrophobicity of PAHs, the main path of surface water contamination is wet or dry atmospheric deposition. The sources of environment contamination with these substances are urban run-off, municipal effluents, industrial effluents and oil spillage or leakage [18]. Despite of their high hydrophobicity, these substances can be found in surface water bodies world-wide and are well studied [18-26].

PAEs are usually used as plasticizers in food packages, building, toys, medical devices such as blood storage bags, intravenous fluid bags and other products [27]. This group of substances can effect on human reproductive health even in environmental friendly level [28]. PAEs are not expected to be highly persistent in environment, but longer half-lives of these substances can be observed under anaerobic conditions, low concentrations and in cold environments [29]. Most studies show that these substances are regularly found in urban environmental compartments at significant level [30-38].

For understanding the global fate of these types of contaminants, it is important to conduct continuous monitoring of each industrial city in the world.

The aims of this study were: (i) determine the contamination levels of PCBs, OCPs, PAHs and PAEs in water samples taken from the Moscow River in the area of high environmental stress; (ii) correlate the contamination results with land use, and (iii) compare the contamination levels of the Moscow River with world levels of this substances in surface water objects.

METHODS

Sampling location and collection

The surface water samples were collected from the four sampling sites along the direction of the Moscow River flow in October 2013. The sampling sites are shown in Figure 1.

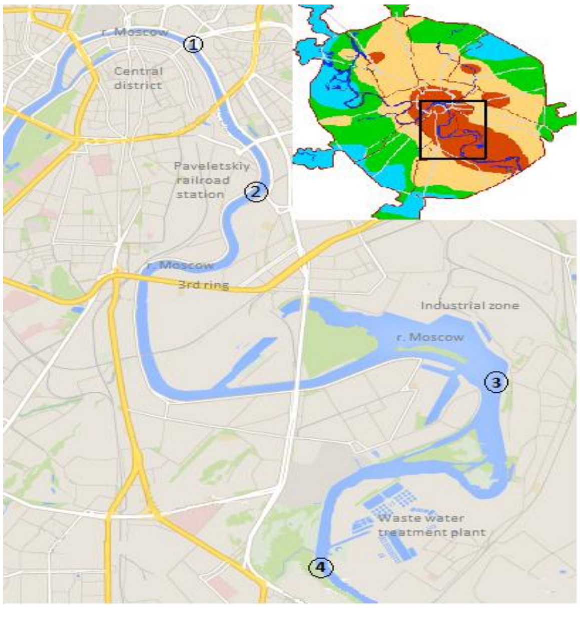

Figure 1. The sampling location in the Moscow River

The four sampling sites were chosen due to the high environmental influence on the Moscow River. Sample 1 (55°44'46.7"N; 37°38'17.2"E) was collected in the center of the city of Moscow near Big Ustinskiy bridge where the traffic is high. Sample 2 (55°43'14.0"N; 37°39'24.3"E) from Krutitskaia bank and sample 3 (55°41'12.4"N; 37°42'53.9"E) from Pechatniki park reflect the situation in the industrial zone. Sampling side 2 was chosen in proximity to the Paveletskiy railroad station. Sampling point 4 (55°38'59.1"N; 37°40'35.4"E) is located a few kilometers downstream from the discharge of the wastewater treatment plant.

All samples were collected at the afternoon to ensure similar environmental conditions (e.g. temperature and humidity). Water samples were collected using 1 liter glass bottle and methanol was added to prevent the target substances adsorption on the bottles’ glass walls. Samples were transported to the laboratory at the same day and were stored at 4 ^{o}C until extraction.

Sample extraction

Extraction procedure of all samples was conducted at the next day after sampling. Polydimethylsiloxane rods were used for extraction of target substances, which were proved as efficient technology for organic contaminants extraction from water [39-42]. A silicon elastomer (O.D. 2 mm) was cut in 2-cm-long pieces. Prior the first use the silicon rods were conditioned by placing into flask containing 100 ml of methanol/dichloromethane mixture (1:1) followed by sonication for 10 min. This procedure was repeated with the fresh solvent mixture, followed by drying step using a lint-free tissue. The rods were then exposed to heating overnight at 250˚C in a nitrogen stream of 30 ml min^{-1}. The silicon rods were then stored during the extraction procedure.

The water samples were brought to room temperature before extraction. Extraction was conducted in the 500 ml triple-neck round-bottom glass flasks. Walls of each flask were rinsed with methanol and 500 ml of water sample was placed directly in the flask. Three silicon rods were put into each water sample. Extraction flasks with water samples were then horizontally shaken (KS15A control, Edmund Bühler GmbH, Hechingen, Germany) at 100 min^{-1} for 24 hours. After extraction silicon rods were dried using a lint-free tissues, put into 1.5 ml vials and stored in the freezer until analysis.

Instrumental analysis

The silicon rods analysis was performed on an Agilent system (Agilent Technologies, Palo Alto, CA, USA) coupled to a Gerstel TDS A thermo desorption device and mass selective detector (5973 network MSD detector, Agilent); see Montero et al. for details. The conditions for the thermodesorption system was as follows: desorption temperature, 300 ˚C; desorption time, 10 min; and helium flow rate, 50 ml min^{-1} (solvent vent mode). The target compounds were determined on an HP-5 (5% phenyl 95% methylsiloxane) capillary column (60m ×250 µm i.d., 0.25 µm film thickness). The GC oven temperature program started from 60 ˚C (5 min) to 180 ˚C at 15˚C/min, to 220 ˚C at 2◦C/min and to 300 ˚C at 15˚C/min. Helium was used as carrier gas. Both single-ion monitoring (SIM) and full ion scanning mode (SCAN) detection methods were established for detection.

An empty thermo desorption glass tubes (Gerstel) were used as containers for silicon rods. Firstly, silicon rods in the tubes were placed in a cold injector (Gerstel) under 30 ml min^{-1} of nitrogen for 1 min to allow evaporation of the solvent (methanol). After that procedure, the tubes were immediately transferred to the thermo desorption device (TDS A) for subsequent analysis.

RESULTS AND DISCUSSIONS

PAHs distribution in water samples of the Moscow River

Among 15 PAHs investigated, only acenaphtene, fluorene, phenantrene, fluoranthene, pyrene, benzo(a)anthracene and crysene were detected in water samples. The water sample from sampling point 2 contains all the determined PAHs (Table 1). Fluorene, phenantrene and pyrene were determined in all analyzed samples. The concentrations of fluorene and phenanthrene in the water samples are ranging from 3.1 ng/L (sample site 1) to 15.5 ng/L (sample site 3) and from 16.5 ng/L (sample site 1) to 45.7 ng/L (sample site 2), respectively. The highest concentrations of these substances in sample site 2 and 3 can be attributed to the nearby industrial area, located on the river bank area between these sampling points. The concentration of pyrene varies slightly in all analyzed sample and can be related to highway proximity. The traffic situation in the city can also influence the fluoranthrene distribution in water samples, which was found at sampling sites 1 and 2, with maximum concentration of 14.9 ng/L in sample site 2.

Table 1: River water PAH concentrations (average±standard deviation; n=2)

	Compound	Concentration, ng/l			
		Sample 1	Sample 2	Sample 3	sample 4
1	Naphtalene	<LOQ	<LOQ	<LOQ	<LOQ
2	Acenaphtene	7.8±0.8	9.6±0.2	11.2±1.5	<LOQ
3	Fluorine	3.1±0.1	8.6±3.0	15.5±1.2	5.6±0.9
4	Phenanthrene	16.5±1.9	45.7±5.4	32.8±2.6	18.2±0.4
5	Antracene	<LOQ	<LOQ	<LOD	<LOD
6	Fluoranthene	3.8±1.8	14.9±2.5	<LOQ	<LOQ
7	Pyrene	19.4±2.4	29.6±1.8	20.8±3.9	28.5±7.9
8	Benzo(a) anthracene	<LOQ	5.5±0.5	<LOQ	<LOQ
9	Chrysene	<LOQ	6.2±0.5	<LOQ	<LOQ
10	Benzo(b) fluoranthene	<LOD	<LOQ	<LOQ	<LOQ
11	Benzo(k) fluoranthene	<LOD	<LOQ	<LOQ	<LOQ
12	Benzo(a)pyrene	<LOD	<LOQ	<LOQ	<LOQ
13	Indeno(123cd) pyrene	<LOD	<LOQ	<LOD	<LOD
14	Dibenzo(ah) anthracene	<LOD	<LOD	<LOD	<LOD
15	Benzo(ghi) perylen	<LOD	<LOQ	<LOD	<LOD
	Σ	50.6	120.1	80.3	52.3

The acenaphtene concentration increases with the river flow from 7.8 ng/L (sample point 1) to 11.2 ng/L (sample point 3) and then decreased to the level of < LOD (sample point 4).

There are many potential sources of environment contamination with PAHs. The main are combustion of organic materials, fires, transportation system and energy production. In light of all the literature reviewed, it appears that there are also many potential sources of PAH associated with railway rails: coal and coal dust from cargo entering, a coal-fired plant, herbicides used to control vegetation along rails, diesel exhaust from diesel electric locomotives, and heated lubricating oils, greases and creosote-treated railway ties, widely used to protect wood [43, 44]. From the figure 2 it can be seen that sampling point 2 is characterized by highest concentrations of almost all determined PAH (except, acenaphtene and fluorene, which concentration are highest in the sample 3). Benzo(a)antracene and chrysene were found only in the sampling site 2. Due to those facts it may be possible that railroad station and rails can be the sources of the Moscow River contamination with PAHs.

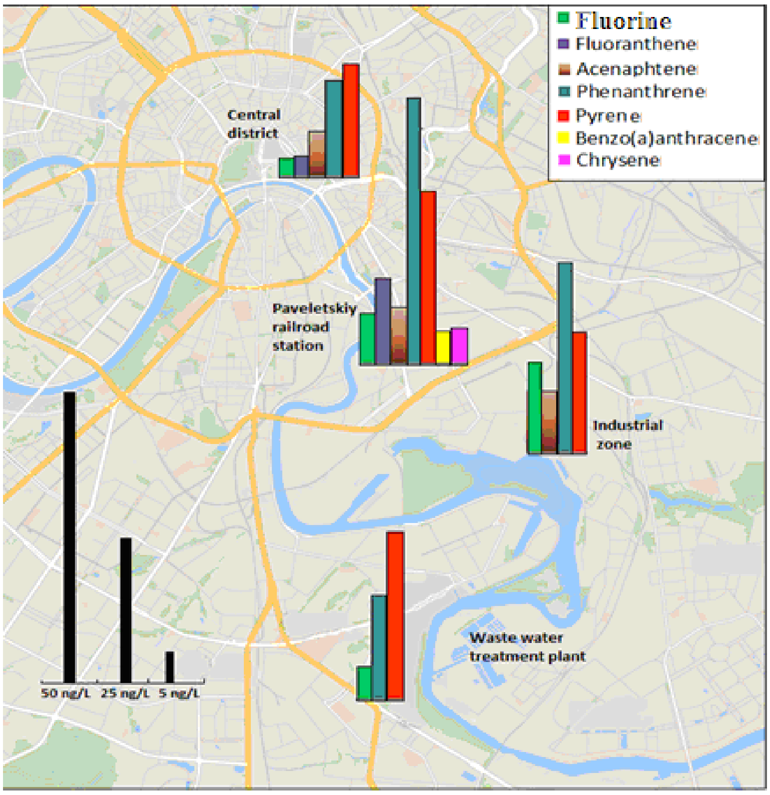

Figure 2. PAHs contamination of the Moscow River water

Only four-ring and three-ring PAHs were presented in analyzed water samples. Three-ring PAHs were most abundant in the water samples 1, 2, 3, accounting for 54 %, 53% and 74 % of ΣPAHs respectively, in contrast with the sample 4, where the abundance of four-ring PAHs is 55%. The absence of high-ring PAHs in water samples can be explained by their low vapor pressure and low water solubility.

OCPs and PCBs distribution in water samples of the Moscow River

Among 11 analyzed OCPs only triclosan was found in the sampling point 4 (51.1±10.4 ng/l). Concentrations of methoxychlor, mirex, α-Hexachlorocyclohexane, o,p-Dichlorodiphenyldichloroethylene, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180 were lower detection limits in all water samples.

Triclosan structure is similar to dioxins, therefore exhibits similar properties such as persistence and bioaccumulation. An environmental half-life of triclosan on the order of 540 days upon deposition in aquatic sediment as suggested the quantitative structure activity relationship (QSAR) models [45]. Due to the use of triclosan in household products of daily use, it can be found in the influents of wastewater treatment plant. It was found that only a part of triclosan can be removed from wastewater during the treatment, while another part can adsorb on the sludge or exits the plant with treated water. It was determined that triclosan concentration in wastewater treatment plants effluents entering the natural water sources ranged from 42-213 ng/L [46].

Because of the proximity of municipal wastewater treatment plant to the sampling site 4 (Figure 3), it may be considered as the source of triclosan contamination of the Moscow River. The main problems connected with triclosan presence in aquatic environment are its toxicity for aquatic organisms and formation of chlorinated dibenzo-p-dioxin congeners during environmental transformation [47].

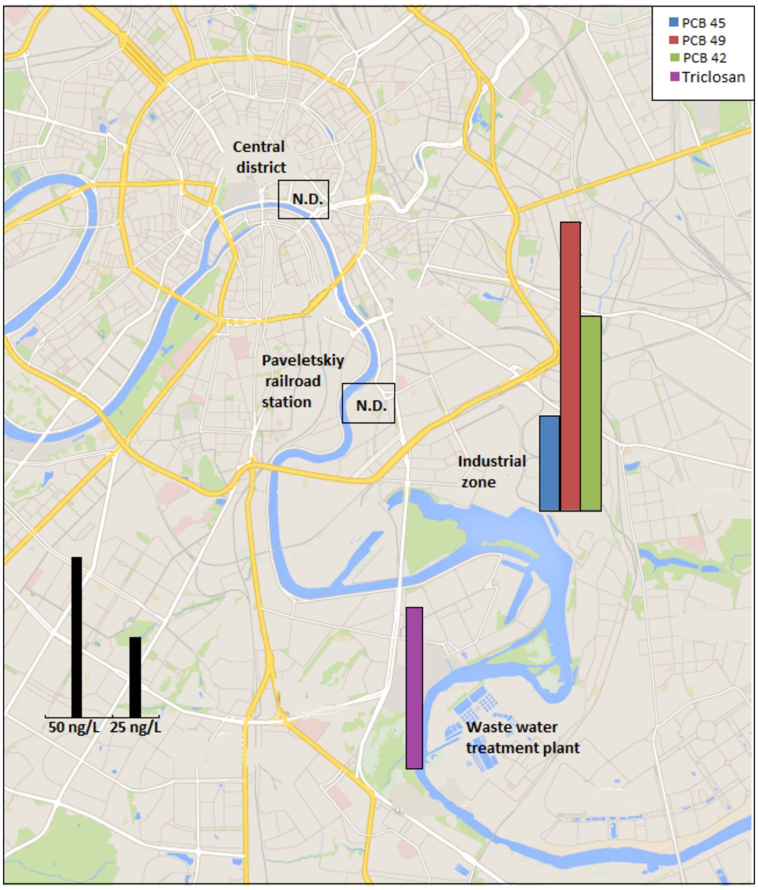

Figure 3. PCBs and OCPS contamination of the Moscow River water

Six European indicator PCB congener (IUPAC № 28, 52, 101, 138, 153 and 180) were not detected in analyzed water samples. As expected, less toxic and low-chlorinated PCBs congeners (IUPAC № 42, 45, 49) were found in water of the sample point 3 (PCB 45 = 29,8±5.8 ng/l; PCB 42= 60.6±3.9 ng/l; PCB 49 = 90,3±4.2 ng/l). According to Shelepchicov et al. the PCBs contamination is typical for the soils in different parts of the Moscow region with extremely high concentrations. Due to the possibility of PCBs leaching from a soil with ground water, rainfalls or runoffs, the presence of low-chlorinated PCBs, determined in this study, can be an indicator of sediments and bank soil contamination with high-chlorinated toxic PCBs. Because there are no known natural PCBs sources, the source of water contamination with PCBs could be the industrial zone on the bank area of the Moscow River nearby the sampling point 3.

PAEs distributions in water samples of the Moscow River

Among 7 analyzed PAEs only 5 were determined in water samples of the Moscow River: Di-n-butyl phthalate (DBP), Di(2-ethylhexyl) phthalate (DEHP), Diisobutyl phthalate (DiBP), n-butyl-isobutyl phthalate (nBiBP) and n-Pentylbenzyl phthalate (PBzP) (see Figure 4). DEHP, DBP and nBiBP were found in all analyzed samples.

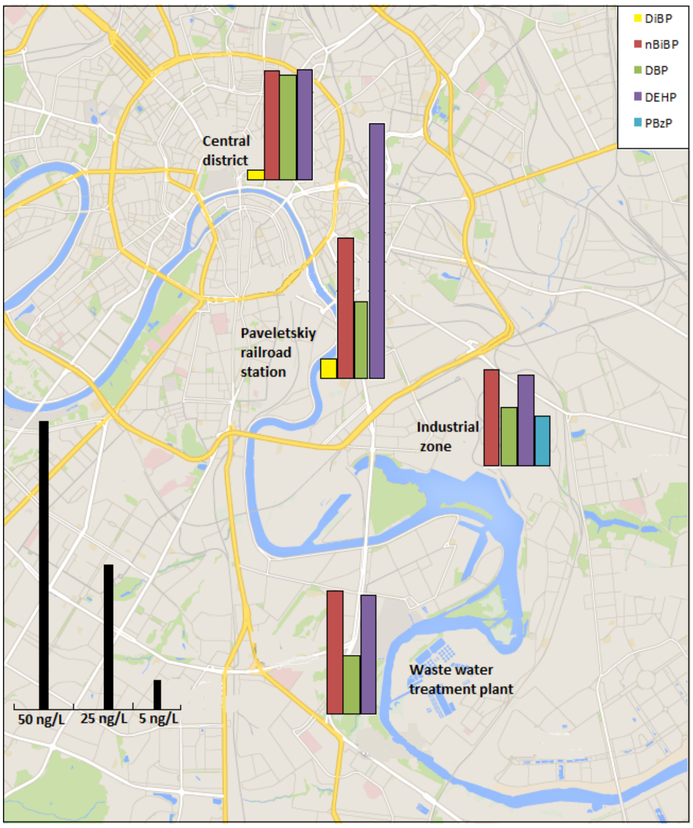

Figure 4. PAEs contamination of the Moscow River water

It is worth mentioning that DBP and nBiBP concentrations are almost equal in all analyzed samples (Table 2). This fact indicates that there is a background contamination of the Moscow River, which is not associated with nearby land use. The DEHP concentration increases along the river flow, reaches maximum at the sampling point 2 and at the sampling points 3 decreases to the level as at the sampling point 1. The DiBP contamination present only in the sampling points 1 and 2 and the PBzP was found only in the sampling point 4.

Table 2: River water PAEs concentrations (average±standard deviation; n=2)

	Compound	Concentration, ng/l			
		Sample 1	Sample 2	Sample 3	Sample 4
1	DBP	18.1±0.6	13.2±1.4	10.1±1.6	10.1±0.8
2	DEHP	18.7±0.9	43.7±0.2	15.7±3.3	20.4±2.7
3	DiBP	1.8±0.6	3.5±0.9	<LOD	<LOD
4	nBiBP	18.8±1.7	24.1±2.4	16.6±0.4	21.2±2.7
5	PBzP	<LOD	<LOD	8.7±1.5	<LOD
	Σ	57.4	84.5	51.1	51.7

Figure 5 shows the distribution of ΣPAHs, ΣOCPs, ΣPCBs and ΣPAEs in the water samples along the direction of the Moscow River flow.

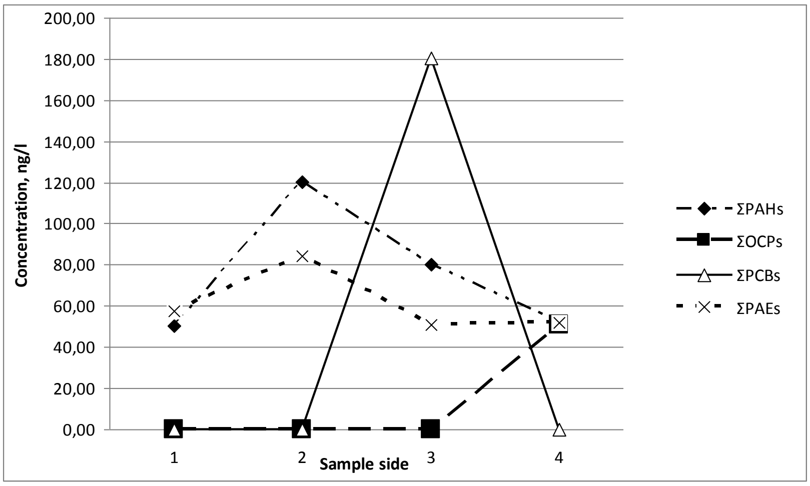

Figure 5. Distribution of ΣPAHs, ΣOCPs, ΣPCBs and ΣPAEs along the direction of the Moscow River flow

Concentration of ∑PAHs varies between the sampling sites. Higher concentrations were observed at the sampling side 2 in the urban area nearby Paveletskiy railroad station. Therefore the concentration of total PAHs gradually decreases along the direction of the Moscow River flow and at sample point 4 reaches the same concentration as before industrial zone (sampling point 1).

OCPs and PCBs were found only in samples point 3 and 4, respectively.

The total PAEs concentration is the highest at the sampling point 2. The total PAEs concentrations in other sampling points are almost equal. It can be possible that there is an input of contaminates in the Moscow River between the sampling sites 1 and 2.

CONCLUSION

By this work, we contribute the documentation of the water contamination by chemicals that were poorly investigated until now in the Moscow River basin. This study shows the impact of urbanized areas on the contamination of the Moscow River water. PAHs, PCBs, OCPs and PAEs concentrations in water sample were determined.

PAHs concentrations in water phase of the Moscow River range from 50.6 to 120.1 ng/l. Only four-ring and three-ring PAHs were presented in analyzed water samples. Higher PAHs concentration was observed at the sampling side in the urban area nearby Paveletskiy railroad station and then gradually decreases along the direction of the Moscow River flow. Determined in this study PAHs concentrations in water of the Moscow River are comparable to those measured in other world’s urban rivers, with the exception of benzo (a)anthracene and chrysene. Concentrations of benzo (a)anthracene and chrysene in the Moscow River are higher, than in other world’s rivers, except the Danube River where the data are comparable. The PAHs contamination sources were determined with the use of characteristic ratio. It was determined that petroleum sources are responsible for the PAHs contamination of all water samples. The sample point 2 is also characterized by combustion source of contamination.

Among 11 analyzed OCPs only triclosan was found in the sampling point near wastewater treatment plant. Due to the fact that trichlosan is presented in effluents of wastewater treatment plants, they can be sources of river water contamination. Measured in this study triclosan concentration is in accordance with contamination levels of world’s rivers.

European indicator PCB congener (IUPAC № 28, 52, 101, 138, 153 and 180) were not detected in analyzed water samples. As expected, less toxic and low-chlorinated PCBs congeners (IUPAC № 42, 45, 49) were found in water sample near large industrial area. The presence of low-chlorinated PCBs, determined in this study, can be an indicator of sediments and bank soil contamination with high-chlorinated toxic PCBs. Different PCBs congeners can be found in water of rivers all over the world, nevertheless the presence of low-chlorinated PCBs, as PCB 42, PCB 45 and PCB 49, in river water are not well studied. The PCB 49 congener concentration in the Moscow River corresponds to the maximum concentration of this congener in the Minjiang River Estuary that is considered as heavily polluted with PCBs.

PAEs were determined in all samples of the Moscow River water. DBP and nBiBP concentrations are almost equal in all analyzed samples. This can be associated with the background contamination of the Moscow River, which is not depended on nearby land use. However, determined PAEs level in the water of the Moscow River are much lower than those in rivers in other parts of the world.

It is planned to determine the seasonal variation of analyzed substances and their presence in another compartment, such as bank soil and sediments, for better understanding of environmental fate and sources of the Moscow River water contamination.

REFERENCES

Wilcke W, Krauss M, Safronov G et al. (2006) *Environmental Pollution, Vol 141*, 327-335
Wilcke W, Krauss M, Safronov G et al. (2005) *Environ. Qual., Vol 34*,1581–1590
Shelepchikov AA, Brodskii ES, Feshin DB et al. (2011) *Eurasian Soil Science , Vol 44,* 286–296
Teil M-J, Tlili K, Blanchard M et al. (2014) *Arch Environ Contam Toxicol, Vol 66*, 41–57
Hawliczek A, Nota B, Cenijn P et al. (2011) *Reprod Toxicol,* doi:10.1016/j.reprotox.2011.11.001
DellaTorre C,Mariottini M,Malysheva A et al.(2013)*Ecotoxicology and Environmental Safety,Vol 94*,104–111
Okay OS, Karacık B, Basak S et al. (2009) *Chemosphere, Vol 76*, 159–166
Schmid P, Gujer E, Zennegg M et al. (2005) *Chemosphere, Vol 58,* 227–234
Thevenon F, Felippe de Alencastro L, Loizeau J-L et al. (2013) *Chemosphere, Vol 90*, 2444–2452
Gong Y, Depinto JV, RHEE G-Y et al., (1998) *Wat. Res., Vol 32,* 2507-2517
Ondarza PM, Gonzalez M, Fillmann G et al. (2014) *Chemosphere, Vol 94*, 135–142
Renaud CB, Alfonso N, Kaiser KLE et al. (2004) *Qual. Res. J. Canada , Vol 39*, 75–82
Zhou Q , Wu W, Xiao J (2013) *International Journal of Environmental Analytical Chemistry,Vol 93*, 894-905
Howell NL, Lakshmanan D, Rifai H et al. (2011) *Science of the Total Environment, Vol 409*, 1867–1888
Qumerais B, Lemieux C, Lum KR (1994) *Chemosphere, Vol 28,* 947-959
Cailleaud K, Forget-Leray J, Souissi S et al. (2007) *Chemosphere, Vol 70*, 270–280
Manoli E, Samara C (1999) *Trends in analytical chemistry, Vol 18,* 417-428
Nagy AS, Simon G, Vass I (2012) *Nova Biotechnologica et Chimica, Vol 11-1*, 27-35
Bourgeault A, Gourlay-Francé C (2013) *Science of the Total Environment, Vol 454–455,* 328–336
Gateuille D, Evrard O , Lefevre I et al. (2014) *Science of the Total Environment, Vol 470–471*, 608–617
Jin G, Cong L, Fang Y et al.(2012) *Atmospheric Environment, Vol 60*, 298-304
Li J, Cheng H, Zhang G et al. (2009) *Environmental Pollution, Vol 157*, 273–279
Ma W-L, Liu L-Y, Qi H et al. (2013) *Environ Monit Assess, Vol 185*, 8399–8409
Patrolecco L, Ademollo N, Capri S et al. (2010) *Chemosphere, Vol 81*,1386–1392
Yunkera MB, Macdonaldb RW, Vingarzanc R et al. (2002) *Organic Geochemistry, Vol 33*, 489–515
Zhang K, Liang B, Wang J-Z et al. (2012) *Environmental Pollution, Vol 167,* 78-84
Magdouli S, Daghrir R, Brar SK et al. (2013) *Journal of Environmental Management, Vol 127*, 36-49
Meng X-Z, Wanga Y, Xianga N et al. (2014) *Science of the Total Environment, Vol 476–477,* 242–249
Xie Z, Ebinghaus R, Temme C et al. (2007) *Environ. Sci. Technol., Vol 41*, 4555-4560
Bergé A, Cladière M, Gasperi J et al. (2013) *Environ Sci Pollut Res , Vol 20*, 8057–8076
Dargnat C, Teil M-J, Chevreuil M et al. *Science of the total environment, Vol 407*, 1235-1244
Dévier M-H, Le Menach K , Viglino L et al. *Science of the Total Environment, Vol 443,* 621–632
Gao D, Li Z, Wen Z et al. (2014) *Chemosphere, Vol 95,* 24–32
Gibson R, Wang M-J, Padgett E et al. (2005) *Chemosphere, Vol 61*,1336–1344
Magdouli S , Daghrir R , Brar SK et al. (2013) *Journal of Environmental Management, Vol 127,* 36-49
Suzuki T, Yaguchik K, Suzuki S et al. (2001) *Environ. Sci. Technol., Vol 35*, 3757-3763
Vikelsøe J, Thomsena M, Carlsenb L (2003) *The Science of the Total Environment , Vol 296*,105–116
Zuo Y, Zhang K, Wua J et al. (2011) *Chemosphere, Vol 83*, 1014–1019
Montero L , Popp P, Paschke A et al. (2004) *Journal of Chromatography A, Vol 1025*, 17–26

Popp P, Paschke A (1997) *Chromatographia, Vol 46,* 419-424.
Paschke A, Brümmer J, Schüürmann G (2007) *Anal Bioanal Chem, Vol 387*,1417–1421
Van Pinxteren M, Paschke A, Popp P (2010) *Journal of Chromatography A, Vol 1217*, 2589–2598
Brooks, Kenneth Res. Pap. FPL-RP-617. Madiso M, 2004, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 53 p.
Ikarashi Y, Kaniwa M-A, Tsuchiya T (2005) *J. of Health Science, Vol 51*, 597-606
Heidler J, Halden RU (2007) *Chemosphere, Vol 66,* 362–369
Singer H, Müller S, Tixier C et al. (2002) *Environ. Sci. Technol., Vol 36,* 4998-5004
Zhao J-L, Zhang Q-Q, Chen F et al. (2013) *Water research, Vol 47,* 395-405

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SUSTAINABLE TREATMENT PROCESS FOR HIGH-STRENGTH INDUSTRIAL WASTEWATERS BY THE APPLICATION OF COMPOSITE COAGULANTS

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ABSTRACT

High-strength industrial wastewater usually contains large concentration of recalcitrant compounds and the coagulation/flocculation process may represent an appropriate technique for their treatment. Composite coagulants (PSiFAC) were produced in this study under various conditions and their efficiency was examined for the treatment of three industrial wastewater samples: (1) a tannery wastewater; (2) Yeast production wastewater, subjected to preliminary anaerobic treatment; and (3) subjected to preliminary anaerobic & aerobic treatment. Certain flocculant aids were added, such as an anionic polyelectrolyte or a combination of an inorganic coagulant and an anionic polyelectrolyte in one unique reagent (PAPEFAC). The optimum treatment of selected wastewaters by various coagulants was carried out; the addition of 100 mg/L PSiFAC in yeast wastewater resulted to a reduction of COD between 21-52%, of turbidity 35-40% and of phosphates 38-42%, respectively; in comparison with 8-20%, 40-46% and 27-41% respectively, with the use of polyelectrolyte. However, higher removal rates were obtained by the same PSiFAC dose in tannery wastewater, resulting to a reduction of COD 50%, 81% of turbidity and 62% of phosphates; compared to 51%, 81% and 52% respectively, with the use of polyelectrolyte; as a result additional cost benefits may arise, including the avoidance of specific equipment for handling the polyelectrolyte.

Key words: *composite coagulants, high strength wastewaters, polyelectrolyte.*

INTRODUCTION

Domestic and industrial wastewaters can contain large concentration of recalcitrant compounds, rather high concentrations of phosphorous, nitrogen and other carbonaceous contaminants that are essential nutrients for the growth of organisms. However, many industrial and food process waste streams are inherently high in nutrients content, and their treatment by the application of simple biological processes is usually not sufficiently effective, resulting to a treated effluent of low quality causing severe eutrophication problems. Very important is considered the case of phosphorous (usually in the form of orthophosphates), which has to be removed efficiently from wastewaters (Kelley & Handley, 2011).

The application of physicochemical pretreatments to industrial wastewater improves the water quality while enhancing the biodegradability. Chemical coagulation is employed to remove suspended colloidal particles within the 0.1-1-nm size range that do not settle out on standing and cannot be removed by conventional physical processes (Metcalf & Eddy, 2003; Eckenfelder, 1999). Chemical coagulation/flocculation (C/F) is an effective and commonly used wastewater treatment option. It involves the addition of chemicals such as alum or ferric salts that coat the colloid with Al^{3+} or Fe^{3+} ions and form positively charged micro-flocs.

THEORY

The Inorganic Polymeric Flocculants (IPFs), or pre-polymerized coagulants, such as polyaluminum chloride (PACl) represent a relatively new category of coagulation reagents, which was developed in order to increase the efficiency of coagulation/flocculation (C/F) process, but there is still need for further improvement of their properties (Sinha et al., 2004; Crittenden et al., 2005).

More recently, composite polymeric aluminum products, such as PASiC (aluminum-silicate polymer composite) (Gao et al., 2002; Zouboulis & Tzoupanos, 2009) and Polyferric silicate sulphate (PFSiS) (Zouboulis & Moussas, 2008)**,** have been also tested in laboratory experiments, as well as in full-scale applications. Latterly, several investigators (Gao et al., 2006; Niu et al., 2011; Sun et al., 2011; Li et al., 2013) have studied the simultaneous addition of Al (III), Fe (III) and polysilicic acid solution (pSi) and the coagulation efficiency of poly-aluminum-ferric-silicate-chloride is mainly affected by the Al/Fe/Si ratio and the respective preparation techniques.

Additionally, synthetic polyelectrolytes have been utilized in C/F process for water purification for more than four decades. Due to their wide usage, it is not surprisingly to consider them as alternative additives in the pre-polymerized coagulants composition for the production of new modified coagulation reagents (Zouboulis & Moussas, 2008).

The aim of this study was the examination of the effectiveness of C/F process using polyaluminum ferric-silicate-chloride coagulants and an anionic polyelectrolyte (Magnafloc-LT 25) as the flocculant aid for the treatment of wastewater samples. Furthermore, the combination of coagulant and polyelectrolyte in one unique reagent was examined in order to increase further their flocculation efficiency, by replacing the inorganic polysilicate additive with the organic polyelectrolyte in their structure. Hence, providing the respective comparison results for the coagulation performance of all the prepared coagulants, applied in wastewater treatment.

METHODS

All chemical reagents used were analytically pure chemicals. De-ionized water with conductivity lower than 0.5 mS/cm was used to prepare all the solutions, except of the solutions used for the preparation of coagulants. In this case, de-ionized water made carbonate free by boiling, was used.

Procedure for the preparation of composite coagulants

Composite polyaluminum ferric silicate chloride (PSiFAC) coagulants were produced in this work at room temperature, according to a procedure proposed by Tolkou et al., 2014a, under various experimental conditions. The used initial solutions were 0.5 M $AlCl_3{\cdot}6H_2O$ (Merck), 0.5 M $FeCl_3.6H_2O$ (Merck), 0.5 M NaOH (Merck) - as the added base - and the prepared polysilicic acid solution (pSi), according to Tzoupanos et al., 2009. The most effective coagulant obtained during preliminary experiments (Tzoupanos et al., 2009; Tolkou et al., 2014a, 2014b), i.e. $PSiFAC_{1.5\text{-}10\text{-}15}$, was used in this study.

A poly-acrylamide co-polymer (Magnafloc LT-25, Ciba SC LTD, commercially available) as an anionic polyelectrolyte (APE) was obtained (0.01 % w/v) and used both as the flocculant aid (in [Al]/[APE] = 10 molar ratio) and the organic additive for the synthesis of composite coagulants (PAPEFAC). The specific polyelectrolyte is commonly used as a flocculant aid in water or wastewater treatment plants, especially in Greece (Mortimer, 1991; Bolto, 1995). Table 1 presents the preparation conditions of all prepared coagulants.

Table 1: Preparation conditions of all laboratory prepared coagulants

Coagulant type	Molar ratios	Procedure
$PSiFAC_{1.5:10:15}$	[OH]/[Al]: 1.5 [Al]/[Fe]: 10 [Al+Fe]/[Si]: 15	Co-polymerization technique: Appropriate amount of $FeCl_3$ solution was added in $AlCl_3$ solution, under vigorous stirring. Then, the resulted FpA solution was added to pSi solution at desired ratios of [Al+Fe]/[Si] and base solution was added slowly (under magnetic stirring) in the mixture at the desired [OH]/[Al] molar ratio.
$PAPEFAC_{1.5-10-15}$	[OH]/[Al]: 1.5 [Al]/[Fe]: 10 [Al+Fe]/[APE]: 15	Co-polymerization technique: Appropriate amount of $FeCl_3$ solution was added in $AlCl_3$ solution, under vigorous stirring. Then, the resulted FpA solution was added to APE solution at desired ratios of [Al+Fe]/[APE] and base solution was added slowly (under magnetic stirring) in the mixture at the desired [OH]/[Al] molar ratio.

Coagulation performance

The pH was measured by using a Metrohm Herisau pH-Metre, the conductivity by using a Crison CM 35 Conductivity Metre and the turbidity measurements were performed by a HACH RATIO/XR Turbidimeter. The UV absorbance at 254 nm, as a convenient indicator of natural organic matter presence, was measured with a Shimadzu UV/Vis spectrophotometer, by using a 1 cm path length quartz cuvette.

Jar-tests

Jar tests were used for the examination of coagulants’ efficiency and the conditions used are shown in Table 2 (Moussas et al., 2011). A jar-test apparatus (Aqualytic) equipped with six paddles was used, employing 1 L glass beakers. Three types of samples were used: (1) a tannery wastewater; (2) Yeast production wastewater, subjected to preliminary anaerobic treatment; and (3) subjected to preliminary anaerobic & aerobic treatment. The properties of all samples are given in the following Table 3.

Table 2: Operating conditions of coagulation experiments

Type of treatment	Rapid mixing period		Slow mixing period		Sedimentation
	Duration (min)	Mixing rate (rpm)	Duration (min)	Mixing rate (rpm)	(min)
Wastewater samples	3	200	30	40	45

Table 3: Major physico-chemical properties of initial wastewater samples

Type of wastewater to be treated	Turbidity (NTU)	Absorbance $UV_{254\ nm}$	COD (mg/L)	Phosphates (mg/L)
Tannery Wastewater	668	2.981	6800	1.76
Yeast wastewater (after anaerobic treatment)	418	3.748	11455	3.49
Yeast wastewater (after anaerobic & aerobic treatment)	143	3.307	4590	2.40

Water samples were collected from the supernatant of each beaker and were analyzed for the determination of: turbidity, absorption at UV_{254nm} that provides an indication of the amount of natural organic matter (NOM, COD (mg/L), and phosphates (mg/L).

Residual contaminant measurements

The residual percentage (RX, %) was expressed as “(1)” :

$$\mathrm{RX}(\%) = (\mathrm{X}/\mathrm{X}_0) \times 100\% \quad (1)$$

where X and X_0 are the parameters (turbidity, absorption at UV254nm, COD, and phosphates) of the treated and raw wastewater, respectively.

FINDINGS & DISCUSSION

Table 4 displays the major physicochemical properties of laboratory prepared composite coagulants. It can be observed that the addition of pSi in an Al-Fe solution (FpA) to induce the formation of composite coagulants, results in the increase of turbidity, in comparison with the addition of APE in the same FpA solution.

Table 4: Properties of laboratory prepared coagulant

Coagulant type	pH	Turbidity (NTU)	Conductivity (mS/cm)
$PSiFAC_{1.5\text{-}10\text{-}15}$	3.7	218.0	26.0
$PAPEFAC_{1.5\text{-}10\text{-}15}$	3.6	137.0	27.0

The most effective coagulant dosage of $PSiFAC_{1\text{-}5\text{-}10\text{-}15}$, obtained during preliminary experiments (Tolkou et al., 2014b), i.e. 100 mg Al/L, as shown in Figure 1, for tannery wastewater sample, was applied for the treatment of the aforementioned wastewater samples to evaluate its coagulation efficiency against these (considered as) relatively high-strength industrial wastewaters.

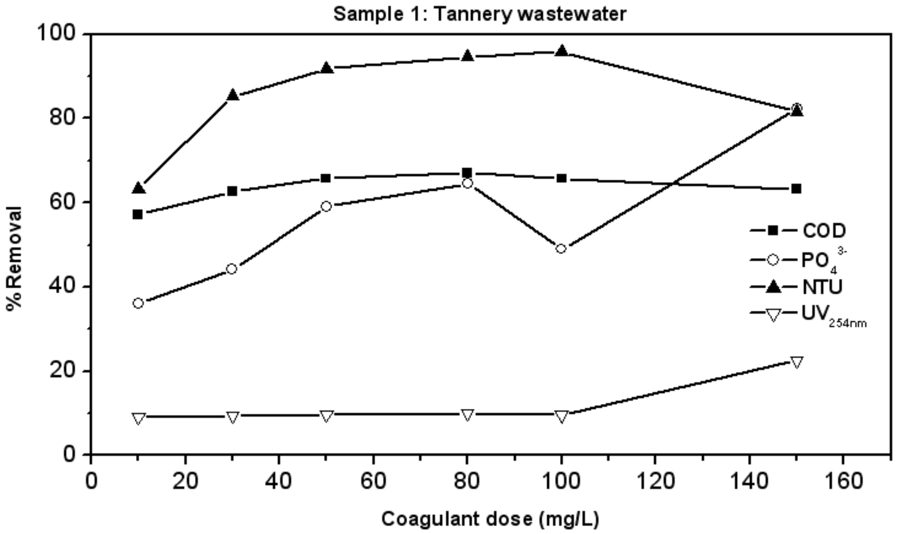

Figure 1. Coagulation experiments for tannery wastewater

The results of coagulation experiments for (%) turbidity, absorption at UV_{254nm}, COD and phosphates removals of wastewater samples are given in Figure 2; the experimental results indicated that, the addition of 100 mg/L of $PSiFAC_{1.5\text{-}10\text{-}15}$, either with or without the addition of the flocculant aid (polyelectrolyte), in tannery wastewater, resulted to a reduction of COD 67%, and 96% for turbidity and 62% for phosphates. Although regarding the UV absorbance at 254 nm, the rates were found to be rather small (10%), as the wastewater sample was not subjected to any pre-treatment stage this is a highly contaminated sample, but coagulation was beneficial to the improvement of its quality.

Additionally, in yeast wastewater the addition of the same $PSiFAC_{1.5\text{-}10\text{-}15}$ dose resulted to a reduction of COD 56%, of turbidity 40%, of UV_{254nm} absorbance 25% and of phosphates 43%; and to a reduction of COD 22%, of turbidity 14%, of UV_{254nm} absorbance 15% and of phosphates 38% respectively to samples 2 and 3. However, from the Figure 2, it is obvious that higher removal rates were obtained when the coagulant and polyelectrolyte were combined in one unique reagent ($PAPEFAC_{1.5\text{-}10\text{-}15}$), but regarding COD removal, the use of $PSiFAC_{1.5\text{-}10\text{-}15}$ without the addition of the flocculant aid (polyelectrolyte), exhibits better and incomparable results.

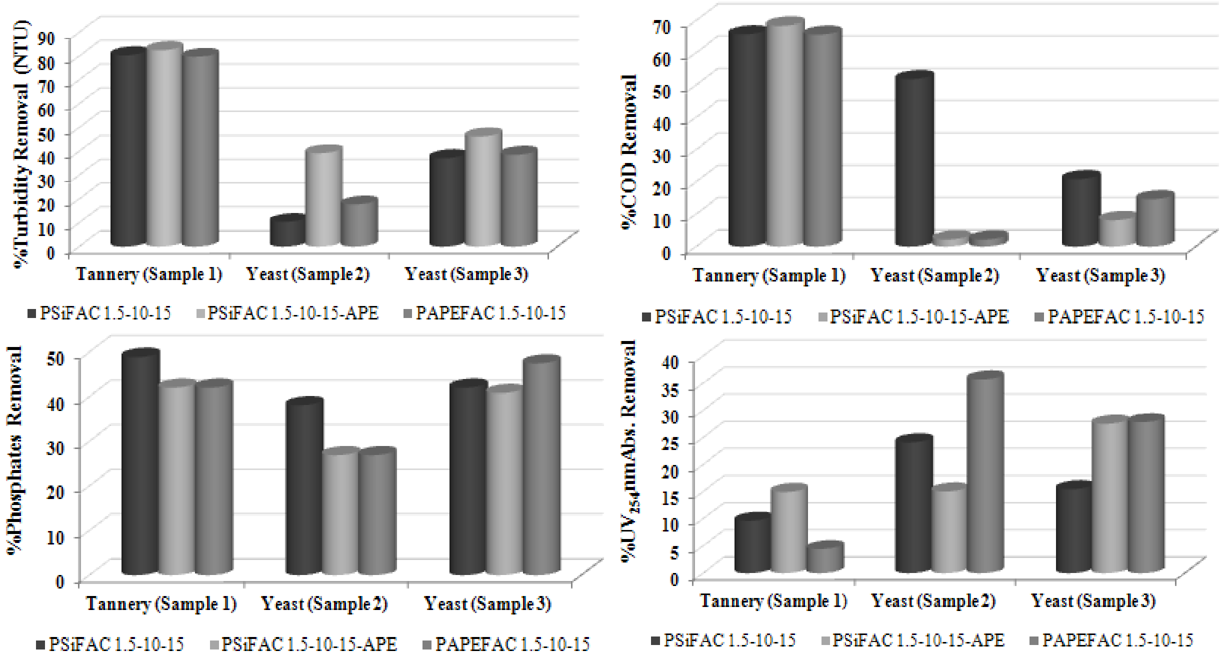

Figure 2. Residual contaminants percentage of the laboratory prepared coagulants (100 mg Al/L) for (1) tannery wastewater; (2) yeast wastewater (after anaerobic treatment); and (3) yeast wastewater (after anaerobic & aerobic treatment)

CONCLUSIONS

In this study, composite polyaluminum ferric silicate chloride (PSiFAC) coagulants were manufactured and their efficiency was studied for treatment of high-strength industrial wastewaters, such as those from tanneries, or from yeast-production (fermentation) plants, as the appropriate and effective coagulant, applied to a developed hybrid MBR system for the control of membrane fouling. At the same time was studied the contribution of polyelectrolyte during the C/F process by two different types of process application; in the first type the polyelectrolyte was added in the sample as flocculation aid and in the second one the coagulant and polyelectrolyte were combined in one unique reagent (PAPEFAC) in order to increase further their flocculation efficiency. The coagulants proved to be quite effective, depending upon the specific wastewater properties; therefore, the addition of 100 mg/L of $PSiFAC_{1.5:10:15}$ in yeast wastewater resulted to a reduction of COD between 22-56%, of turbidity 14-40%, of UV_{254nm} absorbance 15-25% and of phosphates 38-43%, respectively, but higher removal rates were obtained in tannery wastewater (COD 67%, turbidity 96%, phosphates 62%, UV_{254nm} 10%). Conclusively, it was found that the $PSiFAC_{1.5:10:15}$, either with or without the addition of the flocculant aid (polyelectrolyte), provided a better effectiveness of the C/F process, especially regarding COD removal. As a result additional cost benefits may arise by the utilization of this material (i.e. $PSiFAC_{1.5\text{-}10\text{-}15}$), including the avoidance of specific equipment for handling the polyelectrolyte (e.g. dissolution, pumping system). In this way, the overall treatment procedure is simplified and the overall cost-effectiveness is also improved.

IMPLICATIONS

A Membrane Bioreactor (MBR) treatment system can be also effectively applied. The major problem during the operation of any MBR system is membrane fouling. Thus, the ultimate aim of this study is the development and application of efficient alternative composite coagulants to control fouling in membrane bioreactors.

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REFERENCES

Bolto B.A. (1995). Soluble polymers in water treatment. *Progress in Polymer Science*, 20 (6), 987-1041.

Crittenden J.C., Truddel R.R., Hand D.W. & Howe K.J., Tchobanoglous G. (2005). Coagulation, mixing and flocculation, in Water Treatment: Principles and Design. *John Wiley & Sons, 2nd ed.*, New Jersey, 664–691.

Eckenfelder W. (1999). Industrial Water Pollution Control; McGraw-Hill: New York.

Gao B.Y., Yue Q.Y. & Wang. B.J. (2006). Properties and coagulation performance of coagulant poly-aluminum-ferric-silicate-chloride in Water and Wastewater Treatment. *Journal of Environmental Science and Health Part A*, 41, 1281–1292.

Gao B., Hahn H. & Hoffmann E. (2002). Evaluation of aluminum–silicate polymer composite as a coagulant for water treatment. *Water Research*, 36, 3573–3581.

Kelley D. & Handley R.D. (2011). Compositions and methods for wastewater treatment. US7931822.

Li R., He C. & He Y. (2013). Preparation and characterization of poly-silicic-cation coagulants by synchronous-polymerization and co-polymerization. *Chemical Engineering Journal*, 223, 869-874.

Metcalf & Eddy (2003). Wastewater Engineering: Treatment and Reuse; McGraw-Hill: New York.

Mortimer D.A. (1991). Synthetic polyelectrolytes: A review. *Polymer International*, 25 (1), 29-41.

Moussas P.A., Tzoupanos N.D. & Zouboulis A.I. (2011). Advances in coagulation/flocculation field: Al- and Fe based composite coagulation regents. *Desalination and Water Treatment*, 33, 140-146

Niu X., Li X., Ren Y. & Yang Y. (2011). Preparation and coagulation efficiency of polyaluminum ferric silicate chloride composite coagulant from wastewater of high-purity graphite production. *Journal of Environmental Sciences*, 23(7), 1122–1128.

Sinha S., Yoon Y., Amy G. & Yoon J. (2004). Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes. *Chemosphere*, 57 (9), 1115–1122.

Sun T., Sun C.H., Zhu G.L., Miao X.J., Wu C.C., Lv S.B. & Li W.J (2011). Preparation and coagulation performance of poly-ferric-aluminum-silicate-sulfate from fly ash. *Desalination*, 268, 270–275.

Tolkou A. & Zouboulis A. (2014a). Synthesis and coagulation performance of composite poly-aluminum-ferric-silicate-chloride coagulants in water and wastewater treatment. *Desalination Water Treatment*, DOI:10.1080/19443994.2014.933614.

Tolkou A., Zouboulis A. & Peleka E. (2014b). Novel pre-polymerized coagulant agents used for the treatment of industrial wastewaters. In*: 1st IWA Specialized International Conference “EcoSTP- Eco Technologies for Wastewater Treatment*”, Verona, 23-27 June.

Tzoupanos N., Zouboulis A. & Tsoleridis C. (2009). A systematic study for the characterization of a novel coagulant (polyaluminum silicate chloride). *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 342, 30–39.

Zouboulis A. & Tzoupanos N. (2009). Polyaluminum silicate chloride – A systematic study for the preparation and application of an efficient coagulant for water or wastewater treatment. *Journal of Hazardous Materials*, 162, 1379-1389.

Zouboulis A. & Moussas P. (2008). Polyferric silicate sulphate (PFSiS): Preparation, characterization and coagulation behavior. *Desalination*, 224, 307–316.

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DEGRADATION OF PIROXICAM BY ELECTROCHEMICAL OXIDATION AT DSA ELECTRODES

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ABSTRACT

The presence of pharmaceuticals in water is undesirable because of their adverse effects on aquatic organisms even in concentration of ng-µg/L. This paper dealt with the degradation of piroxicam (PXC), a nonsteroidal anti-inflammatory drug (NSAID), by electrochemical oxidation at dimensionally stable anodes (DSA). Two compositions of DSA were used: Ti/RuO2-TiO2 and Ti/RuO2/SnO2-Sb2O5-RuO2. Current densities of 200 and 300 A/m2 were applied for electrolyses time of 60, 120 and 180 minutes in neutral or basic medium. The ultraviolet (UV) spectra of the electrolysed solutions were recorded and total organic carbon (TOC) analyses were carried out to assess the degradation process. The most effective in degradation of PXC was the anodic composition Ti/RuO2-TiO2 in basic medium.

Key words: *degradation, dimensionally stable anodes, electrochemical oxidation, piroxicam.*

INTRODUCTION

Pharmaceuticals are used at large scale and their diversity increases yearly. They are a new class of emerging micropollutants and the concern regarding their presence in water is due to adverse effects towards aquatic organisms even at very low concentration. Pharmaceuticals pass almost unchanged through wastewater treatment plants. Thus, pharmaceuticals enter the water bodies through effluent discharge into aquatic ecosystems where may reach concentrations from ng/L to µg/L (Corcoll et al., 2014).

As a consequence it is strongly necessary to find new ways to remove the pharmaceuticals from wastewaters. Electrochemical technologies are very promising because of their advantages: (a) electrons are clean reagents; (b) effective control of the electron transfer rate (current density); (c) measurement of reaction conditions (current density and electrode potential); (d) the process can be turned on and off via the current; (e) can often use benign (e.g., ambient) conditions of temperature and pressure (Walsh, 2001).

The aim of this paper was the pharmaceuticals degradation by electrochemical oxidation at dimensionally stable anodes (DSA) in order to obtain effluents compatible with the environment. Piroxicam (PXC), a nonsteroidal anti-inflammatory drug, was chosen as model of pharmaceuticals.

THEORY

The areas of application for the electrochemical methods are the pretreatment of biorefractory organic pollutants and the removal of pollutants present at low levels of concentration (in which case traditional methods are affected by slow kinetics) (De Francesco and Costamagna, 2004).

The electrochemical techniques for wastewater treatment also involve electrochemical oxidation (Sires and Brillas, 2012). The electrochemical oxidation provides either the removal of biorefractory organic pollutants or can induce the biodegradability (Martínez-Huitle et al., 2004) and consequently it can be integrated as advanced treatment stage in conventional wastewater treatment schemes.

In this paper the degradation of biorefractory organic pollutants from wastewaters by electrochemical oxidation at DSA is approached. DSA are electrode materials that consist of a layer of conductive metal oxides with electrocatalytic properties deposited on titanium substrate. The introduction of the catalytic reaction in the electrochemical technology, known as electrocatalytic technology, not only causes a significant increase of the efficiency but increases the availability for biorefractory organic pollutants.

The active oxides of DSA are not absolutely the best electrocatalysts, but they are exceptional in terms of their versatility. Transition metal oxides are among the most versatile ever known electrocatalysts (Trasatti, 2000). Titanium, due to the excellent combination of mechanical properties, low density and resistance to corrosion is generally the most used substrate.

Initially designed for the clor-alkali industry, DSA are increasingly studied as electrode material for the electrochemical oxidation of organics. Among the compounds degraded by DSA or modified DSA in the papers are reported dyes (Basiri Parsa et al., 2013; Tavares et al., 2012) or textile effluents (Basha et al., 2012), herbicides (Aquino Neto et al., 2009; Zaviska et al., 2011), 2,4- dichlorophenol (Niu et al., 2013), nitrophenols (Adams et al., 2009) or pharmaceuticals active compounds (Santos et al., 2013).

METHODS

The degradation of PXC by electrochemical oxidation was carried out in a Plexiglas cell. Two DSA anodes and three stainless steel cathodes were used at 1 cm gap. Active surface area was 38 cm2. Experiments were carried out by applying current densities of 200 and 300 A/m2 at 60, 120 and 180 minutes of electrolysis and values of pH: 7 and 10, respectively.

The DSA electrodes had the compositions Ti/RuO2-TiO2 (molar ratio in the precursors solution 30:70) and Ti/RuO2/SnO2-Sb2O5-RuO2 (molar ratio in the precursors solution 94:3:3) and they were prepared by thermal decomposition of appropriate precursors. The DSA electrodes preparation was presented previously (Ihos et al., 2009; Ihos et al., 2011) with the notice that for Ti/RuO2/SnO2-Sb2O5-RuO2 in the mixture of the precursors was also introduced the precursor RuCl3.nH2O (Fluka).
Electrolyses were carried out in solutions of 50 mg/L and 200 mg/L PXC, respectively. The supporting electrolyte was 0.1 M Na2SO4. PXC (4-hydroxy-2-methyl-N-(2-pyridyl)-2H-1,2-benzothiazin-3-caboxyamid-1,1-dioxid) was produced by Nantong Jinghua Pharmaceutical Co. Ltd. The Na2SO4 and NaOH were supplied by Merck and they were reagent grade. The solutions were prepared with distilled water.

The process was followed by recording the UV spectra by using a Specord 205 - Analytik Jena spectrophotometer controlled by computer. TOC was monitored by a TOC analyzer (Shimadzu - TOC-VCPH) computer controlled.

FINDINGS

Fig. 1 shows the chemical structure of the PXC. In Fig. 2 are presented the UV spectra of PXC in 0.1 M Na2SO4 and of the electrolyzed solutions at various electrolysis time. The shape of spectra recorded for other concentration PXC and working conditions and is analogous to those presented in Fig. 2.

The maxima of absorbance of PXC are characteristic to benzene, pyridine and naphthalene derivates: a. ethylene bands with maxima at 193 and 206 nm, that overlap with that of sodium sulphate; b. bands of benzene, pyridine and thia-9-aza-bicycle rings at 253, 274, 280 nm; c. bands due to substituents and condensed ring at 357 and 363 nm [Balaban et al., 1983).

Tables 1-4 shows the UV absorbance bands evolution depending on PXC degradation. Based on data listed in Tables 1-4, the efficiencies of absorbance decrease were calculated corresponding to evolution of absorbance maxima depending on working conditions. These efficiencies are shown in Tables 5-8.

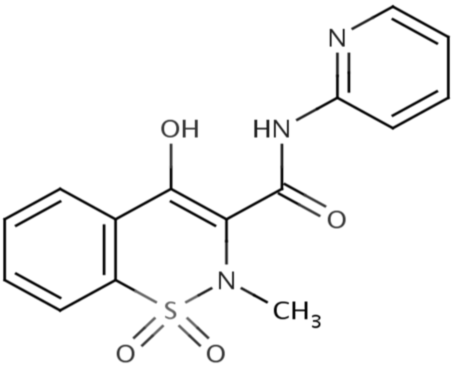

Figure 1. Chemical structure of PXC

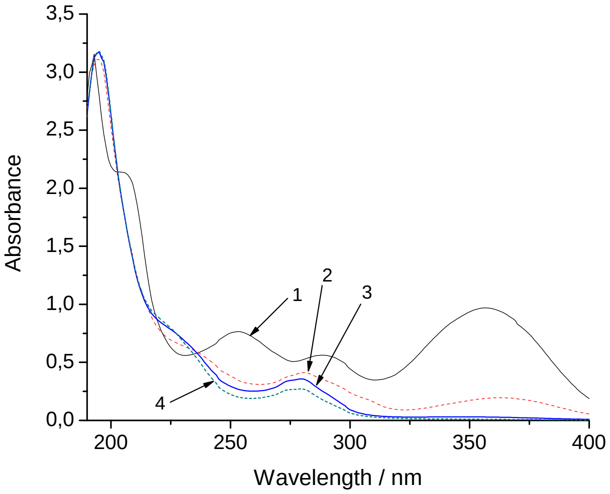

Figure 2. UV spectra of PXC in 0.1 M Na_2SO_4 anode: $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2; c_{ini}= 50 mg/L PXC; pH_{ini}: 7;current density: 200 A/m^2; 1-0 min; 2-60 min; 3-120 min; 4-180 min

Table 1: UV absorbance evolution during the degradation process of PXC at Ti/RuO2-TiO2 anodes and initial pH of 7

Anodic composition/ pHini	PXC concentration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance							
				193	206	253	274	280	288	357	363
			0	2.31	2.11	0.77	0.52	0.52	0.55	0.99	0.94
		200	60	2.87	1.68	0.38	0.41	0.45	0.39	0.20	0.21
			120	2.92	1.66	0.31	0.40	0.43	0.32	0.01	0.01
			180	2.87	1.63	0.25	0.34	0.36	0.25	0	0
	200		0	2.31	2.11	0.77	0.52	0.52	0.55	0.99	0.94
		300	60	2.91	1.69	0.37	0.42	0.44	0.36	0.15	0.15
Ti/RuO2-			120	2.92	1.65	0.24	0.31	0.33	0.23	0.01	0.01
TiO2 /			180	2.90	1.68	0.16	0.21	0.22	0.13	0	0
7			0	3.07	2.12	0.76	0.51	0.51	0.55	0.97	0.94
		200	60	3.15	1.75	0.31	0.37	0.41	0.37	0.13	0.14
			120	3.13	1.76	0.21	0.29	0.36	0.34	0.02	0.02
	50		180	3.15	1.73	0.22	0.30	0.31	0.21	0	0
			0	3.07	2.12	0.76	0.51	0.51	0.55	0.97	0.94
		300	60	3.12	1.70	0.32	0.38	0.40	0.31	0.09	0.09
			120	3.10	1.70	0.15	0.21	0.24	0.20	0	0
			180	3.07	1.70	0.12	0.17	0.17	0.09	0	0

Table 2: UV absorbance evolution during the degradation process of PXC at Ti/RuO2-TiO2 anodes and initial pH of 10

Anodic composition/ pHini	PXC concentration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance						
				193	206	253	274	280	288	355
			0	2.34	2.15	0.77	0.53	0.53	0.58	0.95
		200	60	2.91	1.75	0.42	0.46	0.49	0.40	0.19
			120	2.98	1.70	0.29	0.38	0.42	0.33	0,03
			180	2.94	1.66	0.25	0.33	0.35	0.24	0
	200		0	2.34	2.15	0.77	0.53	0.53	0.58	0.95
		300	60	2.87	1.63	0.33	0.37	0.38	0,31	0.14
			120	2.89	1.63	0.19	0.25	0.26	0.17	0.01
Ti/RuO2-			180	2.85	1.63	0.12	0.17	0.17	0.09	0
TiO2 / 10			0	3.15	2.19	0.76	0.52	0.53	0.58	0.92
		200	60	3.17	1.80	0.39	0.45	0.48	0.38	0.15
			120	3.14	1.75	0.20	0.28	0.34	0.32	0
	50		180	3.10	1.74	0.19	0.26	0.28	0.21	0
			0	3.15	2.19	0.76	0.52	0.53	0.58	0.92
		300	60	3.12	1.68	0.31	0.35	0.37	0.28	0.10
			120	3.08	1.68	0.17	0.23	0.24	0.15	0
			180	3.15	1.78	0.11	0.15	0.15	0.07	0.01

Table 3: UV absorbance evolution during the degradation process of PXC at Ti/RuO2/SnO2- Sb2O5-RuO2 anodes and and initial pH of 7

Anodic composition/ pHini	PXC concentration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance							
				193	197	206	253	280	288	357	363
			0	2.31	2.08	2.11	0.77	0.52	0.55	0.99	0.94
		200	60	2.86	2.64	1.68	0.40	0.49	0.39	0.15	0.14
			120	2.91	2.80	1.73	0.27	0.41	0.38	0.04	0.04
			180	2.94	2.78	1.67	0.28	0.38	0.27	0.01	0.01
	200		0	2.31	2.08	2.11	0.77	0.52	0.55	0.99	0.94
		300	60	2.87	2.64	1.67	0.38	0.46	0.37	0.16	0.15
Ti/RuO2/SnO2-			120	2.93	2.76	1.64	0.28	0.37	0.27	0.02	0.02
Sb2O5-RuO2/			180	2.91	2.75	1.64	0.21	0.28	0.19	0.01	0.01
7			0	3.07	2.49	2.12	0.76	0.51	0.55	0.97	0.94
		200	60	3.10	3.00	1.71	0.34	0.41	0.35	0.19	0.19
			120	3.17	3.08	1.71	0.26	0.35	0.25	0.03	0.02
	50		180	3.18	3.10	1.72	0.20	0.27	0.18	0.01	0
			0	3.07	2.49	2.12	0.76	0.51	0.55	0.97	0.94
		300	60	3.13	3.02	1.70	0.31	0.38	0.31	0.13	0.13
			120	3.08	2.95	1.63	0.16	0.25	0.21	0.01	0.01
			180	3.08	2,90	1,57	0.14	0.19	0.11	0	0

Table 4: UV absorbance evolution during the degradation process of PXC at Ti/RuO2/SnO2- Sb2O5-RuO2 anodes and and initial pH of 10

Anodic composition/ pHini	PXC concen tration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance						
				193	196	206	253	280	288	355
			0	2.34	2.10	2.15	0.77	0.53	0.58	0.95
		200	60	2.67	2.51	1.51	0.37	0.43	0.34	0.18
			120	2.98	2.92	1.76	0.37	0.47	0.36	0.09
			180	2.92	2.88	1.68	0.29	0.39	0.28	0.02
	200		0	2.34	2.10	2.15	0.77	0.53	0.58	0.95
		300	60	2.80	2.69	1.63	0.37	0.44	0.35	0.14
Ti/RuO2/SnO2-			120	2.92	2.86	1.66	0.30	0.39	0.29	0.04
Sb2O5-RuO2/			180	2.92	2.82	1.63	0.23	0.30	0.20	0.01
10			0	3.15	2.68	2.19	0.76	0.53	0.58	0.92
		200	60	3.18	3.14	1.79	0.37	0.45	0.36	0.14
			120	3.14	3.07	1.65	0.27	0.37	0.27	0.02
	50		180	3.10	3.10	1.63	0.21	0.29	0.20	0
			0	3.15	2.68	2.19	0.76	0.53	0.58	0.92
		300	60	3.11	3.07	1.70	0.34	0.42	0.33	0.11
			120	3.11	3.06	1.58	0.20	0.27	0.19	0.01
			180	3.08	3.03	1.59	0.16	0.21	0.13	0

Table 5: Absorbance peak abatement efficiency during the degradation process of PXC at Ti/RuO2-TiO2 anodes and and initial pH of 7

Anodic composition/ pHini	PXC concentration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance abatement efficiency [%]			
				206	253	288	357
			60	20.37	50.64	29.09	79.79
		200	120	21.32	59.74	41.81	98.98
	200		180	22.74	67.53	54.54	100
			60	19.90	51.94	34.54	84.84
		300	120	21.80	68.83	58.18	98.98
Ti/RuO2-TiO2			180	20.37	79.22	76.36	100
/7			60	17.45	59.21	32.72	86.59
		200	120	16.98	72.36	38.18	97.93
	50		180	18.39	71.05	61.81	100
			60	19.81	57.89	43.63	90.72
		300	120	19.81	80.26	63.63	100
			180	19.81	84.21	83.63	100

Table 6: Absorbance peak abatement efficiency during the degradation process of PXC at Ti/RuO2-TiO2 anode and and initial pH of 10

Anodic composition/ pHini	PXC concentration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance abatement efficiency [%]			
				206	253	288	355
			60	18.60	45.45	31.03	80.00
		200	120	20.93	62.33	43.10	96.84
	200		180	22.79	67.53	58.62	100.00
			60	24.19	57.14	46.55	85.26
		300	120	24.19	75.32	70.69	98.95
Ti/RuO2-TiO2 /			180	24.19	84.42	84.48	100.00
10			60	17.81	48.68	34.48	83.70
		200	120	20.09	73.68	44.83	100.00
	50		180	20.55	75000	63.79	100.00
			60	23.29	59.21	51.72	89.13
		300	120	23.29	77.63	74.14	100.00
			180	18.72	85.53	87.93	100.00

Table 7: Absorbance peak abatement efficiency during the degradation process of PXC at Ti/RuO2/SnO2- Sb2O5-RuO2 and and initial pH of 7

Anodic composition/ pHini	PXC concentration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance abatement efficiency [%]			
				206	253	288	357
			60	20.38	48.05	29.09	84.85
		200	120	18.01	64.94	30.91	95.96
	200		180	20.85	63.64	50.91	98.99
			60	20.85	50.65	32.73	83.84
		300	120	22.27	63.64	50.91	97.98
Ti/RuO2/SnO2-			180	22.27	72.73	65.45	98.99
Sb2O5-RuO2/			60	19.34	55.26	36.36	80.41
7		200	120	19.34	65.79	54.55	96.91
	50		180	18.87	73.68	67.27	98.97
			60	19.81	59.21	43.64	86.60
		300	120	23.11	78.95	61.82	98.97
			180	25.94	81.58	80.00	100.00

Table 8: Absorbance peak abatement efficiency during the degradation process of PXC at Ti/RuO2/SnO2-Sb2O5-RuO2 and and initial pH of 10

Anodic composition/ pHini	PXC concentration [mg/L]	Current density [A/m2]	Time [min]	Wavelength [nm] / Absorbance abatement efficiency [%]			
				206	253	288	355
			60	29.77	51.95	41.38	81.05
		200	120	18.14	51.95	37.93	90.53
	200		180	21.86	62.34	51.72	97.89
			60	24.19	51.95	39.66	85.26
		300	120	22.79	61.04	50.00	95.79
Ti/RuO2/SnO2-			180	24.19	70.13	65.52	98.95
Sb2O5-RuO2/			60	18.26	51.32	37.93	84.78
10		200	120	24.66	64.47	53.45	97.83
	50		180	25.57	72.37	65.52	100.00
			60	22.37	55.26	43.10	88.04
		300	120	27.85	73.68	67.24	98.91
			180	27.40	78.95	77.59	100.00

Table 9: TOC evolution during the degradation process of PXC at DSA electrodes electrolysis time: 180 min; TOC of 200 mg/L PXC: 3,81 mg C/L (dil. 1:25); TOC of 50 mg/L PXC: 1,01 mg C/L (dil. 1:25)

PXC concentration [mg/L]	pHini	Anodic composition	Current density [A/m2]	TOC [mg C/L]	TOC abatement efficiency [%]
		Ti/RuO2-TiO2	200	3.420	10.24
200	7		300	3.090	18.90
		Ti/RuO2/SnO2- Sb2O5-RuO2	200	3.570	6.30
			300	3.480	8.66
		Ti/RuO2-TiO2	200	3.340	12.33
200	10		300	2.865	24.80
		Ti/RuO2/SnO2- Sb2O5-RuO2	200	3.200	16.00
			300	3.160	17.07
		Ti/RuO2-TiO2	200	0.837	17.12
50	7		300	0.585	42.07
		Ti/RuO2/SnO2- Sb2O5-RuO2	200	0.881	12.77
			300	0.823	18.51
		Ti/RuO2-TiO2	200	0.740	26.73
50	10		300	0.489	51.58
		Ti/RuO2/SnO2- Sb2O5-RuO2	200	0.887	12.18
			300	0.715	29.21

DISCUSSION

In case of anodic compositions Ti/RuO2-TiO2, at neutral pH it can be observed a low reduction of absorbance at 206 nm as the electrolysis time increased, regardless of the applied current density and the initial concentration of the solution. Thus, the efficiency of absorbance decrease at 206 nm ranged from 20-23% for 200 mg/L PXC and 17-20% for 50 mg/L.

The situation is different for the other wavelengths. Thus, important decreases of the absorbance as the electrolysis time and current density increased were recorded regardless the initial concentration of solution. The best efficiencies of the absorbance decrease were recorded at 357 nm (that practically disappeared from the spectrum), followed by that at 253 nm and 288 nm, respectively. This behaviour could suggest that the structure of the benzene ring was not significantly affected, while the pyridine ring and adjacent substituents to the aromatic ring are degraded with higher efficiencies.

The above findings are valid both for Ti/RuO2-TiO2 anodes and Ti/RuO2/SnO2-Sb2O5-RuO2, both in neutral medium and basic medium. It can be noticed that the best results for both working concentrations were recorded at a current density of 300 A/m2 and 180 minute of electrolysis.

By comparing efficiencies of the absorbance decrease for anodic composition Ti/RuO2-TiO2 in neutral and basic medium it is revealed the absorbance decrease was more significant regardless of the initial concentration.

Not the same aspects were observed for the anodic composition Ti/RuO2/SnO2-Sb2O5-RuO2. Thus, at 206 nm the decrease was higher in basic medium regardless of solution initial concentration, at 253 nm it was higher in neutral medium regardless of solution initial concentration, at 288 nm they were almost the same in neutral and basic medium for the initial concentration of 200 mg/L PXC and higher in neutral medium for the initial concentration of 50 mg/L PXC, and at 357 nm they were almost de same regardless of pH and initial concentration.

TOC analyses were carried out for the electrolyzed solutions. The results are tabulated as follows. It can be noticed a good correlation between the electrochemical degradation and TOC evolution.

The survey of data listed in Table 9 revealed that the advanced degradation of the pollutant occurred with higher efficiencies both in neutral and basic medium for both initial concentrations of the solutions for anodic composition Ti/RuO2-TiO2 as compared with Ti/RuO2/SnO2- Sb2O5-RuO2.

For the anodic composition Ti/RuO2-TiO2, the highest TOC removal efficiencies were recorded in basic medium for both solution initial concentrations. The same behaviour was observed for the anodic composition Ti/RuO2/SnO2- Sb2O5-RuO2.

CONCLUSIONS AND IMPLICATIONS

UV spectra survey revealed a complex degradation process that could be explained by oxidation and bond cleavage between the pyridine and condensed rings, as well as their oxidation. The appearance of new maxima in spectra confirmed the advanced oxidation of PXC.

Based on absorbance abatement efficiencies at wavelength corresponding to absorbance maxima, it can be assumed that the structure of the benzene ring was poorly affected, while the pyridine ring and the adjacent substituents of aromatic ring were degraded with higher efficiencies. The efficiencies of the absorbance decrease corresponding to maxima were higher in basic medium almost in all situations.

Regardless the solution initial concentration, the best removal TOC efficiency was recorded in basic medium for both anodic compositions. The most effective proved to be the anodic composition Ti/RuO2-TiO2 with TOC removal efficiency of 51.58%.

Current facilities do not provide the removal of biorefractory organic pollutants from wastewater treatment and therefore it is necessary to find solutions to provide effluents that meet the conditions of discharge specified by regulations in use.

The research presented in this paper is part of the current concerns existing at European level for providing and developing methods for the treatment of biorefractory organic pollutants effluents so that their transformation into compounds that do not endanger the natural habitat is accomplished.

The international research earmarks important resources to abatement/removal of pollution caused by biorefractory organic pollutants, which is reflected in the extent of research carried out to develop and implement new processes for wastewater treatment. Integrating these processes as advanced treatment steps in wastewater treatment conventional schemes is a condition to obtain effluents compatible with the environment.

REFERENCES

Adams, B., Tian, M., & Chen, A. (2009). Design and electrochemical study of SnO2-based mixed oxide electrodes. Electrochimica Acta, 54, 1491–1498.

Aquino Neto, S., & de Andrade, A.R. (2009). Electrooxidation of glyphosate herbicide at different DSA® compositions: pH, concentration and supporting electrolyte effect. Electrochim. Acta, 54, 2039–2045.

Balaban, A.T., Banciu, M., & Poganz, L. (1983). Aplicații ale metodelor fizice în chimia organică, Editura Ştiințifică şi enciclopedică, Bucureşti, 1983, 39-61.

Basha, C. A., Sendhil, J., Selvakumar, K.V., Muniswaran P.K.A., & Lee, C.W. (2012). Electrochemical degradation of textile dyeing industry effluent in batch and flow reactor systems. Desalination, 285, 188–197.

Basiri Parsa, J., Merati, Z., & Abbasi, M. (2013). Modeling and optimizing of electrochemical oxidation of C.I. Reactive Orange 7 on the Ti/Sb–SnO2 as anode via response surface methodology. Journal of Industrial and Engineering Chemistry, 19, 1350–1355.

Corcoll, N., Acuna, V., Barcelo, D., Casellas, M., Guasch, H., Huerta, B., Petrovic, M., Ponsati, L., Rodriguez-Mozaz, S., & Sabater, S. (2014). Pollution-induced community tolerance to non-steroidal anti-inflammatory drugs (NSAIDs) in fluvial biofilm communities affected by WWTP effluents. Chemosphere, 112, 185–193.

De Francesco, M., & Costamagna, P. (2004). On the design of electrochemical reactors for the treatment of polluted water, Journal of Cleaner Production, 12, 159-163.

Ihos, M., Manea, F., Bocea, G., & Jitaru, M. (2009). Le comportement electrochimique des anodes en SnO2 modifiées en presence des polluants phénoliques. Revue Roumaine de Chimie, 54 (4), 301–307.

Ihos, M., Botau, D., & Andres, L. (2011). Electrochemical methods applied to pharmaceutically active compounds degradation from wastewaters. Book of Proceedings of the International Symposium "The Environment and Industry", 16-18 November 2011, Bucureşti, Romania, vol.I, 61-66.

Martínez-Huitle, C.A., Quiroz, M.A., Comninellis, C., Ferro, S., & Battisti, A.D. (2004). Electrochemical incineration of chloranilic acid using Ti/IrO2, Pb/PbO2 and Si/BDD electrodes. Electrochimica Acta, 50, 949-956.

Niu, J., Maharana, D., Xu, J., Chai, Z., & Bao, Y. (2013). A high activity of Ti/SnO2-Sb electrode in the electrochemical degradation of 2,4-dichlorophenol in aqueous solution. Journal of Environmental Sciences. 25(7), 1424–1430.

Santos, D., Pacheco, M. J., Gomes, A., Lopes, A., & Ciriaco, L. (2013). Preparation of Ti/Pt/SnO2–Sb2O4 electrodes for anodic oxidation of pharmaceutical drugs. Journal of Applied Electrochemistry, 43, 407-416.

Sires, I., & Brillas, E. (2012). Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review. Environment International, 40, 212-229.

Tavares, M.G., da Silva, L.V.A., Sales Solano, A.M., Tonholo, J., Martinez-Huitle, C.A., & Zanta, C. L.P.S. (2012). Electrochemical oxidation of Methyl Red using Ti/Ru0.3Ti0.7O2 and Ti/Pt anodes. Chemical Engineering Journal, 204–206, 141–150.

Trasatti, S. (2000). Electrocatalysis: understanding the success of DSA®, Electrochim. Acta, 45, 2377- 2385.

Walsh, F.C. (2001). Electrochemical technology for environmental treatment and clean energy conversion. Pure and Applied Chemistry, 73 (12), 1819–1837.

Zaviska, F., Drogui, P., Blais, J.F., Mercier, G., & Lafrance, P. (2011). Experimental design methodology applied to electrochemical oxidation of the herbicide atrazine using Ti/IrO2 and Ti/SnO2 circular anode electrodes. Journal of Hazardous Materials, 185, 1499–1507.

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ASSESSMENT OF ENVIRONMENTAL SITUATION OF ORIKUMI LAGOON, ALBANIA, BASED ON DISSOLVED HEAVY METALS CONCENTRATION AND SOME PHYSICAL-CHEMICAL PARAMETERS IN WATER

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ABSTRACT

The study was carried out in Orikumi Lagoon, to evaluate the environmental status and to extent the pollution from different contamination sources in this area. Orikumi Lagoon, situated in the southwestern part of Vlora city, is an environmentally valuable area and presents a particular importance. A water quality survey was performed by the determination of physical-chemical parameters and total heavy metals content in water samples collected according to a network of five sampling points. Total dissolved metal concentrations (Cd, Cu, Cr, Hg, Pb and Zn), were analyzed by graphite furnace AAS (for Cu, Pb, Zn, Cr and Cd determination) and/or CV AAS (Hg) that is known as a very sensitive analytical method. Statistical analysis of the data was carried out using the EXCEL Package Program.Lower physical-chemical parameters resulted in station 4 as the result of the impact of the mixing of lagoon water with fresh water, which probably causes the reduction of salinity and electrical conductivity. The order of the distribution of heavy metal levels in Orikumi Lagoon water resulted as follows: Zn>Cu>Cd>Pb>Cr>Hg. The seawater quality of Orikumi lagoon in terms of heavy metals content in water is quite good and metal levels are lower than the Standard of Seawater Quality Classification.

Key words: *Orikumi Lagoon, environmental assessment, physical-chemical parameters, heavy metals.*

INTRODUCTION

Water is the most important natural resource in the world. The progressive growth of urban wastewater has caused the reduction of water quality of rivers, lakes, coastal areas and the environment in general (Shoshi et al., 2012). The Albanian costal lagoons represent the most sensitive and important environment areas of the Albanian coast. These lagoons are area of multiple ecological and economic values and uses, as provide fish and wildlife habitats, support complex food web, absorb water to reduce flooding and damage from storms, provide erosion control, improve the quality of water (PHARE, 2002). However the above-mentioned socioeconomic advantages may become disadvantageous for the ecological environment if they are not managed and supervised with great care. Lagoons have limited water circulation to compensate for changes in water quality and are susceptible to anthropogenic pollution (Johnson et al., 2007).

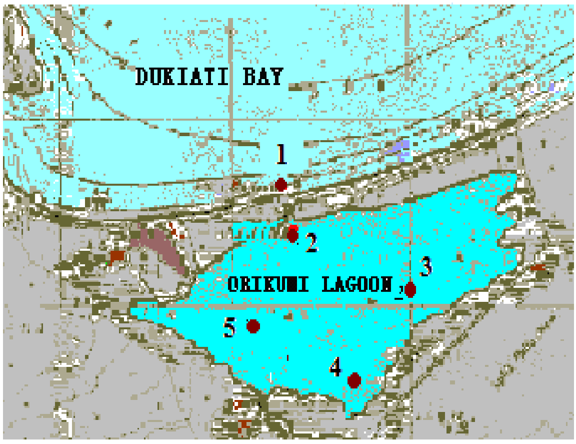
In recent years, significant attention has been paid to the problems of environmental contamination by a wide variety of chemical pollutants including heavy metals (Eldemerdash and Elegamy, 1999). Some of the most important heavy metals from the point of view of water pollution are Zn, Cu, Pb, Cd, Hg and Cr (Rashed, http://faculty.ksu.edu.sa). Heavy metals are of critical ecological significance since they are highly toxic, non-degradable and therefore have the tendency of bioaccumulation (Diagomanolin et al., 2004). The toxic effect of metals depends on their characteristics. Some metals, present in trace quantity, are important for aquatic life. The same metals, however, can cause severe toxicological effects on human health and the aquatic ecosystem, when exceed a certain limit (Bruins et al., 2000) and when complexes are formed with organic compound (Akbulut and Tuncer, 2011).

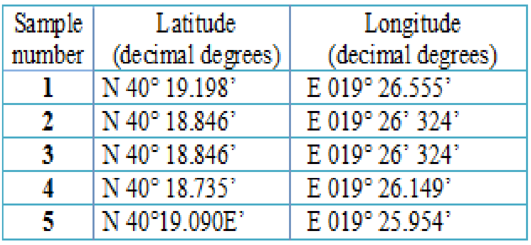
The present study is an attempt to assess the influence of anthropogenic activities in Orikumi Lagoon with specific reference to the concentrations of trace metals and physical-chemical parameters.

MATERIALS AND METHODS

Studied area

Orikumi lagoon is located in the southwestern part of Vlora district with coordinates 40°19’N latitude, 19° 25’ E longitude and an area of 1500 ha (PHARE, 2002). The lagoon has a maximum depth of 3 m and is connected to the sea solely by a 50m-long channel (Shehu et al., 2010). Because of the mixing of lagoon water with fresh water (from a source of fresh water in the southwestern side of the lagoon) salinity of water in various sites varies from 15 to 27 ‰.





Sample number	Latitude (decimal degrees)	Longitude (decimal degrees)
1	N 40° 19.198’	E 019° 26.555’
2	N 40° 18.846’	E 019° 26’ 324’
3	N 40° 18.846’	E 019° 26’ 324’
4	N 40° 18.735’	E 019° 26.149’
5	N 40°19.090E’	E 019° 25.954’

Figure 1. Network of sampling points in Orikumi Lagoon

Sites and sampling methodology

Water samples were collected according to a network of five sampling points in Orikumi Lagoon as following: four samples within the lagoon and another sample in the channel that connect lagoon to the sea. The sampling points are shown in figure 1. Water samples were collected in 50 cm deep and 150 m from the shore. Sample stations were chosen in order to do a better assessment of general environmental situation of Orikumi Lagoon and to evaluate its possible polluting sources. Sample collection, transport and conservation was done according to standard methods recommended (APHA, 1998).

Water samples treatment

Water samples were collected in 1.5 liter PET bottles and were transported during the same day to the laboratory by refrigerated containers under the temperature of 4^{o}C. The physical-chemical parameters of water were determined immediately after the samples were taken to the laboratory. Conductivity, salinity and TDS were determined with a conduct meter (Model DDSJ 308A). pH, temperature, were measured with a pH meter (Model pHS-3BW). Then, the water was filtered (glass filter of 0.42 µm pore size) with the aim to separate all the inert material that can indicate in the results and stored at 4^{o}C until heavy metals analysis. TSS (total suspended mater) was determined by pouring one liter volume of water through a pre-weighed filter of 0.42 µm pore size, then weighing the filter again after drying it at 105^{o}C for 2 hours to remove all water. Heavy metals content were determined by Atomic Absorption Spectroscopy (by using ETA/AAS system or CV-AAS for Hg determination) known as a very sensitive analytical method for many heavy metals. Because of the low content of heavy metals in sea and lagoon water (µg/L) their direct determination by this method is impossible and a pre-concentration and\or separation step before their AAS analysis is indispensable. As an accurate, fast, and inexpensive method for separation of heavy metals from sea water, chloroform extraction after heavy metals complexion with diethyl dithiocarbamates (DDTC) was used as very suitable for this purpose. All measurements were conducted using a Varian SPECTRA 10-Plus atomic absorption spectrophotometer and NovAA 400 equipped with auto sampler.

RESULTS AND DISCUSSION

The results of chemical-physical parameters of Orikumi Lagoon are shown in diagrams of figure 2 and the statistical data of physico-chemical parameters obtained throw the Descriptive Statistic are shown in table 1.

Table 1: Statistical data of physical-chemical parameters

Statitical Parameters	pH	E (mV)	T (^{0}C)	Cond. (mS/cm)	TDS (mg/L)	Sal. (‰)	TSS (mg/L)	DO (mg/L)
Mean	8.04	-56.08	8.7	27.82	15.298	17.48	35.1	9.06
Standard Error	0.052	4.732	0.141	1.740	1.387	0.695	3.896	0.301
Median	8.07	-60.4	8.7	29.6	15.33	17.9	34.8	9.2
Standard Deviation	0.117	10.581	0.316	3.890	3.101	1.553	8.711	0.673
Sample Variance	0.014	111.95	0.100	15.132	9.617	2.412	75.875	0.453
Kurtosis	1.966	4.901	-1.20	-2.207	-2.191	0.559	0.741	-0.667
Skewness	-1.357	2.208	0.000	-0.676	0.189	-0.953	-0.978	-0.599
Range	0.3	24.5	0.8	8.7	7.06	4	21.3	1.7
Minimum	7.85	-61.7	8.3	22.6	12.16	15.1	21.6	8.1
Maximum	8.15	-37.2	9.1	31.3	19.22	19.1	42.9	9.8
EC Directive 78/659	6-9						≤25mg/L	≥ 8mg/L

Chemical-physical parameters present low values of variation and St.Dev/Mean ratios that mean a stable condition in different positions of Orikumi Lagoon. The values of Skewness (close to 0) and Kurtosis (close to 3) indicate more or less a normal distribution of these parameters.

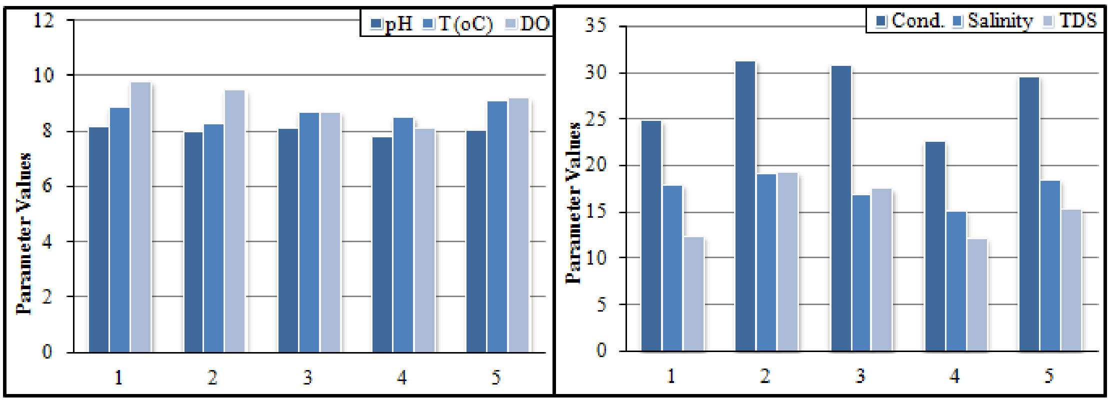


Figure 2. The results of chemical-physical parameters of Orikumi Lagoon (a-pH, T, DO; b-Conductivity, salinity, TDS)

pH:

pH of aquatic ecosystems depends on chemical and biological activity of water. In saline water, pH is near 8.3 and the optimum pH for most of marine animals is usually between pH 7.5 and 8.5 (Boyd, 1998). As we can see from table 1 and figure 2/a, pH values fluctuated between 7.85 -8.15 at station 4 and 1 (the canal that connect the lagoon to the sea) respectively.

Temperature:

As it would be expected, the temperature of surface water of Orikumi Lagoon fluctuated in a low range values between 8.3-9.1°C that is normal for the period of sampling process (during February).

DO (dissolved oxygen):

Dissolved oxygen, O_2, is essential for all animal life. The fluctuations in the dissolved oxygen levels in water can be caused by aquatic vegetation and anthropogenic status of the water. It is well known that the temperature and salinity affect the dissolution of oxygen in water (Saravanakumar et al., 2008). Disolved oxygen in Orikumi Lagoon water resulted between a minimum value of 8.1 mg/L at station 4 and a maximum value of 9.8 mg/L at station 1(see table 1 and Fig. 2/a).

Conductivity, Salinity, TDS:

All these parameters resulted at lower values in station 4 situated in the south-western part of the lagoon. Lagoon water near this station, mix with water of a fresh water source (near Marmiroi Church) which has caused reduction of salinity, electrical conductivity and other physical chemical parameters. Conductivity was found at the levels between 22.6 mS/cm in station 4 to 31.3 mS/cm in station 2. The fluctuation in electric conductivity was due to fluctuations in TDS and salinity (Boyd, 1981). Salinity is the measurement of ionic composition of water and it varies depending on mixing of relatively fresher inland waters with saltier marine waters (Twomeu et al., http://www.eolss.net). In water samples of Orikumi Lagoon, salinity values fluctuated in a range between 15.1-19.1 ‰ (st. 4 and 2 respectively). *TDS* concentration resulted in lower level in station 4 (12.16 mg/L) and in higher level in 2 (19.22 mg/L).

TSS:

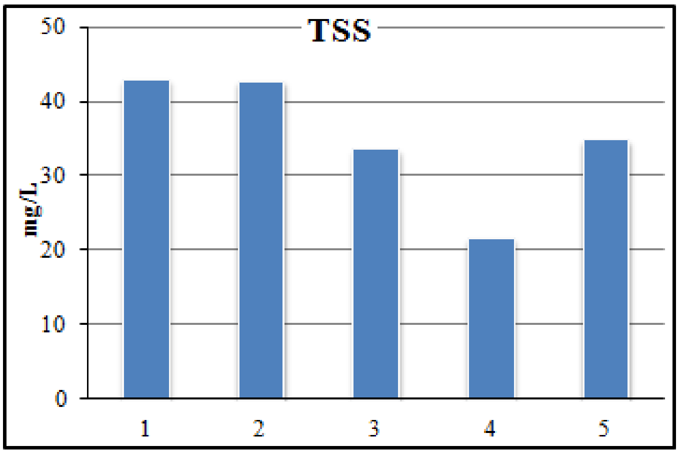


Figure 3. The results of TSS in water of Orikumi Lagoon

High concentrations of TSS have several negative effects, such as decreasing the amount of light that can penetrate the water, thereby slowing photosynthetic processes which in turn can lower the production of dissolved oxygen; high absorption of heat from sunlight, thus increasing the temperature which can result to lower oxygen level. (PHILMINAQ, http://www.aquaculture.asia) TSS content in

Orikumi Lagoon water fluctuated between a minimum value of 21.6 mg/L at station 4 and maximum value of 42.9 mg/L at station 1 (see figure 3).

Red/ox potential:

Redox potential is the activity or strength of red/ox processes in solution. As it can be seen the values of this parameter fluctuated between a minimum of -61.7 mV at station 2 and a maximum of -37.2 mV at station 4. Negative values of the redox potential in all stations indicate the reducing properties of lagoon water (Bellingham, stevenswater.com).

Compared to EC Directive for pH level in cyprinid waters (6-9), CEE 78/659 (EC Fish Directive 44, 2006), pH resulted in normal level. The same for DO content referring to the guide value ($\geq$ 8mg/L) of EC Directive CEE 78/659 (EC Fish Directive 44, 2006) and Seawater Quality Standard of China GB 3097-1997 (Wang et. al., 2011) (DO content in sea water $\geq$ 6). TSS resulted in higher content compared to guide value ($\leq$25mg/L) of EC Directive CEE 78/659 (EC Fish Directive 44, 2006) due to the water currents and swelling during sample collection (samples were collected in winter).

Heavy metals

Determination of heavy metals concentration in saline water is a problem from the analytical point of view because of the low heavy metals content; often lower than detection limits of analysis methods. High salinity of water is another major obstacle for chemical analysis of trace metals due to matrix interferences. Heavy metal levels in water of Orikumi Lagoon exist in the order Hg<Cr<Pb<Cd< Cu<Zn (Figure 4 and Table 2).

Table 2: Statistical data treatment of heavy metals

	Cd	**Cu**	**Cr**	**Pb**	**Zn**	**Hg**
Mean	0.2594	4.059	0.111	0.121	61.765	0.100
St. Error	0.121	1.047	0.017	0.017	9.347	0.014
Median	0.091	3.812	0.104	0.135	61.765	0.096
St.Dev	0.271	2.341	0.037	0.038	20.901	0.032
Sample Variance	0.073	5.479	0.001	0.001	436.843	0.001
Kurtosis	-2.965	1.820	-2.654	0.662	1.310	1.784
Skewness	0.582	0.511	0.164	-1.208	-0.878	1.266
Range	0.58	6.534	0.084	0.089	55.882	0.083
Minimum	0.01 (St.4)	1.04 (St.1)	0.069 (St.1)	0.062(St.4)	29.41(St.5)	0.069(St.1)
Maximum	0.58 (St.5)	7.574(St. 5)	0.153(St.4)	0.151(st.1,2)	85.29(St.1)	0.152(St.2)

Cu, Zn, Pb and Hg present moderate value of variation (CV<75) and low St.Dev/Mean ratios that mean a stable condition in different positions of Orikumi Lagoon. Cd and Cr present high value of variation (CV>75) by explaining an anthropogenic input in this area.

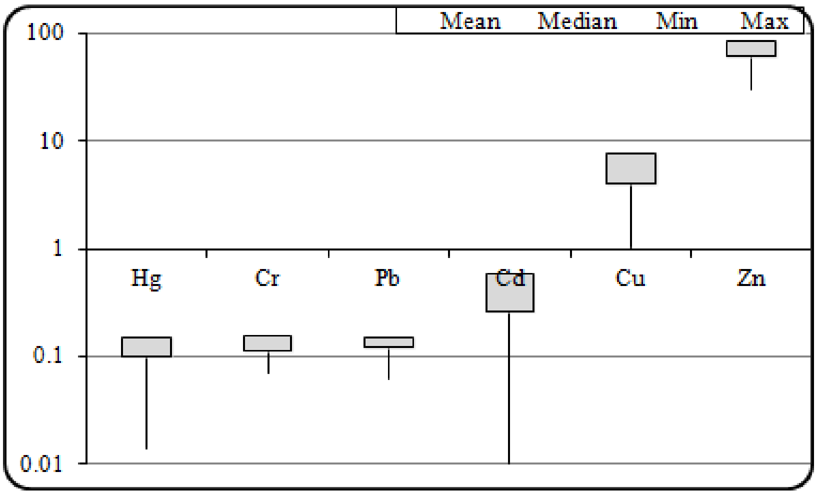


Figure 4. The distribution of heavy metals concentration in all sampling sites of Orikumi Lagoon

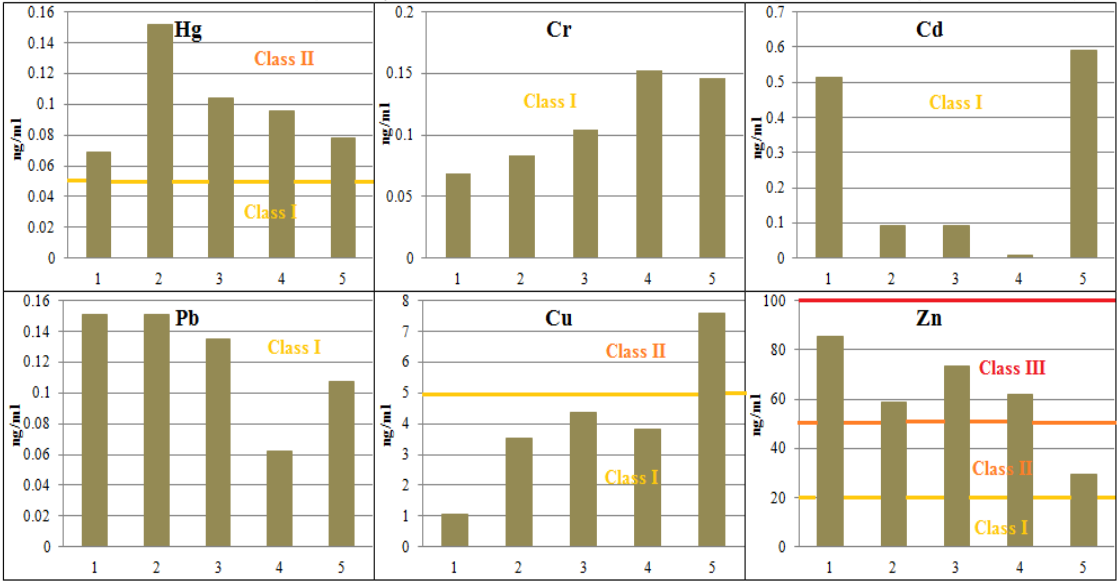


Figure 5. The results of heavy metals concentration in Orikumi Lagoon

As it is shown in figure 5, Pb was found in higher content in station 2 of Orikumi Lagoon and the same for Hg content. Higher content of Cr resulted in station 4 and 5. Cu and Cd were found in higher content in station 5 (situated near Naval base of Pasha Liman) and Zn in station N1. Based on total content of heavy metals in water of Orikumi Lagoon, all the stations studied were classified in class I and II (clean water) of Seawater Quality Standard of China GB 3097-1997 (Wang et. al., 2011) regarding Hg, Cu, Cr, Cd and Pb.

Station 1, 2, 3 and 4 resulted slightly polluted regarding Zn content. The main source of Zn might be the atmospheric sources of dust generated by the erosion of land surfaces (wind transported dusts), but also by direct emission from anthropogenic activities (industry, agriculture, transportation). (Sunda and Huntsman, 1995).

CONCLUSIONS

The assessment of environmental situation of Orikumi Lagoon through this study was quite objective despite the small number of samples analyzed because the sample stations were chosen in order to achieve an effective monitoring of environment situation of this area and to evaluate the possible polluting sources.

In general the physical-chemical parameters including dissolved oxygen (DO), resulted in normal levels. Lower physical-chemical parameters resulted in station 4 (in the south-western part of the lagoon, near Marmiroi Church) as the result of the impact of mixing of lagoon water with fresh water, which causes reduction of salinity electrical conductivity. High concentration of TSS compared to European Directives, might have negative effects in photosynthetic processes and the production of dissolved oxygen in water.

Determination of heavy metals concentration in saline waters makes a difficult problem due to very low content of heavy metals often lower than detection limits of analysis methods and the high salinity of water is the major obstacle for chemical analysis of trace metals due to matrix interferences. The order of heavy metals content in seawater of Orikumi Lagoon resulted Zn >Cu >Cd>Pb> Cr>Hg.
The presence of Cu, Zn, Cr, Pb and other metals in seawater of coastal areas and lagoons are atmospheric deposition due to the heavy traffic in Vlora area, the activity of naval base of Pashaliman and the existing cemeteries of submarine batteries in this area, urban discharges etc. Compared to previous studies (Lazo et al., 2004), the results show stable situation for a long period.

REFERENCES

APHA (American Public Health Assciation) (1998) Standard Methods for the Examination of Water and Wastewater, 20th Edition.

Akbulut, N. E., & Tuncer, A. M. (2011). Accumulation of heavy metals with water quality parameters in Kızılırmak River Basin (Delice River) in Turkey. *Environmental Monitoring and Assessment,* 173, 387–395

Bellingham, K. Physicochemical Parameters of Natural Waters, Stevens Water Monitoring Systems, Inc. http://www.stevenswater.com

Bruins, M. R., Kapil, S., & Oehme, F. W. (2000). Microbial resistance to metals in the environment. *Ecotoxicology and Environmental Safety*, 45, 198–207.

Boyd, C.E. (1981): Water Quality in warm water fish ponds. Anburn University, Alabama. Craftmaster Printer, Inc. Opelika, Alabama.

Boyd, C. E. (1990). Water quality in ponds for aquaculture. Alabama Agricultural Experiment Station, Auburn University, Alabama

Council Fish Directive 2006/44/EC of the European Parliament and of the Council of 6 September 2006 on the quality of fresh waters needing protection or improvement in order to support fish life. *Official Journal of the European Union.* 264/20—264/31 (http://rod.eionet.europa.eu/show.jsv?id=626&mode=S)

Diagomanolina, V., Farhanga, M., Ghazi-Khansaria, M., Jafarzadehb, N. (2004). Heavy metals (Ni, Cr, Cu) in the Karoon waterway river, Iran. *Toxicology Letters*, 151, 63–68

Directives of European Community BMZ (ed), Environmental Handbook: Documentation on monitoring and evaluation impacts, CEE/CEEA/CE 78/659 “Quality of fresh waters supporting fish life”, Vieweg, Leverkusen, 1995

El-demerdash, F. M., Elegamy E. L. (1999). Biological effects In Tilapia nilotica fish as indicators of pollution by cadmio and mercury. *Int. J. Environ. Health Res.,* 9(1999): 173-186

Johnson, D.E., Bartlett, J., Nash, L.A., (2007). Coastal lagoon habitat re-creation potential in Hampshire, England. *Mar. Policy* 31, 599–606

Lazo, P., Lubonja, F., Arapi, A., Pjeshkazini, L. (2004). An evaluation of heavy metals content in Orikumi, Dukati Bay-Ionian Sea–Albania, *International Journal of Chemistry, (IJCS)* Vol.2(1), 101-107

Twomeu, L. J., Piehler, M. F. and Paerl, H. W. Priority Parameters for monitoring of freshwater and marine systems, and their measurement. *Institute of Marine Sciences, University of North Carolina at Chapel Hill, USA* http://www.eolss.net/sample-chapters/c09/e6-38a-04-01.pdf

Rashed, M.N. Biomarkers as indicators for water pollution with heavymetals in rivers, seas and oceans http://faculty.ksu.edu.sa/Adham/My%20documents/Impact%20of%20hazardous%20(citation%201).pdf

PHARE, (2002). PHARE Programme Albania. Strategy for Albanian Lagoon Management. *Government of Albania, European Commission, Final Report*, 155p

PHILMINAQ, Annex 2. Water Quality Criteria and Standards for Freshwater and Marine Aquaculture http://www.aquaculture.asia/files/PMNQ%20WQ%20standard%202.pdf

Saravanakumar, A., M. Rajkumar, J. Sesh Serebiah and G.A. Thivakaran (2008). Seasonal variations in physico-chemical characteristics of water, sediment and soil texture in arid zone mangroves of Kachchh-Gujarat. *J. Environ. Biol.*, 29, 725-732

Sunda, W. G. and Huntsman, S. A. (1995). Cobalt and zinc interreplacement in marine phytoplankton: biological and geochemical implications. *Limnol. Oceanogr.*, 40(8), 1404–1417

Wang B., Xie L., and Sun X. (2011). Water Quality in Marginal Seas off China in the Last Two Decades. *International Journal of Oceanography*,Volume 2011, Article ID 731828, 6 pages, doi: 10.1155/2011/731828)

Shoshi, O., Sulçe, S., Rada, Z., Vllamasi, N. (2012). The Pollution Level in the Urban Wastewater Discharge**.** *BALWOIS, 2012. International Conference on water climate and environment, 28 May–2 June, Ohrid, Republic of Macedonia;* USB ISBN 978-608-4510-10-9 http://www.balwois.com/2012

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ANALYSIS OF THE DYNAMICS OF PB (II) IONS ADSORPTION PROCESS ONTO NATURAL ZEOLITE BY APPLICATION OF RESPONSE SURFACE METHOD

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ABSTRACT

This paper presents an experimental study on the dynamics of adsorption of Pb(II) ions from aqueous solutions in a fix bed adsorbent (natural zeolite) system. The influence of the operating parameters - initial Pb(II) ions concentration, adsorbate flow rate and adsorbate bed height on the effluent Pb(II) ions concentration was determined through the experimental analysis. The initial concentration of Pb(II) ions in the aqueous solution was varied from 50-250 mg/dm^3, the flow rate of adsorbate was varied from 10-20 cm^3/min, while the bed height of adsorbent was changed from 8-23 cm. The corresponding targets was proven to be satisfactory with a correlation coefficient of 0.99987 for three model variables used in this study.

Key words: *Pb (II) ions, adsorption, zeolite, response surface method (RSM-3D).*

INTRODUCTION

Fresh water supply is a necessity for the modern world and becomes a concerning issue for many countries nowadays. Drinking water, urban wastewater, industrial wastewater and groundwater are subjected to different types of treatment for removal of present pollutants.

In recent years the interest for purification of industrial wastewater containing heavy metals that are hazardous to human health as well as the environment represents a growing interest within the scientific community.

Heavy metals industry (heavy metallurgy) is characterized by large water consumption which comes from the washing process during production and many other indirect applications, which produce wastewater with complex composition. Therefore, the wastewater produced during washing processes of cadmium, zinc and lead has a huge concentration of these metals which should be reduced to maximal allowed concentrations included in various regulatives. The metals can accumulate in toxic concentrations and can cause environmental damage. In aquatic systems, the metals are present as complex ions, suspended and colloidal ions and solid components in sediments. The concentrations of these metal ions are highly dependent on biological processes, their redox potential, ionic strength, pH of organic and inorganic solvents and cleaning processes.

The biggest source of metals pollution comes from municipal water (especially As, Cr, Cu, Mn and Ni), coal burning plants (As, Hg and Se), smelters of Cd, Ni, Pb and Se, iron and steel plants (Cr, Mo, Sb and Zn), communal waste removal (As, Mn and Pb), ceramics, electro polishing, metallurgy, glass industry, mining, coating industry etc. There are different methods that are commonly applied for wastewater purification: flotation, flocculation, filtration, ultra-filtration, precipitation, chlorination, reverse osmosis, aeration and adsorption (M. Singanan (2011), S. Khaoya et al. (2012), l. Tofan et al. (2004), Z. Sarkar et al. (2013), M. Moyo et al. (2013), F. Pavan et al. (2008), J. Acharya et al. (2011),

J. Mbadcam et al. (2011), M. Saidi et al. (2010), I. Mobasherpour et al. (2014), I. Vassilis et al. (2010)).

The application of the adsorption processes for elimination or reduction of the water pollution has several advantages: smaller investments in terms of initial costs and costs for land, simple design and operation management, no side effects from toxic substances, as superior extraction of organic waste materials and heavy metals. Several adsorbents can be applied for wastewater treatment including granular activated carbon, silica gel, activated alumina, bauxite, zeolites and ion exchange resin, peat, clay, chitosan, different microorganisms, chimney rice and peanut shell, metal oxides, peat, ash etc. (E. Ivanova et al. (2010), C. Oliveira et al. (2007), S. Abdullah et al. (2013), A. Chojnacka et al. 2004), J. Guo et al. (2013)).

Natural zeolites are materials with big specific surface area due to their big porosity. Zeolite crystals have many active centers which can interact with heavy metals or organic compounds through ion exchange or adsorption.

Clinoptilolite is a commercially available natural zeolite with a chemical composition based on a hydrate sodium calcium alumosilicate. It has a unique crystal structure in order to particle size. These unique properties make this adsorbent applicable in the wastewater treatment industry (P. Johnson et al. (2008), N. Medvidovic et al. (2006), B. Amarasinghe et al. (2011)).

MATERIALS AND METHODS

Preparation of the Adsorbate

The adsorbate used in experiments is hydrated lead nitrate salt ($Pb(NO_3)_2{\cdot}7H_2O$) with different initial concentrations of lead ions in aqueous solution.

Adsorbents Characteristics

Natural zeolite (NZ) was used as adsorbent in the dynamic experiments in the frames of this work. Natural zeolite (90% clinoptilolite) was supplied by “Nemetali”,Vranjska Banja, Serbia. Prior to the performing of the experiments the NZ was dried at 330°C for 48 h. The chemical composition of natural zeolite is given in table 1 and some of the properties of the utilized adsorbent are listed in table 2.

Table 1: Chemical composition of natural zeolite (NZ)

Ingredients	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**Ignition loss**
Natural zeolite (mass %)	64.88	12.99	2.00	0.37	3.26	1.07	0.95	0.89	13.59

Table 2: Natural zeolite (NZ) properties

Properties	**Natural zeolite**
Particle diameter, (mm)	1-3
Bed porosity	0.325
Particle density, (g/cm^3)	2.12
Bulk density, (g/cm^3)	1.43
Surface area, (cm^3/g)	20-40

Working Conditions

For the purpose of dynamics experiments, the initial concentration of lead in aqueous solution were set at: 50, 100, 150, 200 and 250 mg/dm^3. The flow rate of adsorbate in the fixed bed column was set at 10, 15 and 20 cm^3/min and the bed height of adsorbent was set at 8, 16 and 23 cm of natural zeolite (NZ). All of the dynamics experiments were conducted in continuous conditions.

The adsorbate by certain initial Pb(II) ions concentration is located in a vessel. By pump the adsorbate entered into fixed bed column and by certain flow rate passes through column with certain bed height (figure 1).

Concentration of lead ions at the outlet of fixed bed column was measured using AERL 3520 Atomic Absorption Spectrophotometer.

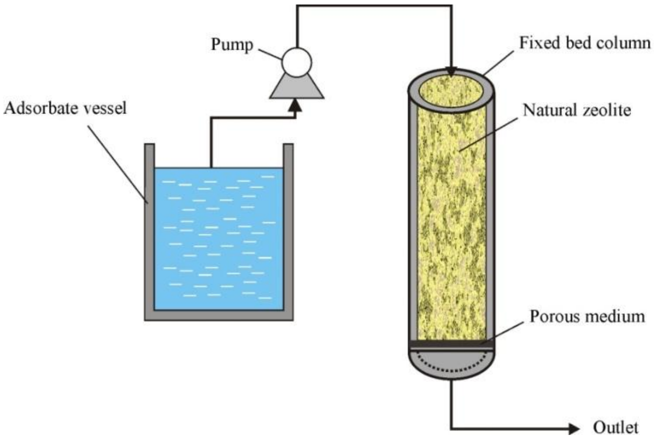
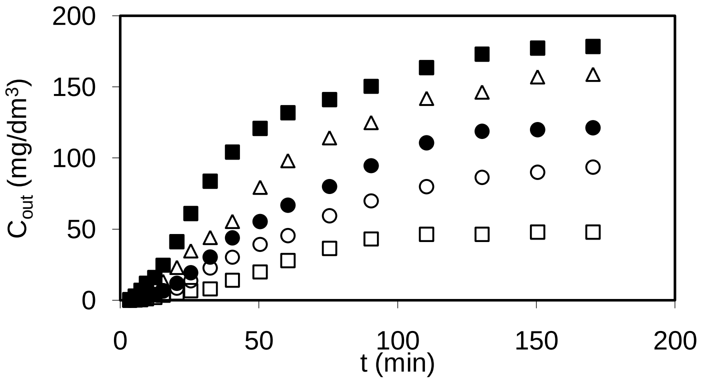


Figure 1. Fixed bed column

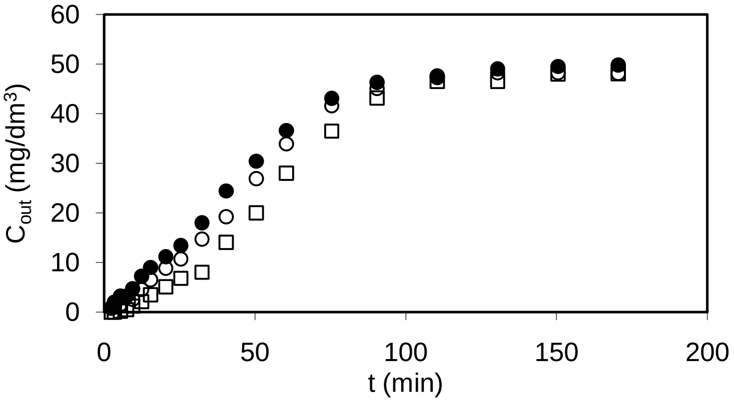
RESULTS AND DISCUSSION

Experimental data of adsorption dynamics of Pb (II) ions are shown on figure 2, 3 and 4. On figure 2 dependence of initial Pb(II) concentration as a function of time for constant flow rate F=10 cm^3/min and constant bed height of NZ adsorbent L=23 cm are given.



□ - c_o = 50 mg/dm^3 ; ○ - c_o = 100 mg/dm^3; ● - c_o = 150 mg/dm^3;
△ - c_o = 200 mg/dm^3; ■ - c_o = 250 mg/dm^3

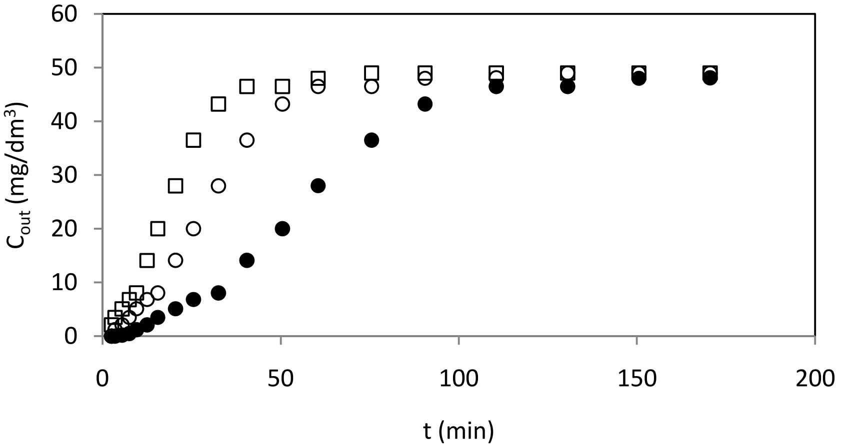
Figure 2. Dependence of initial Pb(II) concentration as a function of time for constant flow rate F=10 cm^3/min and constant bed height of NZ adsorbent L=23 cm



□ - F = 10 cm^3/min ; ○- F = 15 cm^3/min; ●- F = 20 cm^3/min

Figure 3. Dependence of adsorabte flow rate as a function of time for constant initial Pb(II) ions concentration C_0=50 mg/dm^3 and constant bed height of NZ adsorbent L=23 cm

On figure 3 dependence of adsorabte flow rate as a function of time for constant initial Pb(II) ions concentration C_0=50 mg/dm^3 and constant bed height of NZ adsorbent L=23 cm are given.
On figure 4 dependence of bed height of NZ adsorbent as a function of time for constant initial Pb(II) ions concentration C_0=50 mg/dm^3 and constant flow rate of adsorbate F=10 cm^3/min are given.



□ - L = 8 cm ; ○ - L = 16 cm; ● - L = 23 cm

Figure 4. Dependence of bed height of NZ adsorbent as a function of time for constant initial Pb(II) ions concentration C_0=50 mg/dm^3 and constant flow rate of adsorbate F=10 cm^3/min

The results obtained through the optimization were entered in Statgraphic Centurion in order to define a mathematical model of the dynamic adsorption process.

Optimization of Output Pb(II) Ions Concentration by Statgraphic Centurion

To determine the model of adsorption dynamics of Pb (II) ions in the aqueous solution Statgraphic Centurion was used. This software import values for initial concentration of Pb (II) ions in solution, contact time, the bed height of NZ adsorbent and the adsorbate flow rate as input parameters and have their separate influence, and their interaction of outlet concentration of Pb (II) ions from the column with a fixed bed adsorbent.

In order to initiate the response surface method (RSM-3D) optimization of the investigated system within Statgraphics Centurion, it is essential to define the initial concentration levels of lead in the aqueous solution, contact time, bed height of natural zeolite adsorbent and the adsorbate flow rate.

Values obtained from the created model were used as output data. The Statgraphic Centurion analysis produced the regression coefficients, Pareto chart of the influence of inlet values and their interactions on the output Pb(II) concentration for different initial Pb(II) ions concentration, different bed height of NZ adsorbent and different adsorbate flow rate.

The regression coefficients from Statgraphic Centurion analysis are given in table 3.

Table 3: Regression coefficients from Statgraphic Centurion analysis

Coefficient	***Estimate***	***Coefficient***	***Estimate***
constant	0.111766	AD	-0.000941548
A:time	0.873415	BB	0.000395673
B:Co	-0.00576467	BC	0.00306347
C:flow rate	-0.981977	BD	-0.0000805333
D:bed height	-0.473325	CC	0.0102213
AA	-0.00427571	CD	0.036232
AB	0.00444395	DD	-0.00461274
AC	-0.000208846		

The overall model will be:

C_{out} = 0.111766 + 0.873415***time** - 0.00576467***Co** - 0.981977***flow rate** - 0.473325***bed height** - 0.00427571***time**^2 + 0.00444395***time*****Co** - 0.000208846***time*****flow rate** - 0.000941548***time*****bed height** + 0.000395673***Co**^2 + 0.00306347***Co*****flow rate** - 0.0000805333***Co*****bed height** + 0.0102213***flow rate**^2 + 0.036232***flow rate*****bed height** - 0.00461274***bed height**^2

where: **C_{out}**-output concentration of Pb(II) ions (mg/dm^3); **Co**-initial Pb(II) ions concentration in aqueous solution (mg/dm^3), **flow rate**-flow rate of adsorbate (cm^3/min), **bed height**- bed height of Zeolite adsorbent (cm) and **time**-contact time between adsorbate and fixed bed adsorbent.

The Pareto chart represents the influence of operating parameters and their interaction on the output values of the adsorption dynamics which is given on figure 5. From Pareto chart (figure 5) and regression coefficient (table 3) it can be seen which coefficients are positive and which are negative. On figure 5 the dark tapes are negative coefficients and bright tapes are positive coefficients. But the important thing is that influential and non-influential coefficients. It is best seen from the Pareto diagram (figure 5).

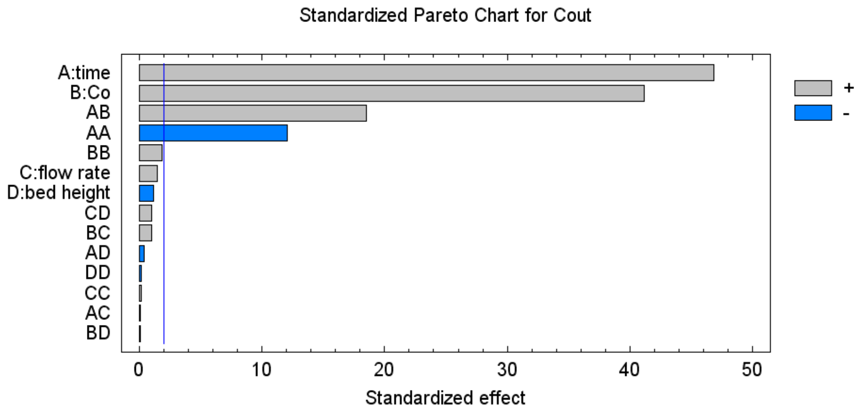


Figure 5. Pareto chart for the influence of operating parameters and their interaction on the output values of the adsorption dynamics

The odds must be greater than the vertical line drawn on the chart, so influential are only 4 coefficients, as follows: A-**time**, B-**initial concentration of Pb (II) ions in solution**, AB-**interaction of contact time and the initial concentration of Pb (II) ions in solution** and AA- **squared contact time**. This means that the resulting model will be reduced and will be in the following form:

$$\mathbf{C_{out}}=0.111766+0.873415*\mathbf{time}-0.00576467*\mathbf{Co}-0.00427571*\mathbf{time}^\wedge 2+0.00444395*\mathbf{time}*\mathbf{Co}$$

or:

$$\mathbf{C_{out}} = 0.111766 + 0.873415\cdot\mathbf{t} - 0.00576467\cdot\mathbf{C_o} - 0.00427571\cdot\mathbf{t}^2+0.00444395\cdot\mathbf{t}\cdot\mathbf{C_o}$$

The coefficient of correlation for the founded model by Statgraphics Centurion is R=0.95385.
The 3D response surface for constant bed height of NZ adsorbent (L=23 cm) and constant flow rate of adsorbate (F=10 cm^3/min) is given on figure 6 which provides the dependence of output Pb(II) ions concentration from contact time and the initial Pb(II) ions concentration in aqueous solution.

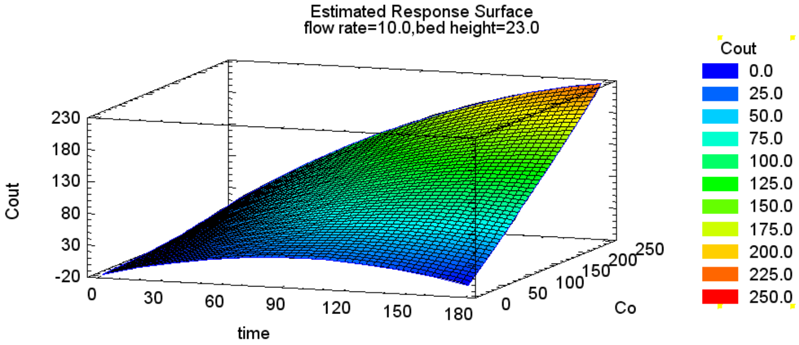


Figure 6. 3D response surface for the dependence of output Pb(II) ions concentration from the contact time and the initial Pb(II) ions concentration in aqueous solution in the same time (constant bed height of NZ adsorbent, L=23 cm) and constant flow rate of adsorbate (F=10 cm^3/min).

The contours of estimated response surface for constant bed height of NZ adsorbent and constant flow rate of adsorbate F=10 cm^3/min is given on figure 7.

To achieve complete purification of wastewater from Pb (II) ions with fixed bed adsorbent (if working with a fixed bed adsorbent of 23 cm and a flow rate of 10 cm^3/min) column can works up to 25 min for initial concentrations of 0-240 mg/dm^3. To achieve 10% of the input concentration, eg. 25 mg/dm^3 (From the main entrance concentration of 250 mg/dm^3), the column can works 170 min. For smaller initial concentrations as initial concentration, eg. 50 mg/dm^3, the column should be works only 35 min to reach 5 mg/dm^3.

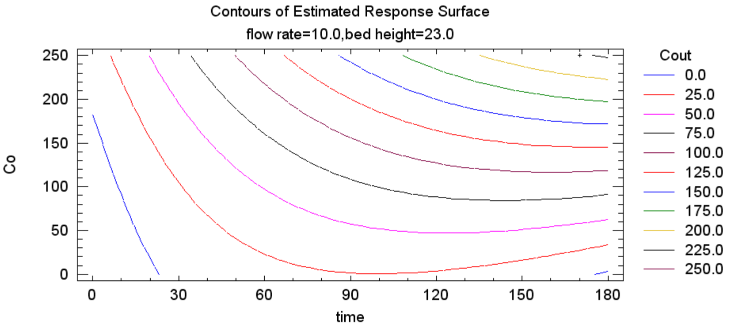


Figure 7. Contours of estimated response surface for constant bed height of NZ adsorbent (23 cm) and constant flow rate of adsorbate (F=10 cm^3/min)

The 3D response surface for constant bed height of NZ adsorbent (L=8 cm) and constant flow rate of adsorbate (F=10 cm^3/min) is given on figure 8 which provides the dependence of output Pb(II) ions concentration from contact time and the initial Pb(II) ions concentration in aqueous solution.

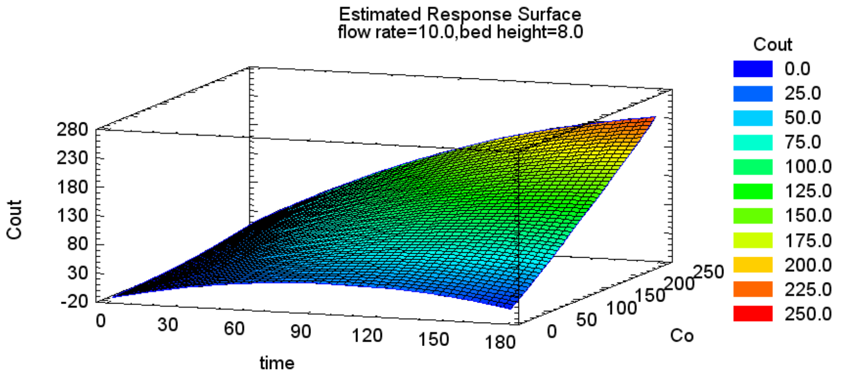


Figure 8. 3D response surface for the dependence of output Pb(II) ions concentration from the contact time and the initial Pb(II) ions concentration in aqueous solution in the same time (constant bed height of NZ adsorbent, L=8 cm) and constant flow rate of adsorbate (F=10 cm^3/min)

The contours of estimated response surface for constant bed height of NZ adsorbent (8 cm) and constant flow rate of adsorbate F=10 cm^3/min is given on figure 9.

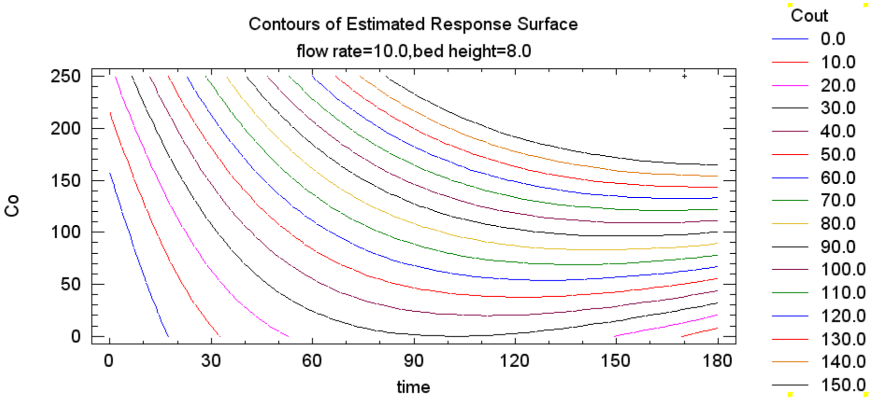


Figure 9. Contours of estimated response surface for constant bed height of NZ adsorbent (8 cm) and constant flow rate of adsorbate (F=10 cm^3/min)

To achieve complete purification of wastewater from Pb (II) ions with fixed bed adsorbent (if working with a fixed bed adsorbent of 8 cm and a flow rate of 10 cm^3/min) column can works up to 19 min for initial concentrations of 0-200 mg/dm^3. To achieve 10% of the input concentration, eg. 25 mg/dm^3 (From the main entrance concentration of 250 mg/dm^3), the column can works 80 min. For smaller initial concentrations as initial concentration, eg. 50 mg/dm^3, the column should be works only 25 min to reach 5 mg/dm^3.

The 3D response surface for constant bed height of NZ adsorbent (L=23 cm) and constant flow rate of adsorbate (F=20 cm^3/min) is given on figure 10 which provides the dependence of output Pb(II) ions concentration from contact time and the initial Pb(II) ions concentration in aqueous solution.

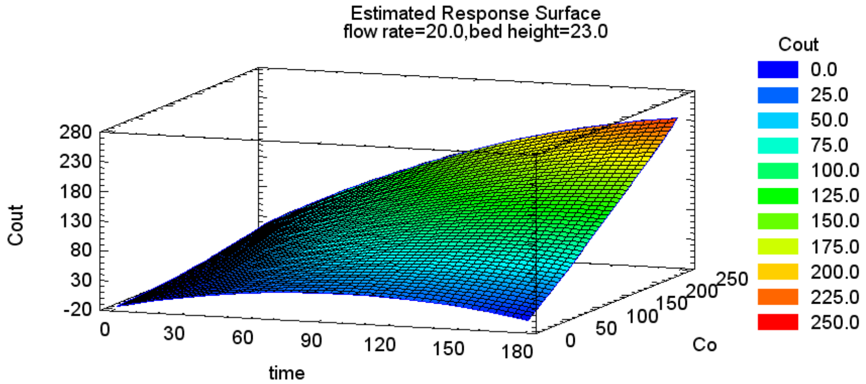


Figure 10. 3D response surface for the dependence of output Pb(II) ions concentration from the contact time and the initial Pb(II) ions concentration in aqueous solution in the same time (constant bed height of NZ adsorbent, L=23 cm) and constant flow rate of adsorbate (F=20 cm^3/min)

The contours of estimated response surface for constant bed height of NZ adsorbent (23 cm) and constant flow rate of adsorbate F=20 cm^3/min is given on figure 11.

To achieve complete purification of wastewater from Pb (II) ions with fixed bed adsorbent (if working with a fixed bed adsorbent of 23 cm and a flow rate of 20 cm^3/min) column can works up to 25 min for initial concentrations of 0-180 mg/dm^3. To achieve 10% of the input concentration, eg. 25 mg/dm^3 (From the main entrance concentration of 250 mg/dm^3), the column can works 115 min. For smaller initial concentrations as initial concentration, eg. 50 mg/dm^3, the column should be works only 32 min to reach 5 mg/dm^3.

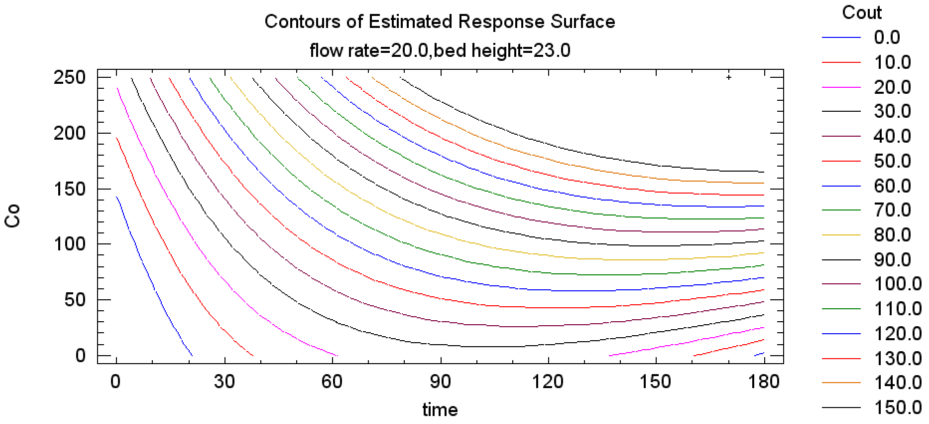


Figure 11. Contours of estimated response surface for constant bed height of NZ adsorbent (23 cm) and constant flow rate of adsorbate (F=20 cm^3/min)

The 3D response surface for constant bed height of NZ adsorbent (L=8 cm) and constant flow rate of adsorbate (F=20 cm^3/min) is given on figure 12 which provides the dependence of output Pb(II) ions concentration from contact time and the initial Pb(II) ions concentration in aqueous solution.

The contours of estimated response surface for constant bed height of NZ adsorbent (8 cm) and constant flow rate of adsorbate F=20 cm^3/min is given on figure 13.

To achieve complete purification of wastewater from Pb (II) ions with fixed bed adsorbent (if working with a fixed bed adsorbent of 8 cm and a flow rate of 20 cm^3/min) column can works up to 21 min for initial concentrations of 0-190 mg/dm^3. To achieve 10% of the input concentration, eg. 25 mg/dm^3 (From the main entrance concentration of 250 mg/dm^3), the column can works 85 min. For smaller initial concentrations as initial concentration, eg. 50 mg/dm^3, the column should be works only 30 min to reach 5 mg/dm^3.

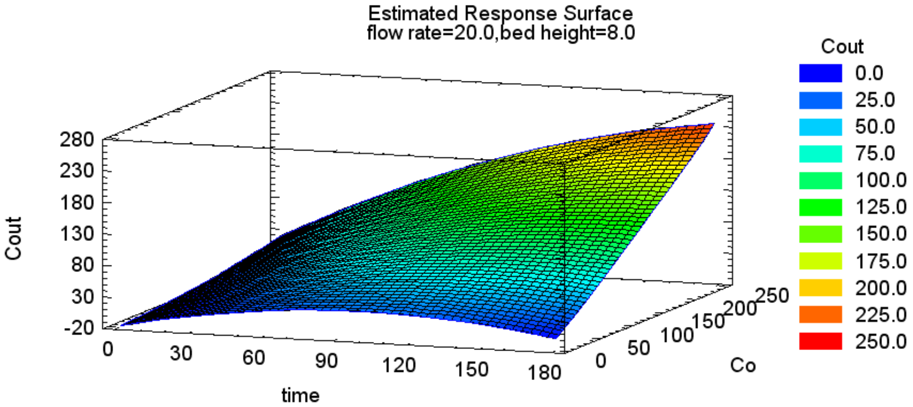


Figure 12. 3D response surface for the dependence of output Pb(II) ions concentration from the contact time and the initial Pb(II) ions concentration in aqueous solution in the same time (constant bed height of NZ adsorbent, L=23 cm) and constant flow rate of adsorbate (F=20 cm^3/min)

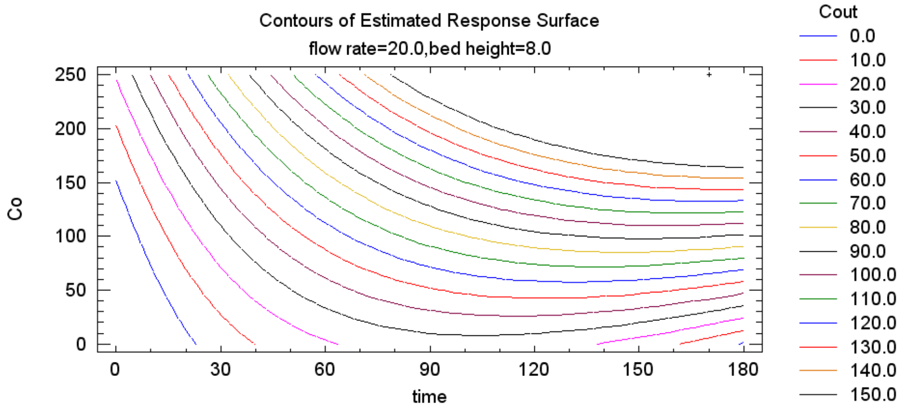


Figure 13. Contours of estimated response surface for constant bed height of NZ adsorbent (23 cm) and constant flow rate of adsorbate (F=20 cm^3/min)

CONCLUSIONS

The natural zeolite used as an adsorbent showed a good adsorption performance for removal of Pb(II) ions from aqueous solutions. The effect of various operational parameters on the adsorption of Pb(II) ions onto natural zeolite was investigated and optimized. When the fixed bed column works with a fixed flow rate of 10 cm^3/min, changing the bed height of the adsorbent from 8-23 cm, the time to work on the column (with an initial concentration of 50 mg/dm^3) changes from 19 min (height 8 cm), to 25 min (with a height of 23 cm). Changing the adsorbate flow rate does not affect much on the operation of the column, it can run 20 min for complete purification of wastewater with an initial concentration of Pb(II) ions of 50-190 mg/dm^3. So, the fixed bed column can works 25 min with complete purification of wastewater from Pb(II) ions (with outlet concentration zero) by adsorbate flow rate 10 or 20 cm^3/min, adsorbent bed height 23 cm and the initial concentration of Pb(II) ions in aqueous solution from 50-180 mg/dm^3.

Obtained model correlated the output concentration of Pb(II) ions in aqueous solution as a function from the initial concentration of Pb(II) ions in aqueous solution, the adsorbate flow rate and the height of natural zeolite adsorbent as well as their interactions.

REFERENCES

Abdullah S. R., Abustan I., Ibrahim A. N. M., (2013). Wastewater treatment using bentonite, the combinations of bentonite-zeolite, bentonite-alum, and bentonite-limestone as adsorbent and coagulant, *International Journal of Environmental Sciences, Vol. 4, (3)*, 379-391.

Acharya J., Kumar U., Meikap B.C., (2011). Thermodynamic characterization of adsorption of lead(II) ions on activated carbon developed from tamarind wood from aqueous solution, South African *Journal of Chemical Engineering,vol.18, no. 1*, 70-76.

Amarasinghe B.M.W.P.K., (2011). Lead and Cadmium Removal from Aqueous Medium Using Coir Pith as Adsorbent: Batch and Fixed bed Column Studies, *Journal of Tropical Forestry and Environment Vol. 1, No. 1*, 36-47.

Chojnacki A., Chojnacka K., Hoffmann J., Gorecki H ., (2004). The application of natural zeolites for mercury removal: from laboratory tests to industrial scale, *Minerals Engineering 17*, 933–937.

Guo J., Yang C., Zeng G., (2013). Treatment of swine wastewater using chemically modified zeolite and bioflocculant from activated sludge, *Bioresource Technology 143*, 289–297.

Ivanova E., Karsheva M., Koumanova B., (2010). Adsorption of ammonium ions onto natural zeolite, Journal of the University of Chemical Technology and Metallurgy, 45, 3, 295-302.

Johnson P.D., Girinathannair P., Ohlinger K. N., Ritchie S., Teuber L., Kirby J., (2008). Enhanced Removal of Heavy Metals in Primary Treatment Using Coagulation and Flocculation, *Water Environment Research, Vol. 80, (5)*, 472-479.

Mbadcam J.K., Anagho S.G., Nsami J.N., Kammegne A.M., (2011). Kinetic and equilibrium studies of the adsorption of lead (II) ions from aqueous solution onto two Cameroon clays: Kaolinite and smectite, *Journal of Environmental Chemistry and Ecotoxicology Vol. 3(11)*, 290-297.

Medvidovic N. V., Peric J., Trgo M., (2006). Column performance in lead removal from aqueous solutions by fixed bed of natural zeolite–clinoptilolite, *Separation and Purification Technology 49*, 237–244.

Mobasherpour I., Salahi E., Asjodi A., (2014). Research on the Batch and Fixed-Bed Column Performance of Red Mud Adsorbents for Lead Removal, *Canadian Chemical Transactions, Vol. 2 (1)*, 83-96.

Moyo M., Chikazaza L., (2013). Bioremediation of Lead(II) from Polluted Wastewaters Employing Sulphuric Acid Treated Maize Tassel Biomass, *American Journal of Analytical Chemistry, 4*, 689-695.

Oliveira C.R., Rubio J., (2007). New basis for adsorption of ionic pollutants onto modified zeolites, *Minerals Engineering 20*, 552–558.

PavanF.A. , MazzocatoA.C. , JacquesR.A. , DiasS.L.P. . (2008). Ponkan peel: A potential biosorbent for removal of Pb(II) ions from aqueous solution, *Biochemical Engineering Journal 40*, 357–362.

Saidi M., (2010). Experimental studies on effect of Heavy Metals presence in Industrial Wastewater on Biological Treatment, *International Journal of Environmental Sciences Volume 1, No 4*, 666-676.

Sarkar Z.K., Sarkar F.K., (2013). Selective Removal of Lead (II) Ion from Wastewater Using Superparamagnetic Monodispersed Iron Oxide (Fe_3O_4) Nanoparticles as a Effective Adsorbent, *Int. J. Nanosci. Nanotechnol., Vol. 9, No. 2*, 109-114.

Singanan, M. (2011). Removal of lead(II) and cadmium(II) ions from wastewater using activated biocarbon, *ScienceAsia 37*, 115–119.

Tofan L., Paduraru, C. (2004). Sorption Studies of AgI, CdII and PbII Ions on Sulphydryl Hemp Fibers, *Croatica Chemica Acta CCACAA 77 (4)*, 581-586.

Vassilis I.J., (2010). Ion Exchange and Adsorption Fixed Bed Operations for Wastewater Treatment- PART I: Modeling Fundamentals and Hydraulics Analysis, *Journal of Engineering Studies and Research, Vol. 16 (3)*, 29-41.

Khaoya,S., Pancharoen U. (2012). Removal of Lead (II) from Battery Industry Wastewater by HFSLM, *International Journal of Chemical Engineering and Applications, Vol. 3, No. 2*, 98-103.

IV International Conference
„ECOLOGY OF URBAN AREAS“ 2014

ADSORPTION PROPERTIES OF NATURAL ZEOLITE - CLINOPTILOLITE

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ABSTRACT

The natural zeolite - clinoptiolite is isotype of hollandite with chemical formula $(NaKCa)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12\ H_2O$. *The formula shows that the structure of clinoptilolite beside* AlO_4^- *and* SiO_4^- *tetrahedrons includes* Na^+, K^+ *and* Ca^+ *cations. This zeolite has a high dehydration stability and is thermally stabile at 700* ^oC *at the air environment and it differs from the other zeolites with similar chemical structure. Its structure is three-dimensional grid made up of tetrahedrons of Si and Al. Rocks rich with clinoptilolite contain 60 -90% pure clinoptilolite, feldspars, clay and quartz as major mineral impurities. The zeolite is used as odors adsorbent, for making the membranes and filters for purification of municipal and industrial waste waters. Because of this our studies will be oriented to analyze the adsorption properties of clinoptilolite. The static-gravimetric method is applied. The adsorption isotherm is Langmuir type of isotherm and the linear plot of the isotherm is used to determine the specific surface of zeolite which value is 268* m^2/g. *Obtained results will be presented in table and as graphic and also the structure of clinoptilolite will be shown with FTIR spectrum. It can be concluded that this natural zeolite - clinoptilolite can be exploited for purification of muddy rivers and wastewaters which contain a high percentage of heavy metals (Cr, Ni, Fe).*

Key words: *Clinoptilolite, adsorption, Langmuir isotherm, specific surface.*

INTRODUCTION

The zeolites are porous crystals, characterized by specific structure of the frame and regulated pore geometry. The zeolites have high ion exchange capacity and selective adsorption capacity, thermal and mechanical stability (Passaglia and Sheppard 2001). There are natural and synthetic zeolites. The zeolite - clinoptilolite is natural zeolite. Natural zeolites are obtained by performing the excavation while synthetic zeolites are obtained through chemical processes based on chemicals with carbon fundament. The natural zeolites have higher ratio of silicon and aluminum unlike the synthetic zeolites. SiO_4 and AlO_4 tetrahedrons in the zeolites are connected in skeletal structure. The aluminosilicate structure has negative charge that attracts the inside positive cations. The zeolites in their structure have large cavities where cations like K, Na, Ba or Ca (Peric et al., 2001), large molecules of organic compounds, cationic groups of ammonia, carbonate and nitrate ions, can penetrate and can be adsorbed. In some types of zeolites the cavities are interconnected and form wide and long channels with different sizes. These channels allow easy movement of ions and molecules into and out of the zeolites structure (Breck 1984). Also, zeolites feature the ability to adsorb or desorb the water molecules without damaging of their crystal structure. In the nature are found about 50 zeolite minerals so far, of which only 6 of them are in significant amount in sedimentary deposits and they are clinoptilolite, chabazite, modernite, erionite, hollandite and phillipsite. Rocks rich in clinoptilolite contain more than 90% pure clinoptilolite and other mineral impurities. In this study, characterization of clinoptilolite by chemical and FTIR analysis is given and specific surface applying statistic gravimetric method is determined.

EXPERIMENTAL PART AND RESULTS DISCUSSION

The clinoptilolite used for experimental analysis is in the form of granules. The results of chemical composition of clinoptilolite determined by classical silicate chemical analysis are presented in Table 1.

Table 1: Chemical composition of clinoptilolite

Oxides	SiO_2	Al_2O_3	CaO	H_2O	Fe_2O_3	MgO	Na_2O	MnO	Cr_2O_3	P_2O_5
Mass [%]	72	12	3,7	3,8	1,9	1,2	0,5	0,8	0,01	0,03

The chemical analysis show that the percentage of SiO_2 in the clinoptilolite is 72. The presence of the colored oxides is minimal, and Al_2O_3 percentage is above 10%.

The structure of clinoptilolite is determined by Fourier transform infrared (FTIR) spectroscopy (Goryainov et al., 1995; Krivacsy and Hlavay 1995), and FTIR spectrum is given in Figure 1. The assignation of FTIR spectrum showed that: at the wave number from 3600 cm^{-1} to 3200 cm^{-1} with peak at 3435 cm^{-1} occurs a line which comes from the hydroxyl groups; in the range of 1800 cm^{-1} to 1600 cm^{-1} with peak at 1635 cm^{-1} the line occurs as a result of valence vibrations of molecular water; the line from 1200 cm^{-1} to 1000 cm^{-1} with peak at 1058 cm^{-1} occurs due to vibrations of the Si(Al) - O bond; the line from 1000 cm^{-1} to 800 cm^{-1} with the peak at 796 cm^{-1} as well as the lines that occur from 800 cm^{-1} to 400 cm^{-1} with peaks at 609 cm^{-1}, 525 cm^{-1} and 471 cm^{-1} are symmetrical and result from the vibrations that arise in the structure of the zeolites.

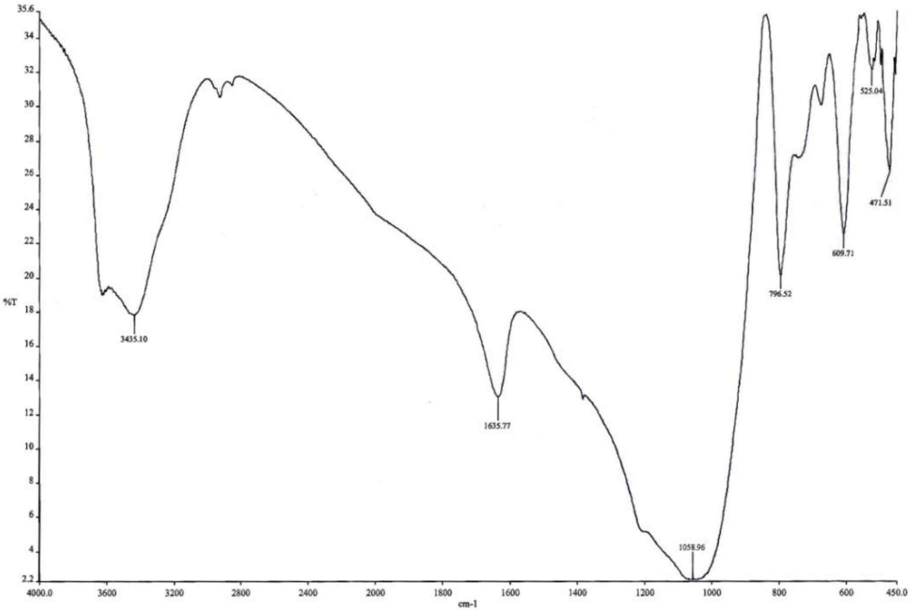

Figure 1. FTIR spectrum of clinoptilolit

The structure of the clinoptilolite is made up of AlO_4 and SiO_4 interconnected with oxygen bridge. They can connect to each other in different ways creating rings that interconnect forming geometric figures building the sodalite units. Zeolites vary in geometric channels. The entrance to the channel of the zeolite is an orifice (pore) made up of 6, 8, 10 or 12 rings and therefore there are zeolites with small, medium or large pores. The pores are with diameter of 0, 3 to 1,2 nm. The structure of the zeolite - clinoptilolite is given in Figure 2 and natural clinoptilolite is shown in Figure 3.

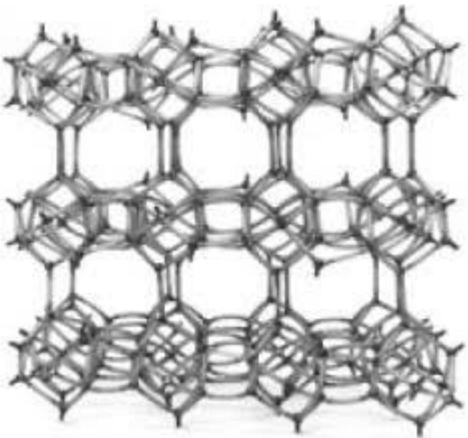

Figure 2. Structure of clinoptilolite

Figure 3. Natural clinoptilolite

Determination of adsorption properties of clinoptilolite

The adsorption properties of clinoptilolite are determined using static gravimetric method. The material was ground to a particle size of 0,09 mm. The monolayer capacity and specific surface of clinoptilolite are evaluated from data of equilibrium adsorption of water vapor. The adsorption isotherm obtained at 298K is shown in Figure 4.

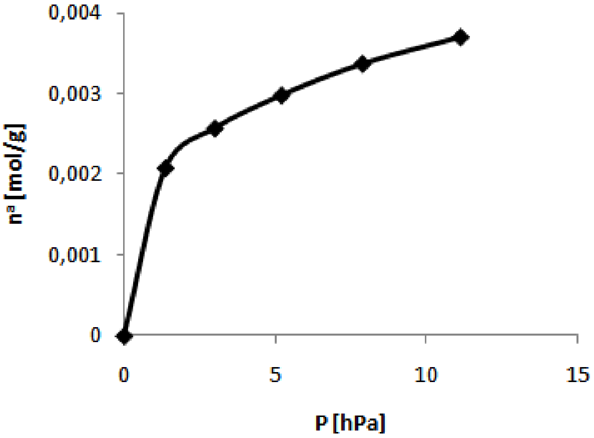

Figure 4. Adsorption isotherm of water vapor on clinoptilolite obtained at 298K

The adsorption isotherms at 298K are interpreted by linear form of Langmuir equation.

$$\frac{P}{n^a} = \frac{1}{n_m^a b} + \frac{P}{n_m^a} \qquad (1)$$

where P is equilibrium pressure of water vapor, n^a is amount of adsorbed water vapor, n_m^a is monolayer capacity of adsorbent and b is a constant.

The diagram of the linear form of the equation is given in Figure 5.

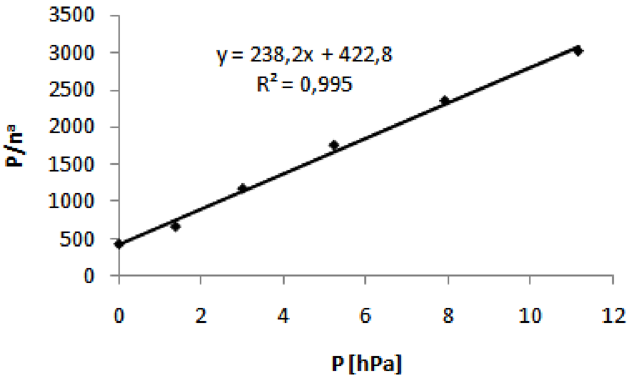

Figure 5. Plot of linear form of Langmuir equation for adsorption of water vapor on clinoptilolite

The linearity of the plot and high value of regression coefficient, R^2 = 0,996, show the good fit of the experimental isotherm to the Langmuir equation. The value of monolayer capacity is used to calculate the specific surface of clinoptilolite by the equation:

$$a_s = n_m^a N_A a_m 10^{-18} \tag{2}$$

where a_s is the specific surface, a_m is surface of adsorbent occupied by one molecule of adsorbate, which for water is 0,106 nm^2.

The values of the parameters of the Langmuir equation, monolayer capacity, n_m^a and constant *b*, and the specific surface, a_s are 4,2 · 10^{-3} mol/g, 0,56, and 268 m^2/g, respectively. The high value of specific surface of clinoptilolite enables it to be used as adsorbent for heavy metals removal from industrial wastewaters (Milicevic et al., 2013).

CONCLUSION

Performed analysis and the results presented in this work lead to the conclusion that the natural zeolite - clinoptilolite with its structure shows good adsorption properties as confirmed by Langmuir adsorption isotherm. The specific surface, determined by linearization of Langmuir isotherm, shows that clinoptilolite can be applied as adsorbent for heavy metals and other toxic materials. Clinoptilolite, with its adsorption ability, can be used in the future for selective adsorption removal of ammonium ion. Furthermore clinoptilolite can be exploited for industrial wastewaters purification.

REFERENCES

Breck, D. W. (1984). Zeolite molecular sieves. *Krieger Publ. Comp.* Malabar, Florida

Goryainov, S. V., Stolpovskaya, V. N., Likhacheva, A. Y., Beltisky, I. A., & Fursenko, B. A. (1995). Determination of clinoptilolite and heulandites in tuffaceous deposits by infrared spectroscopy. Natural Zeolites 93: Occurrence, properties, use. Ming, D. W., and Mumpton, F. A. International committee on netural zeolites, New York

Krivacsy, Z., & Hlavay, J. (1995). A Simple method for the determination of clinoptilolite in natural zeolite rocks. *Zeolites, Vol. 15(6).* 551 - 555

Milicevic, S., Milosevic, V., Povrenovic, D., Stojanovic, J., Martinovic, S., & Babic, B. (2013). Removal of heavy metals from aqueous solution using natural and Fe(III) oxyhidroxide clinoptilolite. *Clays and Clay Minerals, Vol. 61.* 231 - 257

Passaglia, A. & Sheppard, R. A. (2001). Crystal chemistry of zeolites. In Bish, D. L., Ming, D. W. (eds.). Natural zeolites: Occurrence, properties, application, Reviews in mineralogy and geochemistry. The Mineralogical Society of America, Washington DC

Peric, J., Trgo, M. & Cerijan - Stefanovic, S. (2001). The sorption equilibria in natural zeolite - aqueous solutions systems, *Zeolites and Mesoporous Materials at the Down of the 21 st Centery,* Amsterdam. London, Elsevier

IV International Conference
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ANALYSIS OF EMERGING SUBSTANCES IN URBAN WASTE AND SURFACE WATER

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ABSTRACT

Four screening and two target analysis of emerging and priority pollutants have been done as a part of NATO Project, in surface and wastewater samples at selecting sampling locations on the river Danube in the vicinity of Novi Sad. The research presented in this paper has been focused on detection of pesticides, especially on DDT and its metabolites. p,p`-DDD, was detected in almost all the samples with extremely high values at sampling sites GC1'' and RO', which confirms historical contamination, but also recent contamination inputted upstream of the city of Novi Sad. This could be cause of concern because DDT was banned in Serbia since 1972. as in the EU countries. The quantitative analyses conducted in this study could serve as a base for monitoring of ecological and chemical water status in order to establish a quality overview of drinking water sources and the occurrence of “emerging” organic substances along the Danube in the vicinity of Novi Sad. Presented study of the surface water quality was performed for the first time in Novi Sad and its surroundings, where municipal and industrial wastewaters are directly discharged, without any treatment, into the Danube River.

Key words: *emerging contaminants, urban water quality, pesticides.*

INTRODUCTION

In the last decade, considerable interest has grown concerning the presence of the so called “emerging substances (EmS)”. EmS are contaminants that have been recently discovered in the environment, due to their continuous increased use and above all due to the fact that they were not considered as contaminants before.

Most of them are widespread in everyday life and applied in different fields such as pharmaceuticals (for both human and animal uses), hormones, household chemicals, personal care products, secondary by-products from industry.

EmS are ubiquitous, persistent/pseudo-persistent and biologically very active molecules that occur in the environment as a result of natural, industrial and human activities. Low doses and pseudo-persistency effects are recognized as powerful chemical eco stressors onto total biosphere with unknown eco toxicology implication, fate, behavior, distribution and partitioning as well as transport through all environmental media.

EmS are mostly present in waste, surface and receiving water bodies (Grujic Letic et al., 2012, Milic et al., 2014, Barcelo et al., 2008, Loos et al., 2012). EmS could be released into the environment through the wastewater discharges, application of sewage sludge, landfill leachate, accidents and other ways (Kümmerer, 2009; Verlicchi et al., 2010). The water effluents are then discharged into rivers and sludge are spread on the soil as fertilizers. Therefore these compounds can reach all the environmental compartments. The distribution, partitioning processes, transport, ecotoxicity and the fate of EmS in the environment are close related to their physico-chemical characteristics.

According to NORMAN EmS can be defined as substances that have been detected in the environment, but which are currently not included in routine monitoring programs at EU level and whose fate, behavior and (eco)toxicological effects are not well understood and which may be candidates for future regulation. Emerging environmental substances are not the new chemicals. They are substances that have often long been present in the environment but whose presence and significance are now recognized and being elucidated. Data for emerging substances are often scarce and measurement methods are often at the research and development stage or have not yet been harmonized at the European level.

This work was carried out using guidelines set by the Water Framework Directive aimed at improving the ecological quality of surface waters and NORMAN list of emerging substances. Four screening and two target analysis of emerging and priority pollutants have been done as a part of NATO Project, in surface and wastewater samples at several sampling locations on the river Danube in the vicinity of Novi Sad. Novi Sad has joint collector for both industrial and municipal wastewaters, directly discharged into the Danube. The Novi Sad Municipality Water Supply System generally uses groundwater from alluvial aquifers of the Danube. Thus, the quantitative analyses conducted in this study could serve as a base for monitoring of ecological and chemical water status in order to establish a quality overview of drinking water sources and the occurrence of “emerging” organic substances along the Danube in the vicinity of Novi Sad. The work presented in this paper has been focused on detection of pesticides in wastewater and Danube surface samples in the vicinity of Novi Sad. This research was conducted within NATO Science for Peace Project, ESP.EAP.SFP 984087.

MATERIAL AND METHODS

Samples of surface and waste water were collected in urban area of Novi Sad. The selected sampling points include waste water directly from the collectors of four sewage discharges GC1, GC2, Ratno ostrvo (RO) and Rokov potok (RP), while samples of surface water from Danube River were taken 100 meters downstream of the each discharge: 45°15'5,42"N, 19°51'22,95"E (100 m downstream of the discharge GC1), 45°15'44,4"N, 19°51'28,46"E (100 m downstream of the discharge GC2), 45°15'11,84"N, 19°54'40,18"E (100 m downstream of the discharge Ratno ostrvo) and 45°15'2,2"N, 19°54'9,92"E (100 m downstream of the discharge Rokov potok).

Collected water samples were analysed by GC-MS. Screening and target analyses were performed at Institute of Analytical Chemistry STU in Bratislava. A 800 ml aliquot of water sample were spiked with internal standard (phenanthrene-D10) to achieve final concentration of 1µg/l and extracted with two 50 ml portions of dichloromethane for 20 minutes. After extraction, both extracts were combined and dried with anhydrous sodium sulfate. A small aliquots of copper powder were added into obtained extract to remove elementary sulphur. After filtration, the combined extract was evaporated using Kuderna-Danish apparatus to final volume 1 ml. A 50 µl of extract was injected into Agilent 6890 gas chromatograph coupled to Agilent 5973 mass spectrometric detector. The GC system was equipped with PTV injector that was ramped from 60˚C to 260˚C (5 minutes) at a rate of 40 ˚C/min. Helium was used as carrier gas. The MSD was used in the scan mode (m/z 45–600) for all samples. Identification of compounds was performed using Wiley7n and NIST08 mass spectrum libraries. According to the results of screening analysis target compounds were selected for quantitative analysis with GC/MS.

RESULTS AND DISCCUSION

Four screening campaigns in the river Danube in the vicinity of Novi Sad have been performed within the NATO Project ESP.EAP.SFP 984087 in order to determine occurrence of EmS, priority and hazardous substances of interest for Danube basin and to proceed with target analysis of Danube surface water and wastewater discharged directly into Danube, which is the fundamental basis for the broader knowledge of the newly recognized properties of EmS.

Within screening analyses more than 150 organic compounds in surface water were detected as the first screening results of the occurrence of EmS in the river Danube in the vicinity of Novi Sad (Milic et al., 2014). The most frequently compounds occurring in studied water samples were phthalates, pesticides, PAHs, terpenes and fatty acids.

This study was then focused on the target analysis of pesticides. Organochlorine pesticides are included in the list of Priority Substances and Certain Other Pollutants according to Annex II of Directive 2008/105/EC and DDT is included in Annex B of the Stockholm convention.

Pesticides were detected in the highest concentrations in the first target campaign, especially in the wastewater at sampling point RO', indicating pollution from agricultural activities, households and farms. The most lipophilic metabolite of p,p`-DDT, p,p`-DDD, was detected in almost all the samples with extremely high values at sampling sites GC1" and RO' (Table 1), which confirms historical contamination, but also recent contamination inputted upstream of the city of Novi Sad.

Table 1: Pesticides concentrations in waste and surface water in the vicinity of Novi Sad

Compound	GC1'	GC1"	GC2'	GC2"	RO'	RO"	RP'	RP"	average	SD
Dieldrin	<10	270	<10	100	70	30	<10	<10	118	106
Endrin	<10	<10	<10	<10	20	100	<10	<10	60	57
Endosulfan alpha	<5	230	<5	<5	60	<5	<5	<5	145	120
Endosulfan beta	<5	<5	<5	<5	80	40	<5	<5	60	28
p,p`-DDD	230	400	240	<25	620	220	220	<25	322	162
p,p`-DDE	80	25	80		110	80	80	<25	76	28
p,p`-DDT	260	310	<10	<10	500	<10	<10	<10	357	127

DDT was banned in Serbia since 1972, as in the other EU countries; however DDT is still determined in high concentrations. This unexpected trend of high DDT concentrations has been registered in other research studies and could be the evidence of uncontrolled usage of DDT. Some pesticides like endosulfan, dieldrin and endrin were identified in significantly higher concentrations at RO' which is located in agricultural area, thus such pollution can be expected.

Figure 1. presents the sum of DDT concentrations in waste and surface water in the vicinity of Novi Sad. The highest concentration of sum of DDT metabolites in Danube surface water was detected at sampling site GC2".

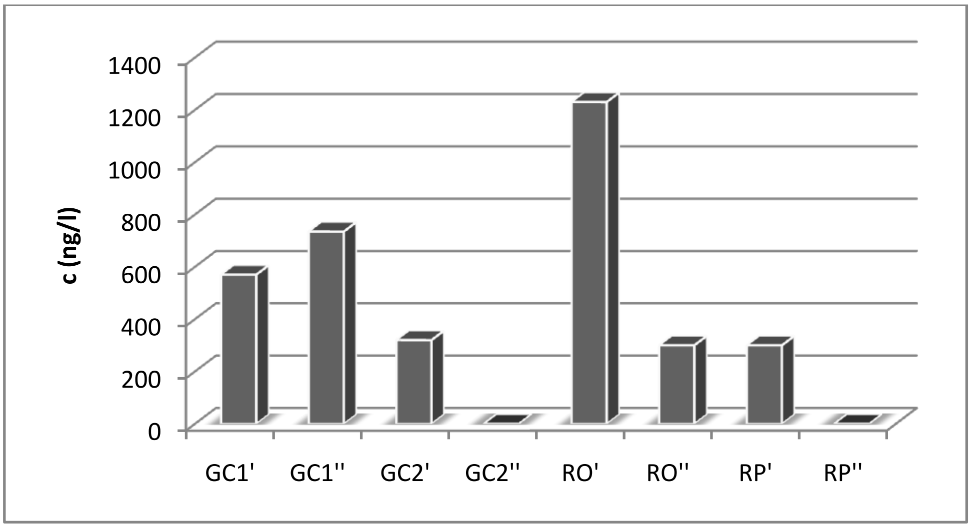

Figure 1. Sum of DDT concentrations in waste and surface water in the vicinity of Novi Sad

CONCLUSIONS

In screening analyses more than 150 different organic and inorganic chemicals were registered. Within the target analyses, the most of the detected organic compounds from the groups of PAH, phenols, phthalates and pesticides; therefore special attention should be focused to those compounds. Pesticides were detected in target analyses of waste and surface water in urban area of Novi Sad. p,p`-DDD, the metabolite of DDT, was detected in the highest concentrations, especially in the agricultural area of Novi Sad. Presented study of the surface water quality was performed for the first time in Novi Sad and its surroundings, where municipal and industrial wastewaters are directly discharged, without any treatment, into the Danube River.

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REFERENCES

Barcelo, D., Petrovic, M. (2008): Emerging contaminants from industrial and municipal waste, Water pollution, Springer,Volume 5/S.

Grujić Letić, N., Milić, N., Turk Sekulić, M., Radonić, J., Milanović, M., Mhajlović, I., Vojinović-Miloradov, M. (2012). Quantification of emerging organic contaminants in the Danube River samples by HPLC, Chemicke Listy, 106, 264-266, ISSN 1213-7103.

Kümmerer K (2009): Antibiotics in the aquatic environment—a review—part I, Chemosphere, 75, 417–34.

Loos R, Locoro G, Contini S. (2010). Occurrence of polar organic contaminants in the dissolved water phase of the Danube River and its major tributaries using SPE-LC-MS^2 analysis. Water res, 44(7), 2325-2335.

Milić, N., Milanović, M., Grujić Letić, N., Turk Sekulić, M., Radonić, J., Mihajlović, I., Vojinović Miloradov, M. (2012). Occurrence of antibiotics as emerging contaminant substances in aquatic environment. Int J Environ Health Res. 1-15, DOI:10.1080/09603123.2012.733934.

Milić N, Spanik I, Radonić J, Turk Sekulić M, Grujić N, Vyviurska O, Milanović M, Sremački M, VojinovićMiloradov M (2014): Screening analyses of wastewater and Danube surface water in Novi Sad locality, Serbia. Fresenius Environmental Bulletin, 23, 372-377.

NORMAN (accessed 2 May 2013).http://www.norman-network.net/index_php.php

Verlicchi P, Al Aukidy M, Zambello E. (2012). Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment—a review. Sci Total Environ. 429, 123–155.

Vojinović Miloradov, M., Turk Sekulić, M., Radonić, J., Milić, N., Grujić Letić N., Mihajlović, I., Milanović, M. (2013). Industrial emerging chemicals in the environment. Chem Ind. DOI:10.2298/HEMIND121110028V.

Vojinović Miloradov, M., Miloradov, M., Turk Sekulić, M., Radonić, J., Stošić, M. (2012). Low doses effects of emerging substances, pseudopersistancy and hazard consequences to aquatic environment and public health. 2 International conference “Ecology of urban areas”, Invited plenary lecture, Zrenjanin.

IV International Conference
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SELECTED PHARMACEUTICALS LOAD IN URBAN WASTEWATER FOR THE CITY OF NOVI SAD

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ABSTRACT

There has been an increasing concern in recent years about the occurrence, fate, and adverse effects of pharmaceutical residues in the aquatic environment. Since most of the pharmaceutical residues and metabolites are not completely removed during conventional wastewater treatment, especially in the Republic of Serbia where only 15% of wastewater is treated, significant amount of compounds belonging to the selected group reaches the surface water. Due to the rather poor wastewater management practice, with less than 10% of all being biologically treated, and less than 2% of all being tertiary treated, most of the contaminants present in wastewaters can represent a significant environmental concern. This fact is crucial, and represents the basis for one of the first attempts to identify and determine concentration levels of selected pharmaceuticals in municipal wastewater from the city of Novi Sad. The sampling site was urban wastewater discharge GC2. This site was selected as representative, due to the fact that the city of Novi Sad has three clinical Centres connected to the sewerage system and discharging wastewater without any treatment. This paper describes the research and preliminary results of detection and average load and consumption of selected pharmaceuticals.

Key words: *Pharmaceuticals, wastewater, load, consumption, Novi Sad.*

INTRODUCTION

Wastewater represent one of the main input routes of anthropogenic organic and inorganic contaminants into the environment. Due to their distinct differences in chemical structure and related specific treatment requirements, urban and industrial wastewaters are often kept in separate wastewater collection and treatment systems, which allows a more efficient source control and specific pollutant mitigation strategies (Terzić et al., 2008.) In contrast, municipal wastewaters in the developing countries such as Republic of Serbia are mainly of mixed type and include both, domestic and industrial wastewaters (Kaštelan-Macan et al., 2007). Moreover, a vast majority of wastewaters in the Republic of Serbia is released to the environment either without any treatment or after being treated only mechanically. Since most of the pharmaceutical residues and metabolites are not completely removed during conventional wastewater treatment, especially in the Republic of Serbia where only 16% of wastewater is treated, significant amount of compounds belonging to this group reaches the surface water. Due to the rather poor wastewater management practice, with less than 10% of all being biologically treated, and less than 2% of all being tertiary treated, Figure 1.

The identification and determination of many previously undetected organic anthropogenic compounds in wastewaters, including a large number of pharmaceuticals and personal care products, has seen a dramatic progress in recent years along with a rapid development of new analytical techniques (e.g. Gros et al., 2006a; Gonzalez et al., 2007; Richardson, 2007).

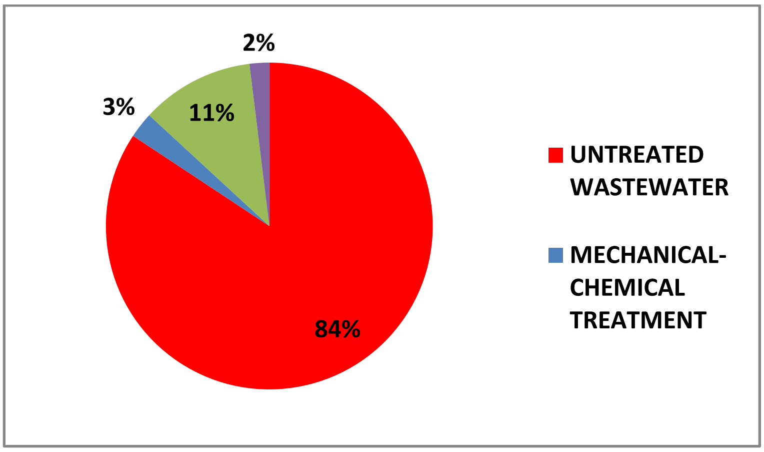

Figure 1. Treated wastewater in the Republic of Serbia
(Republical Statistical Office - Serbia, Used and treated water, 2012.)

To the best of our knowledge, there are no reports in the open literature, documenting the occurrence of emerging contaminants in domestic and industrial wastewaters in Serbia, except (Terzić et al., 2008.) for city of Belgrade and (Petrović et al., 2014) for Obrenovac municipial wastewater) and especially for the city of Novi Sad. Along these lines, this paper aims to fill the existing gap by providing for the first time a comprehensive report on the occurrence of organic wastewater contaminants in municipal and industrial wastewaters from city of Novi Sad.

THEORY

Pharmaceuticals, usually used in human and veterinary medicine, can enter the aquatic environment as parent compounds, metabolites or conjugates of both. Sometimes, these compounds are not managed properly and are discharged directly into drains, while at other times they are not completelymetabolized by the human body and are excreted via urine and feces. Thus, the occurrence of pharmaceuticals in the environment leads to various unanswered questions with regard to their biological potency in flora, fauna, and humans. Generally, very little is known about the long-termeffect and behavior of pharmaceutical residues in the aquatic environment, and in groundwater in particular (López-Serna et al., 2010). Also, it is unknown if the combination of drugs that share a common mechanism of action exhibits toxic synergistic effect (Hernando et al., 2004).

An innovative method of estimating drug consumption utilising the measuring of drug residues in wastewater was initially proposed by Daughton in 2001 (Daughton, 2001), implemented by Zuccato et al. In 2004 (Zuccato et al., 2005) and followed by others. The method assumes that drugs, after they are consumed and metabolised in the human body, are excreted into the sewage systemas parent compounds and metabolites. These residues reach the WWTP where the wastewater is sampled before treatment.

The metabolic pathways of many pharmaceuticals are understood, with several metabolites known in many cases. Therefore, this approach assumes that the measured residue concentrations present in sewage can be correlated with the amount of drug consumed by a population served by a WWTP. Obvious parameters required to calculate such usage on this scale include: (a) the concentration of suitable target species in wastewater; (b) the flow rate of sewage through the WWTP at/across the time of sampling (in this case wastewater efluent, because city of Novi Sad has no WWTP) and (c) the population served by the wastewater collection system.

This approach offers significant opportunities to aid in the monitoring of pharmaceutical usage at a community level, however to date this concept has received relatively little validation. If an excretion product is stable in wastewater and efficiently conveyed to the wastewater outlet, it is reasonable to

assume that the amount collectively excreted in a given period should be reflected by the amount reaching the wastewater outlet in the corresponding interval (Daughton 2001).
This paper presents, for the first time, the results of estimation of pharmaceutical consumption in Republic of Serbia using wastewater analysis.

METHODS

Chemicals and materials

Analyzed target compounds belong to different medical classes. They were selected taking into account different selection criteria. First of all, there is a need for comprehensive study of as wide range of PhAC in the Serbian wastewaters, particularly in those from the northern part of Serbia, which is dominated almost entirely by the drainage basin of the river Danube and could therefore reflect water contamination by pharmaceuticals. Within the analyzed groups of compounds, some were selected because of their high consumption and ubiquity in the aquatic environment while some were targeted due to their known persistency (carbamazepine, β-blockers, diclofenac, etc.).

Table 1: List of analyzed pharmaceuticals (LOD, LOQ, analysis method)

Pharmaceuticals	**LC/MS^2**	
	LOD (ng·L^{-1})	**LOQ (ng·L^{-1})**
Trimethoprim	0.4	1.2
Sulfametoksazole	2.3	7.6
Azytromicin	0.8	2.8
Doksicyklin	2.0	6.8
Eritromicin	0.8	2.5
Bromazepam	0.3	0.9
Karbamazepin	0.1	0.2
Lorazepam	0.2	0.7
Diazepam	0.5	1.6
Dikolofenak	1.4	4.7
4-formilaminoantipirine (4-FAA)	0.3	1.0
N-acetil-4-aminoantipirin (4-AAA)	0.4	1.3
Enalapril	0.6	1.9
Atorvastatin	1.8	6.1
Amlodipin	4.0	13.3
Cilazapril	0.6	2.0
Metoprolol	0.3	1.0
Bisprolol	0.5	1.6
Simvastatin	1.3	4.2

High purity (>90%) analytical standards of drugs were provided by domestic pharmaceutical companies (Hemofarm and Zorka-Pharma, Serbia). The individual standard solutions were prepared in methanol at the concentration of 300 gml^{-1}. The working standard solutions were prepared at 10 gml^{-1} and 100ngml^{-1} by mixing the appropriate amounts of the individual standard solutions and dilution with methanol. All solutions were preserved at −4°C. For the pH-value adjustment of the water samples, concentrated acetic acid and ammonia were used. All solvents used were HPLC grade from Fluka or Sigma−Aldrich, and all other reagents were of analytical grade. Deionized water was obtained by passing the tap water through a GenPure ultrapure water system (TKA, Niederelbert, Germany).

Sampling location and collection procedures

Over a 2-day period in March 2013, wastewater was collected as 24 h-composite samples from a wastewater outlet GC 2 (Figure 2) in city of Novi Sad. Composite sampling was performed continuously (every 180 min, from 07:00 am to 22:00 pm). This urban wastewater outlet is supplied with sewage primarily from a combined sewer infrastructure as well as a small proportion from separate sewers. Pumping stations are used to deliver sewage to this outlet. The population is 321.282 inhabitants (RSO 2012). The measured flow rate of influent wastewater through this wastewater collection system across the week was between 114912 and 128995 $m^3 day^{-1}$. All samples were collected in PET bottles. Samples were subsequently transported back to the laboratory in a dark and refrigerated storage, and stored at −4 °C until analysis.

Figure 2. Location of wastewater outlet GC 2 (google earth)

Analytical methodology

The selected pharmaceuticals were analyzed by solid phase extraction (SPE) followed by liquid chromatography–tandem mass spectrometry analysis (LC–MS^2) according to a method described in the literature (Grujić et al., 2009). The SPE method consisted of the loading of the water sample (100 ml, pH = 6) on the Oasis HLB cartridge (200 mg/ml), followed by 10 min. drying by vacuum suction, cartridge elution with 15 ml of methanol, and finally, extract evaporation to dryness and reconstitution with 1 ml of methanol. As for the LC–MS^2 method, the chromatographic separation of compounds was performed on a reverse-phase Zorbax Eclipse® XDB–C18 column, 75 mm × 4.6 mm ID and 3.5 µm particle size (Agilent Technologies, Santa Clara, CA, USA). The mobile phase was composed of methanol (A), deionized water (B) and 10% acetic acid (C) and gradient was changing as follows: 0 min, B 33%, C 2%; 12 min, B 98%, C 2%; 15 min, B 98%, C 2%. The initial conditions were then re-established and held for 15 min. The flow rate of the mobile phase was 0.6 ml min^{-1}. The injection volume was 10 µl. The mass spectrometric measurements were obtained using the LCQ Advantage quadrupole ion trap mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Electrospray ionization was used to perform the mass spectrometric analysis operating in the positive ionization mode.

RESULTS AND DISCUSSION

Measured concentrations ($ng{\cdot}L^{-1}$) of target analytes in wastewater influent were used to back-calculate pharmaceutical usage in local areas. The following description and formulas describe the method by which estimates were calculated. The concentration ($ng{\cdot}L^{-1}$) of selected pharmaceutical was firstly multiplied by the flow rate ($L{\cdot}day^{-1}$) of influent. Assuming no loss of sewage water along the pipes (no new as recorded either as a planned overflow or outage during this period), this provided an estimate of the load ($g{\cdot}day^{-1}$) of a selected pharmaceutical arriving at a selected wastewater outlet GC2. The formula used to calculate daily loads is shown in Equation (1). The formula used to calculate consumption is shown in Equation (2).

$$Load = Concentration \cdot Flow \qquad (1)$$

$$Consumption = 1000 \cdot Load \cdot \left(\frac{1000}{Population} \right) \qquad (2)$$

Where: Concentration corresponds to the pharmaceutical concentration (ng·L^{-1}),Flow to the wastewater influent volume over a 24 hour period (m^{3}·day^{-1}).Load (g·day^{-1}), Consumption (mg·day^{-1}·1000people^{-1}).

Corresponding loads (g•day) and average wastewater derived consumption estimates of analytes in wastewater are listed in Table 2. Several pharmaceuticals were frequently quantified at sometimes relatively high concentrations in both wastewater samples. These concentrations were extrapolated to estimate loads of target analytes and consumption in local communities.

Table 2: Average load (g day^{-1}) of target analytes in samples, and average wastewater derived consumption estimates

Pharmaceutical compound	**Loads (g·day^{-1})**		**Consumption (mg·day$^{-1\cdot}$1000people $^{-1}$)**	
	15.03.2013.	*16.03.2013.*	*15.03.2013.*	*16.03.2013.*
Trimethoprim	31.4	31,15	97.7	96.96
Sulfamethoxazole	10.3	8,05	32.3	25
Azithromycin	n.d	n.d.	n.d.	n.d.
Doxycycline	n.d	n.d.	n.d.	n.d.
Erythromycin	36.3	37	112.9	115.2
Bromazepam	n.d	n.d.	n.d.	n.d.
Carbamazepine	33.5	41,6	104.2	129.5
Lorazepam	n.d	n.d.	n.d.	n.d.
Diazepam	n.d	n.d.	n.d.	n.d.
Dicolofenac	n.d	n.d.	n.d.	n.d.
4- formyl aminoantipyrine (4 -FAA)	75.1	62,6	233.7	194.8
N-acetyl-4-aminoantipyrine (4-AAA)	150.9	73,3	469.7	228.1
Enalapril	n.d	30,3	n.d.	94.3
Atorvastatin	37.2	9,5	115.8	29.6
Amlodipine	2.8	n.d.	8.7	n.d.
Cilazapril	n.d	n.d.	n.d.	n.d.
Metoprolol	n.d	27,58	n.d.	85.8
Bisprolol	25.8	14,13	80.3	43.9
Simvastatin	9.4	n.d.	29.2	n.d.
Clopidogrel	n.d	n.d.	n.d.	n.d.

The results obtained indicate that the Azithromycin, Doxycycline, Bromazepam, Lorazepam, Diazepam, Dicolofenac, Enalapril, Cilazapril, Metoprolol, Clopidogrel were not detected. Average usage of Trimethoprim in the area studied was estimated to be between 96.96 and 97.7 mg·day^{-1}·1000 people^{-1}, The daily results of the monitoring study showed that almost same amounts of trimethoprim were consumed during the weekend (16.03.) and weekdays (15.03.). For Sulfamethoxazole average uptake is about three times lower between 25 and 32.3 mg day^{-1} 1000 people^{-1}. For Erythromycin average usage was estimated to be between 112.9 and 115.2 mg day^{-1} 1000 people^{-1}, The daily results of the monitoring study showed that almost same amounts of Erythromycin were consumed during the weekend and weekdays. Average uptake of Carbamazepine was estimated to be between 104.2 and 129.5 mg day^{-1}. Almost the same amounts were consumed during the weekend and weekdays. Metamizole metabolites 4-formylaminoantipyrine (4-FAA) and N-acetyl-4-aminoantipyrine (4-AAA), have largest average usage, 4–FAA was estimated to be between 194.8 and 233.7 mg·day^{-1}·1000 people^{-1}, and also (4-AAA) was estimated to be between 228.1 and 469.7 mg·day^{-1}, significant difference between the weekend and weekdays that maybe indicate larger consumption of analgesics during weekdays and stress period.

Cardiovascular pharmaceuticals such as Atorvastatin, Bisprolol, Metoprolol and Simvastatin have average usage and it was estimated to be between 29.2 for Simvastatin and 115.8 for Atorvastatin mg·day^{-1}·1000 people^{-1}. Also there is as difference between the weekend and weekdays.

CONCLUSIONS

The above results show the usefulness of wastewater analysis in order to provide estimates of local community pharmaceutical consumption. Potential reasons for discrepancies were discussed above for each compound, but in general, these factors include: sales of pharmaceuticals sold without prescription and not included within data, different consumption patterns in different areas. It is noticeable that using a metabolite (and not a parent drug) as a biomarker leads to higher certainty of obtained estimates. With regard to pharmaceuticals, consistent and logical results were reported. Monitoring of these compounds over two days is not enough. This period did not highlighted the expected occasionally use of many of these pharmaceuticals and the more consistent use of others. Wastewater analysis provides near-real time data, with sample collection, analysis and data reporting achieved in around 24 h (depending on the time of sample collection). The analysis of wastewater may provide a more reliable estimation of selected pharmaceuticals usage; as data is generated from a direct source rather than indirect sources such as population surveys in which participants may (for example) be untruthful about their pharmaceutical consumption.

Wastewater analysis for selected pharmaceutical usage estimation is a promising tool. However, this methodology will never be a stand-alone approach due to inherent limitations. Estimations through wastewater analysis cannot provide data with regard to the individuals taking the pharmaceuticals. Neither can data be provided on the dose, frequency or method of administration (although the method of administration may be determined for some compounds in which differentiating metabolites can be identified). In reality, it is likely that wastewater estimations will be complimentary to classical socio-epidemical studies, with wastewater analysis allowing authorities the important capacity to generate rapid consumptions estimates when required.

REFERENCES

Daughton CG. Illicit Drugs in Municipal Sewage: Proposed New Nonintrusive Tool to Heighten Public Awareness of Societal Use of Illicit/Abused Drugs and Their Potential for Ecological Consequences. In: Daughton C, Jones-Lepp T, editors. Pharmaceuticalsand Personal Care Products in the Environment: Scientific and Regulatory Issues. ACS Symposium SeriesWashington, D.C.: American Chemical Society; 2001. p. 348–64.

Gonzalez S, Petrović M, BarceloD.Advanced liquid chromatography/ mass spectrometry (LC-MS) methods applied to wastewater removal and the fate of surfactants in the environment. Trends Anal Chem 2007; 26(2):116–24.

Grujić S, Vasiljević T, Laušević M. Determination ofmultiple pharmaceutical classes in surface and ground waters by liquid chromatography–ion trap–tandem mass spectrometry. J Chromatogr A 2009; 1216:4989–5000.

Gros M, Petrović M, Barcelo D. Multi-residue analytical methods using LC-tandem MS for the determination of pharmaceuticals in environmental and wastewater samples: a review. Anal Bioanal Chem 2006a; 386(4):941–52.

Hernando MD, Mezcua M, GómezMJ, Malato O, Agüera A, Fernández-Alba AR. Comparative study of analytical methods involving gas chromatography–mass spectrometry after derivatization and gas chromatography–tandem mass spectrometry for the determination of selected endocrine disrupting compounds in wastewaters. J Chromatogr A 2004; 1047:129–35.

Kaštelan-Macan M, Ahel M, Horvat AJM, Jabučar D, Jovančić P. Water resources and waste water management in Bosnia and Herzegovina, Croatia and the State Union of Serbia and Montenegro. Water Policy 2007; 9:319–43.

Kovačević S., Miloradov M.V., Petković A., , Radonić J., Sremački M., Dimkić M., Occurance of selected pharmaceuticals in municipial wastewater from city of Novi Sad, 14th European Meeting on Environmental Chemistry, 4-7.12.2013., Budva, Montenegro, ISBN 978-9940-9059-1-0.

López-Serna R, Pérez S, Ginebreda A, Petrović M, Barceló D. Fully automated determination of 74 pharmaceuticals in environmental and waste waters by online solid phase extraction– liquid chromatography-electrospray–tandem mass spectrometry. Talanta 2010; 83:410–24.

Petrović M., Škrbić B., Živančev J., Ferrando-Climent L.,, Barcelo D., Determination of 81 pharmaceutical drugs by high performance liquid chromatography coupled to mass spectrometry with hybrid triple quadrupole–linear ion trap in different types of water in Serbia, Science of the Total Environment 468–469 (2014) 415–428.

Richardson SD. Water analysis: emerging contaminants and current issues. Anal Chem 2007; 79(12):4295–323

Republical Statistical Office - Serbia, Used and treated water, 2012.

Terzić S, Senta I, Ahela M, Gros M, Petrović M, Barceló D, et al. Occurrence and fate of emerging wastewater contaminants in Western Balkan Region. Sci Total Environ 2008; 399:66–77.

Zuccato E, Castiglioni S, Fanelli R. Identification of the pharmaceuticals for human use contaminating the Italian aquatic environment. J Hazard Mater 2005; 122:205–9.

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DETECTION OF EMERGING AND PRIORITY SUBSTANCES IN SURFACE WATER – GC-MS SCREENING METHOD OPTIMISATION

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ABSTRACT

The screening analysis makes a powerful analytical tool for determination, identification and prioritization of organic substances and pollutants in surface water. The analysis of surface water samples should be modified to fit the purpose and optimized to extract the most important and valuable information. The screening analysis is a process that comprises of extraction, isolation, detection and identification of selected substance or a group of substances within a minimum number of steps and relatively short period of time. For the purpose of screening analyses, gas chromatography coupled with mass spectrometry was selected as an analytical method. During the optimisation of the method different solvents have been utilised during extraction process to obtain the optimum solvent for specific sample. The chemical species that have been detected in surface water during the year of 2012 belong to emerging and priority groups of substances – flammables, irritants, toxic and cancerogenic compounds, EDCs, industrial chemicals, plasticizers, aliphatic (fatty) alcohol, higher alkanes, wood preservatives, flavour and fragrances, personal care products, pesticides, antifoaming agents, additive residues and others. The identified substances open the possibility for specification of target analyses in the future and better organisation and prioritisation of surface water monitoring system specific for the selected location.

Key words: *Emerging and priority compounds, method optimization, GC-MS, surface water.*

INTRODUCTION

In the natural aquatic environment diverse physical, chemical and biological processes occur and directly affect the content, transformation, diffusion and dispersion of different constituents in water. A significant number of chemical substances that can be found in surface water have divers impact onto the environment and human health.

The priority pollutants are a set of chemical pollutants that are regulated by law, and for which there are developed analytical tests and monitoring methods and quality standards. The current list of 129 Priority Pollutants is presented in Appendix A to 40 Code of Federal Regulations, Part 423. The Priority Pollutant list makes the list of toxic pollutants more usable, in a practical way, for the purposes assigned to EPA by the Clean Water Act (US EPA).The Annex X of the Water Framework Directive established provides a list of 33 Priority Substances (11 priority hazardous substances, 14 priority substances under review and 8 priority substances). The first list was replaced by Annex II of the Directive on Environmental Quality Standards, which set environmental quality standards for the substances in surface waters and confirmed their designation as priority or priority hazardous substances (Directive 2000/60/EC, Directive 2008/105/EC).

Emerging substances, present another level of concern, as low dose and pseudo-persistence can have a very strong chemical and ecological stress in a long period of time, which can completely and irreversibly change the balance in the ecosystem, as well as in the environment (*Miloradov* Vojinović, M. et al. 2012). Emerging substances are present in environment for a long period of time but their effects, presence and significance is rediscovered as the detection of such low doses have just been enabled due to the progress in analytical detection techniques. Data about emerging substances are scarce and measurement techniques and methods are often at the research and development stage or have not yet been harmonized at the European level. The low concentrations of emerging substances present in environment and scarce detection possibilities are making it difficult to interpret and evaluate results and represents a major difficulty for regulatory bodies in their decision-making (NORMAN, 2014) The importance of the low doses should be emphasized, especially for emerging substances from group of endocrine disruptive substances – EDS, in nano to pikogram (ppb to ppt, respectively) concentrations, which mimic function and cycle of natural hormone like substances (Miloradov Vojinović, M. et al. 2012). Some of the emerging substances despite the low doses have significant effect onto the environment and human health.

The screening analysis methodology for surface water samples was modified to fit the specific purpose and optimized to extract the most important and valuable data from the analyzed samples. During the screening analysis optimization of sample preparation and analytical method was performed using the traditional “one variable at a time” (OVAT) methodology to increase organic compounds recoveries during chromatography in screening procedure.

For the purpose of this research the surface water samples were collected from Skadar Lake and River Morača in Montenegro.

THEORY

Sample preparation process

Liquid-liquid extraction of analytes from surface water samples

Liquid-liquid extraction or solvent extraction is one of the most widely utilized sample preparation technique for qualitative and quantitative analysis, which is why this method has been selected as a preparation method for all samples. Among the advantages of this technique there are large linear sample capacities and the organic extract itself can be directly subjected to the quantitative analytical measurement step such as gas chromatography. Also LLE is a classical sample preparation technique with the vast literature background, accumulated over many years, which provides useful information on choices of organic solvents, pH, type and concentration of reagents and other (Moldoveanu, S.C. and David, V., 2002). The solvents of different properties were used to determine the optimal procedure for meat processing industry sample matrix.

Evaporation of prepared extract – Kuderna Danish concentrator

Kuderna Danish concentrator is widely used to concentrate samples before instrumental analysis, in this case for GC-MS. KD concentrator includes a two- or three-ball Snyder column, a flask and a spring-mounted collection tube for convenient access to samples. Complete apparatus consists of a Snyder column 150 mm long (with Standard Taper 24/40 joints), a flask (with Standard Taper24/40 tops and Standard Taper19/22 lower joint) a graduated tube (with Standard Taper 19/22 joints) and two joint springs. The extract has to be constantly stirred and heated during the process of concentration. Kuderna Danish concentrator is used for enhancement of extract, precisely, evaporation of excess solvent (Motteran F. et al. 2013). Jacketed Kuderna-Danish concentrator tubes circulate hot water through the jacket to boil the solvent dry during extraction/concentration. The bottom portion of the tube is never heated, so samples won't boil dry. The concentration automatically stops when the solvent sinks below the jacket. Tubes have either serrated tabulations or screw thread connections. The temperature of evaporation was set according to boiling point of solvent used during preparation.

Analytical process – gas chromatography coupled with mass spectrometry

The principal function of the gas chromatograph is to provide those conditions required by the column for achieving a separation without adversely affecting its performance in any way. Operation of the column requires a regulated flow of carrier gas; an inlet system to vaporize and mix the sample with the carrier gas; a thermostatted oven to optimize the temperature for the separation; an on-line detector to monitor the separation; and associated electronic components to control and monitor instrument conditions, and to record, manipulate and format the chromatographic data (Poole C.F. 2002). A chromatogram provides information about the complexity (number of components), quantity (peak height or area) and identity (retention parameter) of the components in a mixture. A mass spectrometer produces a mass spectrum, a fingerprint of the molecule, which is a histogram of the relative abundance of the ions generated by ionization of the sample and their subsequent separation, based on their mass-to-charge ratio (m/z) (Poole C.F. 2002).

METHODS

Sampling campaigns, sample types, transportation and storage

Surface water samples were taken during sampling campaign in the year of 2012 from the downstream of River Morača. The three specific locations of sampling were near the settlement Vukovci, the lower course of the river Morača at resort Petrović, and from Skadar Lake.

Sample type was grab sample, and it was taken in the middle of the River flow in prewashed and prepared glass bottles with plastic lids, volume of 2l. Surface water samples were placed in movable refrigerate systems and transferred to the Laboratory of Department of analytical chemistry, Faculty of chemistry and food technology, Slovak Technical University in Bratislava. Samples were prepared for analysis within 48h, and stored prewashed and rinsed with suitable solvent glass vial.

Sample preparation procedure

LLE procedure was used as a sample preparation procedure for all samples. A 500 ml aliquot of water sample was spiked with an internal standard (benzophenone), after that the sample is placed in a 1000 ml glass separatory funnel and extracted with two 50 ml portions of solvent for 30 minutes using automatic shaker device at 700 rpm. Collected extracts were concentrated in Kuderna-Danish apparatus to final volume 1.0 ml. Injection volume of 2 µl was used for introduction of extract to GC-MS system.

Development and optimization of this procedure was carried out by utilisation of solvents with different polar properties – non-polar solvent n-pentane (≥99.8% purity), polar aprotic solvent dichloromethane (≥99.5% purity), polar protic solvent n-methanol (≥99.9% purity), manufacturer Sigma Aldrich. Ideally, an extraction solvent should obey the following properties:
it has to cover a broad range of chemical properties of metabolites to enable extraction of all metabolites in high yields with good reproducibility (Liebeke M. and Bundy J.G. 2012),

- and solvent system should not affect the stability of metabolites extracted (Rubin A.L. and Evert S. 2006).

Screening analysis procedure

The screening analysis is represented as a process that extracts, isolates, detects and identifies a selected substance or a group within a minimum number of steps and relatively short period of time.

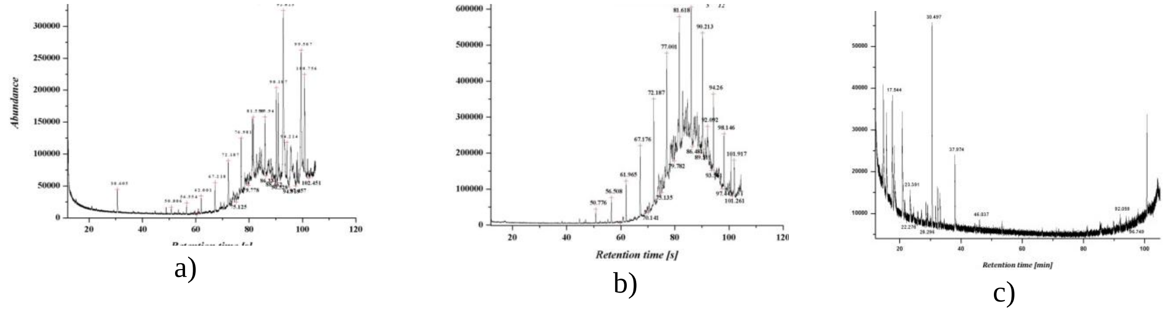
For the performance of screening analyses of surface water samples, gas chromatography coupled with mass spectrometry was selected as the suitable method. The GC-MS screening analysis was performed using Agilent 6890 gas chromatograph coupled to the Agilent 5973 mass spectrometric detector. The GC system was equipped with the programmed temperature vaporization (PTV) injector, known to be suitable for large volume samples. Prepared extract of 2 µl was injected into the gas chromatography system. The capillary GC analysis was done on a 30 m x 250 mm I.D., 0.25 mm df DB-FFAP column. Helium was used as a carrier gas. The mass selective detector (MSD) was used in the scan mode (m/z 45-600) for all the samples. Hold time for solvent delays of 15, 12 and 10 minutes in oven programs during GC-MS screening analyses procedure were fitted to n-pentane, dichloromethane and n-methanol boiling points of 36, 40, 65ºC, respectively. The optimisation of temperature gradient for oven programme to achieve the maximum operational temperature of 230 ºC was set to 2ºC/min, 3ºC/min and 4ºC/min to 230. The evaluation of obtained data in mass spectres and identification of compounds has been done using Wiley7n and NIST08 mass spectral libraries.

FINDINGS, DISCUSSION AND RESULTS

According to operation time of sample preparation, n-pentane has shown to be the most efficient, as it’s boiling point is the lowest, 36°C, with the average of 1 hour and 15 minutes needed for concentration of extract, but the average difference of 15 minutes between n-pentane and dichloromethane is acceptable in correspondence with the higher quality of peaks obtained during analyses of samples prepared with dichloromethane. Boiling point of dichloromethane is 40°C, and n-methanol 60°. Another disadvantage of n-pentane and n-methanol is their density of 0.626 g/ml and 0.791g/ml respectively, in relation to surface water sample, which reflects as a technical difficulty during the extraction process. As the whole volume of sample fluid has to be removed from the extraction funnel first, there is a higher possibility of extract volume lose. As the dichloromethane has a density of 1.3266 g/ml, which is higher density than water, this is not the case whit the dichloromethane as solvent. Dichloromethane has the higher density, so the extract is concentrated on the bottom of extraction funnel and is removed first, which prevents loss of extracts and time. Methanol was disregarded after conclusion that the concentration procedure was not optimal in relation to time consumption, as the average concentration process for selected solvent was at least 4 hours.

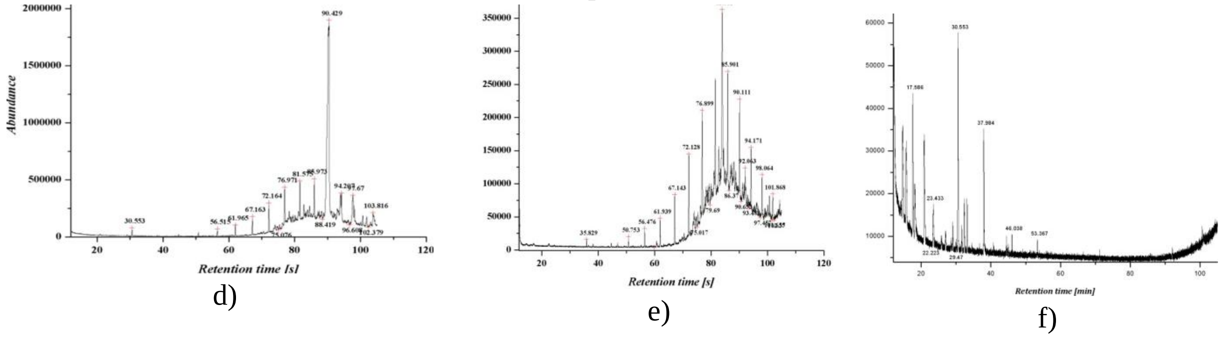
During this phase dichloromethane has shown as the optimal solvent for this type of samples, being the solvent which made possible to extract the largest quantity of compounds, had the cleanest base line with low level of interference, the least amount of peak distortion, and clearest peak separations in chromatogram out of all 3 solvents used. The liquid-liquid extraction into dichloromethane favours the transport of hydrophobic organic compounds from water to an extraction solvent, while the extraction efficiency depends on the compound partitioning coefficient (Progress Report DriWAQ-NS, 2012).
Optimal oven program during GC-MS screening analyses procedure was concluded to be 10 minutes of hold time as solvent delay on 40ºC, and gradient of temperature set on 2ºC/min, to maximum operational temperature of 230ºC, for selected optimal solvent, dichloromethane. Hold time of 10 minutes set for a boiling point temperature of used solvent was enough time for solvent vaporization. The lowest temperature gradient of 2ºC/min has shown to be the most effective one in sense of separation and acquisition of peaks from samples.

Surface water samples near resort "Petrović"



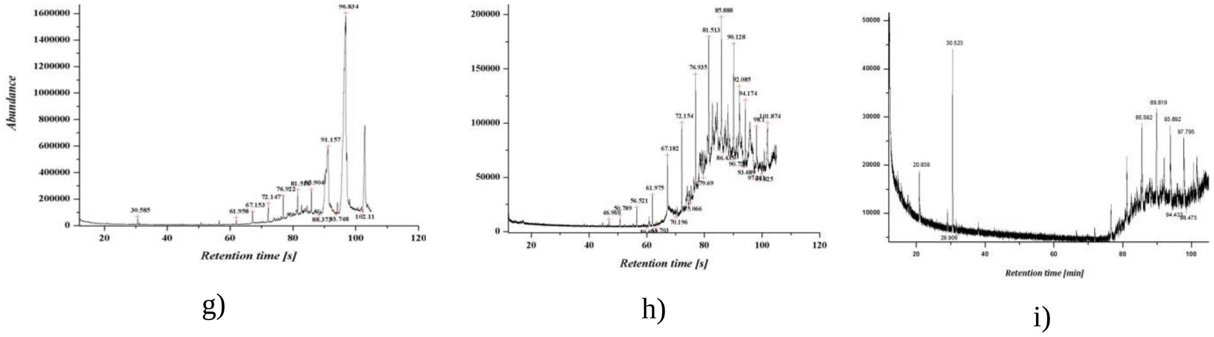
a) b) c)

Surface water samples from Skadar Lake



d) e) f)

Surface water sample from River Morača near Vukovci



g) h) i)

Figure 2. Chromatograms of surface water samples prepared with DCM (a,d,g), n-pentane(b,e,h) and n-methanol(c,f,i)

According to the overall shape of chromatograms and peaks, chromatograms obtained from surface water samples prepared for analysis with dichloromethane as solvent have cleaner base line which facilitates the calculation of the peak areas and the concentration of the components can be calculated with greater accuracy. Samples prepared with dichloromethane have better peak separation with less peak slopes and shape distortion which suggests that dichloromethane is the optimal and best solution for screening analyses of selected surface water sample matrix.

N-pentane as solvent has shown as good solvent for alkanes and higher alkanes extraction, which is shown by the chromatogram shape, which suggests a high content of crude oil pollution. N-methanol is disregarded as it has shown a high base line distortion and interference with a low extraction capacity, confirmed with significantly low number of peaks.

CONCLUSION AND IMPLICATIONS

The optimised screening analysis method for surface water sample is an important phase in the process of detected compound prioritization. The prioritization process is significant step for selection of single chemical spices or groups of compounds for target analysis and monitoring system design. Overall around 542 peaks were detected by GC-MS in all 3 samples during 9 screening analyses performed, using two different solvents. The number of peaks detected from samples prepared with DCM is 275, n-pentane 190, and n-methanol 77. From detected peaks only 124 substances that have shown quality match index (QMI) greater than 60% during spectral search, were identified using relevant library. Optimal solvent has been selected as dichloromethane, according to observations of overall shape of chromatograms and peaks, cleaner base line which facilitates the calculation of the peak areas and the concentration of the components can be calculated with greater accuracy, better peak separation with less peak slopes and shape distortion.

Optimal oven program during GC-MS screening analyses procedure was concluded to be 10 minutes of hold time as solvent delay on 40 ºC, and gradient of temperature set on 2ºC/min, to maximum operational temperature of 230ºC, for selected optimal solvent, dichloromethane.

Monitored target pollutants are specific and differ from the location to location, which is why the good optimisation of screening method and prioritization of obtained data is necessary, for preparation and design of appropriate monitoring system.

This type of research and screening analysis was conducted for the first time in Montenegro, on surface water samples.

REFERENCES

US EPA http://water.epa.gov/scitech/methods/cwa/pollutants.cfm, (20th September 2014)

Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy, Water Framework Directive (WFD) (2000) http://ec.europa.eu/environment/water/water-framework/index_en.html (24th September 2014)

Directive 2008/105/EC of the European Parliament and the Council on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC, was published in the Official Journal on 24 December 2008., Directive on Environmental Quality Standards (EQSD)(2008) (24th September 2014)

Miloradov Vojinović, M., Miloradov, M., Sekulić-Turk, M., Radonić, J., Stošić, M., (2012) Low doses effects of Emerging substances, pseudopersistancy and hazard concequences to aquatic enviromentt and public heslth, *2nd International Conference "Ecology of urban areas 2012",* Zrenjanin

NORMAN http://www.norman-network.net/?q=node/19 (25th September 2014)

Moldoveanu, S.C., & David, V. (2002) Sample Preparation in Chromatography, *Journal of Chromatography*, Elsevier, Vol.65, 272-282

Motteran, F., Pereira, E. L., Campos, C. M. M. (2013) The behaviour of an anaerobic baffled reactor (ABR) as the first stage in the biological treatment of hog farming effluents, *Brazilian Journal of Chemical Engineering*, 30 (2), 299 - 310

Poole C.F. (2002) "The Essence of Chromatography", 1st Edition, Elsevier Science, Print Book, ISBN: 80444501981

Liebeke, M., & Bundy, J.G. (2012) Tissue disruption and extraction methods for metabolomic profiling of an invertebrate sentinel species, *Metabolomics*, Vol. 8, pp. 819–830

Rubin, A.L., & Evert, S. (2006) Risk characterization document for Carbofuran, rapport, California environmental protection agency. (www.cdpr.ca.gov/docs/risk/rcd/carbofuran/pdf)

Progress Rapport for Project Drinking Water Quality Risk Assessment and Prevention in Novi Sad municipality, Serbia, Project number ESP.EAP.SFP 984087, DriWAQ-NS, The Science for Peace and Security Programme, NATO

IV International Conference
„ECOLOGY OF URBAN AREAS“ 2014

HUMAN EXPOSURE TO INORGANIC ARSENIC FROM DRINKING WATER IN THE CITY OF ZRENJANIN

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ABSTRACT

Supplying people with hygienically correct drinking water is one of the basic requirements of a good health, and the right on drinking water is a basic human right. The population from the City of Zrenjanin has no this right across decades. Due to its very complex physical and chemical composition, the crucial issue of drinking water in Zrenjanin is elevated concentration of inorganic arsenic. Chronic exposure to arsenic is a concern primarily because of its carcinogenic effects. In this paper will be present increasing trend malignancy, in last decade, in the target organs between exposed and unexposed populations. It will be observed the emergence of malignant disease in skin, lung and bladder in relation to sex during the reporting period. Malignant diseases are multifactorial etiology, and so the arsenic from drinking water is only one of the possible risk factors.

Key words: *inorganic arsenic, exposure, drinking water, malignancy, Zrenjanin.*

INTRODUCTION

The quality of supplying drinking water is of vital importance, not only because consumers are ensured with water which is essential for their life, but at the same time there is a risk of unwanted distribution of hazardous substances as well as microorganisms. The hygienically correct drinking water is the basic postulate for good health. The water used for drinking, food preparation and for personal and global hygiene, must satisfy the basic health and hygiene requirements: sufficient quantities of safe water, i.e. the water that must not contain toxic and carcinogenic substances as well as pathogenic microorganisms. Drinking water must be without colour, smell and any kind of taste (WHO, 2011).

Access to safe drinking water is a critical health issue in the City of Zrenjanin for more than five decades. It all begans with the construction and establishment of water supply network in 60s of the twentieth century. Water supply system abstracted groundwater from the second and third aquifer, which entailed with itself arsenic from deep underground rocks. Groundwater arsenic contamination is of geogenic origin released from soil under conditions conducive to dissolution of arsenic from solid phase on soil grains to liquid phase in water (Ghosh and Singh, 2009). Before 60s, population of the City of Zrenjanin was using water from the phreatic aquifer for drinking and cooking, which has no arsenic in it content. People in this affected area have chronically been exposed to drinking arsenic contaminated water (Kiurski et al., 2013). There are serious health problems related to the consumption of groundwater with extremely high arsenic concentrations.

Inorganic arsenic is one of the few substances proven to cause cancer in humans through consumption of drinking water. It takes 10 years for cancer to develop. Arsenic can cause skin, bladder and lung cancer. There are also limited evidence that it can cause kidney, liver and prostate cancer, too. International Agency for Research on Cancer (IARC) has classified arsenic and arsenic compounds as carcinogenic to humans (Group 1), which means that there is sufficient evidence for their carcinogenicity to humans (IARC, 2004).

The subject of the analysis in this paper is to determine if there is a relationship between elevated concentrations of arsenic in drinking water and the occurrence of malignant diseases in the exposed and unexposed populations. The exposed population included people living in the City of Zrenjaninin, known to contain drinking water arsenic concentrations ranging from 2 to 349 µg/l, and the unexposed population that included people living in Sečanj municipality, known to contain drinking water arsenic below 10 µg/l. It will be observed the emergence of malignant disease in skin, lung and bladder in relation to sex from 2003-2011. Inorganic arsenic will be examined only as one of many factors that increase the risk of developing cancer in target organs.

THEORY

Arsenic has no known nutritional requirement to the biological world, yet the metabolic process of this element in the biological species, including humans has been evolved. It is likely that metabolism of arsenic, like other toxic metals, is associated with the conversion of the most potentially toxic forms of this element to the less toxic form, followed by accumulation in or excretion from the cell (Roy & Saha, 2002).

Inorganic arsenic forms (arsenite, As (III) and arsenate, As (V)) from drinking water are readily absorbed in gastrointestinal tract after ingestion. However, the arsenic absorption varies depending on the solubility of certain arsenic compounds (the higher aqueous solubility → greater absorption) and the presence and composition of other ingredients of the food and nutrients in the gastrointestinal tract (EFSA, 2009). Absorption rate estimates range from 40 to 100% for humans. As (V), whether inorganic or organic, is better absorbed than As (III), because As (V) is less reactive with membranes of the gastrointestinal tract. Arsenic in drinking water is mostly in the arsenate form, and complete absorption of arsenic from water may occur (Saha et al., 1999). High absorption of arsenic through the gastrointestinal tract is supported by the fact that people who generally ingest drinking water with elevated concentrations of arsenic has elevated concentrations of arsenic in the urine.

Metabolism of arsenic in humans involves two processes of methylation and is illustrated in the Figure 1. After entering a cell, arsenate is reduced to arsenite. Arsenite is then methylated to form monomethyl arsenic (MMA) and dimethyl arsenic (DMA), primarily in the liver. By the combination of oxidative methylation and other pathways, arsenate (As (V)) is transformed to dimethylarsinous acid (DMA (III)); arsenate (As (V)) → arsenite (As (III)) → monomethylarsonic acid (MMA(V)) → monomethylarsonous acid (MMA(III)) → dimethylarsinic acid (DMA (V)) → dimethylarsinous acid (DMA (III)) (Agusa et al.,2011). In mammals, As (III) falls out oxidative methylation in the liver, by adding a methyl group from S-adenosylmethionine (SAM) in the presence of a catalyst arsenic-methyltransferase (As3MT). As a product of this process occurs MMA (V). As (V) in MMA is further reduced to the MMA (III) in the presence of the enzyme glutathione-S-transferase, also known as metilarsenat reductase (Tseng, 2007). Methylation has been considered as a detoxification process of inorganic arsenic, because toxicities of MMA (V) and DMA (V) are much lower than that of inorganic arsenic. On the other hand, later studies revealed that MMA (III) or DMA (III) are more cytotoxic and genotoxic than inorganic arsenic (Petrick et al., 2000; Styblo et al., 2000), suggesting that oxidative methylation of inorganic arsenic is a bioactivation process.

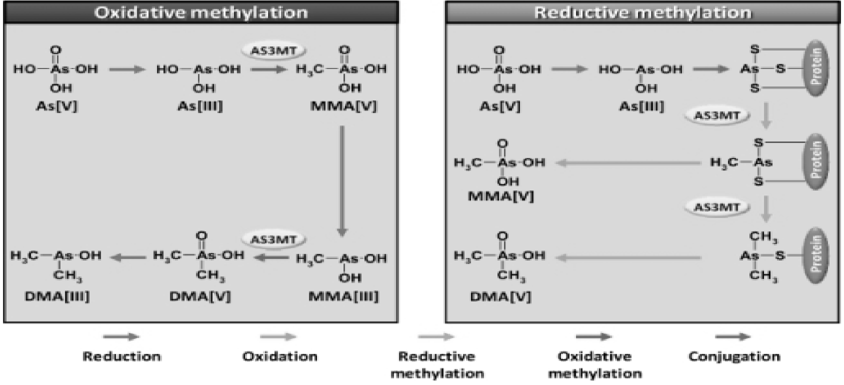

Figure 1. Inorganic arsenic metabolism by oxidative and reductive methylation (Agusa et al.,2011)

Inorganic As (V) and As (III) have different mechanisms of action. Arsenate behaves very much like phosphate consequently it can substitute for phosphate in normal cell reactions, interesting with normal cell functions. In contrast, arsenite has a high affinity for thiol (-SH) groups in proteins, causing inactivation of a variety of enzymes. Because arsenate is reduced in the body to arsenite, arsenate in drinking water may have a biological effect identical to arsenite.

The form of arsenic significantly affects the rate at which arsenic is excreted from the body. Some of the inorganic arsenic is excreted primarily via urine as the parent form of the ingested arsenic. After methylation, it is also excreted as MMA and DMA. Humans rapidly excrete most blood arsenic, with 50 to 90% cleared in two to four days. The remainder is cleared 10-100 times more slowly (Saha et al., 1999). DMA (V) is detected as a major arsenical in the urine of humans.

METHODS

To test the hypothesis that chronic exposure to inorganic arsenic from drinking water may result in increasing malignancy in human, we analyzed data on trend of the occurrence of malignant diseases in the two populations: City of Zrenjanin and Sečanj municipality. People from Zrenjanin area are chronically exposed to this extremely hazardous pollutant from the 60s of last century. In the experimentally populations were examined the emergence of malignant disease in skin, lung and urinary bladder in relation to sex from 2005-2011. These organs are observed as target organs with regard to intoxication with inorganic arsenic from drinking water. Arsenic concentrations in drinking water supply system, in Sečanj municipality, are below the permissible limits by current legislation (Book of Regulations on the Hygienic Correctness of Drinking Water, 1999).

The City of Zrenjanin occupies an area of 1,326 km^2, which represents around 8 % of the total square area of the region of Vojvodina and 15% of the square area of region Banat, which belongs to Serbia. The observed population consists of 123362 inhabitants (as per 2011 census) and it involves the city itself and 22 nearby settlements. The unexposed population has 13,267 inhabitants (as per 2011 census) in the Sečanj municipality. It covers an area of 523 km^2 with 11 nearby settlements.

Institute of Public Health Zrenjanin monitors, investigates and analyzes the health condition and health behaviour of the population, quality of the environment, the safety of water, air and food, causes, occurrence and spread of infectious and other diseases of the socio-medical importance, the impact of environmental factors on health, as well as the organization, operation and development of health services. The Institute keeps track of health condition of the overall population from Central Banat District (Figure 2), a north-eastern district of Serbia. It encompasses the municipalities of: Novi Bečej, Nova Crnja, Žitište and Sečanj and the City of Zrenjanin. The Institute statistically processed data on the occurrences of overall morbidity in overall Central Banat District. The relevant data on malignancy for this research were taken from this institution.

Figure 2. Area of Central Banat District

Data on the studied populations are summarized in Table 1 and Table 2.

Table 1: Morbidity of malignant diseases by specific localization in the City of Zrenjanin

Target organs	Morbidity of malignant neoplasms													
	2011		2010		2009		2008		2007		2006		2005	
	M	F	M	F	M	F	M	F	M	F	M	F	M	F
Skin	35	38	68	44	70	59	32	47	70	70	64	53	49	45
Lung	62	20	86	18	72	21	81	25	79	16	63	15	66	17
Urinary bladder	13	5	30	-	21	7	18	-	22	-	24	11	38	9

*M-male; F-female

Table 2: Morbidity of malignant diseases by specific localization in the Sečanj municipality

Target organs	Morbidity of malignant neoplasms													
	2011		2010		2009		2008		2007		2006		2005	
	M	F	M	F	M	F	M	F	M	F	M	F	M	F
Skin	-	5	5	5	6	10	2	1	3	8	6	4	2	3
Lung	6	3	6	5	9	2	9	-	2	-	6	-	7	2
Urinary bladder	2	1	5	-	2	1	2	2	2	-	5	2	2	1

*M-male; F-female

FINDINGS AND DISCUSSION

When we look at the trend of newly diagnosed malignancies in relation to their localization of occurrence, shown in Tables 1 and 2, we see that the most common cancers are in skin, lung and bladder respectively. In regard to gender, a leading localization of malignant diseases in male is lung cancer, and skin cancer in women in both the unexposed and exposed populations. From all malignant neoplasms, it can be seen that men have greater incidence on cancers than women in both researched populations.

Figures 3-5 represent the overall morbidity of malignant diseases in target organs in experimentally populations from 2005-2011. These figures reveal that there is significantly higher morbidity of malignancy in target organs in exposed population compared to unexposed population, in the observed period.

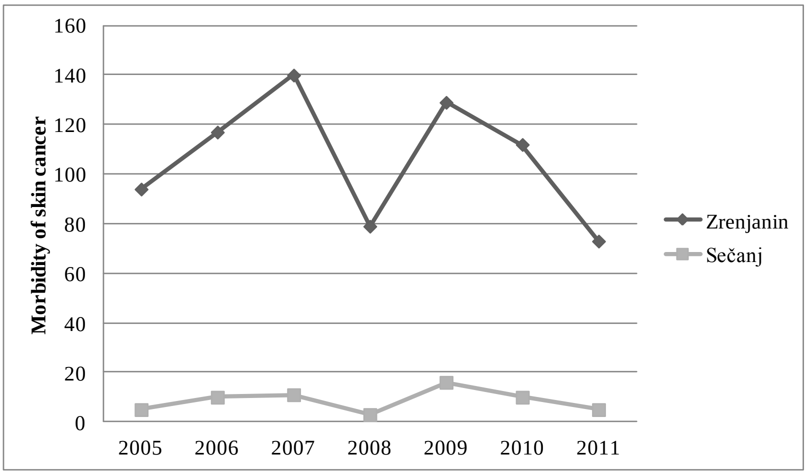

Figure 3. Overall morbidity of skin cancer in experimentally populations for researched period

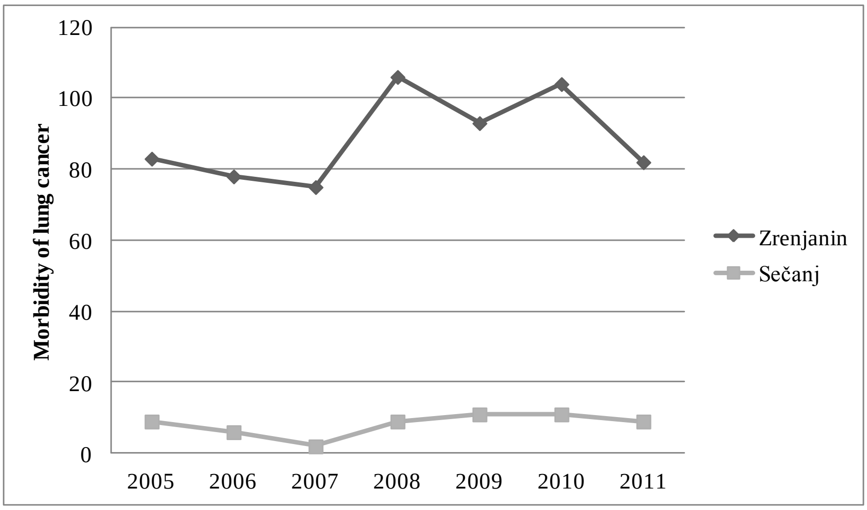

Figure 4. Overall morbidity of lung cancer in experimental populations for researched period

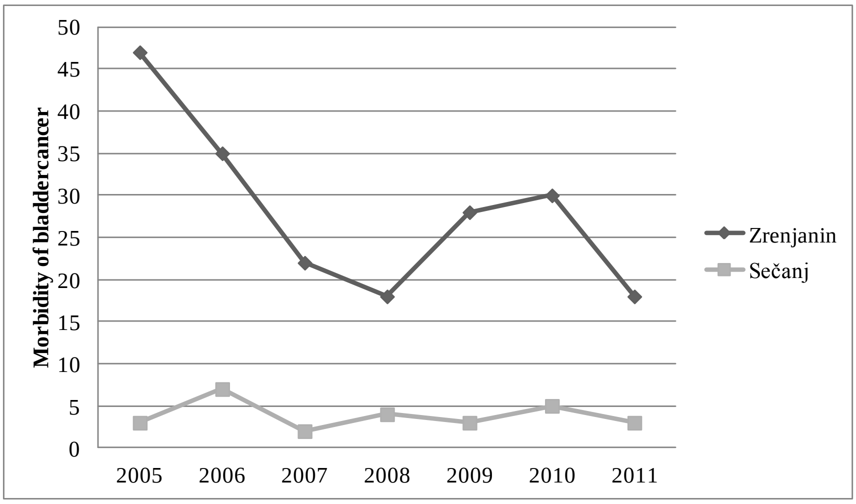

Figure 5. Overall morbidity of bladder cancer in experimental populations for researched period

Based on the statistics of the data from the Institute, it can be concluded that leading malignant neoplasms are of the skin and lungs in both men and women. The skin is primary target organ associated with intoxication of inorganic arsenic from drinking water. The emergence of an enormous number of malignant neoplasms of the lung correlated with elevated concentrations of arsenic in drinking water can be explained by the fact that lungs are organs with the highest number of blood vessels. As the arsenic is transmitted through blood the greatest amount of it just gets into the lungs.

However, there is a great difference in the number of newly diagnosed malignancy in relation to sex. In men, there is a dramatically increased occurrence of malignant diseases compared to women. Such statement indicates that women have a greater capacity of arsenic methylation than men in localization characteristic for arsenic intoxication. Lindberg et al. (2008) have documented the protective effect of estrogens in women in the methylation of arsenic as the cause of the small quantities of MMA in the urine of women as opposed to men.

Related results have been obtained in other recently studies showing strong positive associations between the consumption of drinking water containing inorganic arsenic and the occurrence of various cancers. Christoforidou et al. (2013) carried out a systematic review of the occurrence of risk of bladder cancer in humans associated with exposure to arsenic through drinking water from 2000-2013. Most of the cases were from southwestern and northeastern Taiwan, Pakistan, Bangladesh, Argentina (Cordoba Province), USA (southeastern Michigan, Florida, Idaho) and Chile. Celik et al. (2008) also conducted a systematic review of the literature examining the association between arsenic in drinking water and the risk of lung cancer in humans through April 2006. The majority of the studies were conducted in areas of high arsenic exposure (100 μg/L) such as southwestern Taiwan, the Niigata Prefecture, Japan, and Northern Chile. Prasad et al. (2014) investigated cancer risk associated with inorganic arsenic consumption by human particularly in arsenic contaminated drinking water areas of Katihar district of Bihar, India. Arsenic concentrations measured in examined area were 50-827 μg/L. They concluded that ingestion of arsenic has been definitely linked to increased incidence of cancer in skin, lung, bladder, kidney, liver, and potentially prostate.

National Research Council (NRC, 1999) presented a correlation between daily intake of high concentrations of arsenic via drinking water and the overall risk of cancer, as shown in the Table 3.

Table 3: Correlation between daily intake of high concentrations of arsenic via drinking water and the overall risk of cancer

Arsenic from drinking water (ppb)	Overall risk of cancer at the average intake of 2l of water per day
0.5	1 in 10000
1	1 in 5000
3	1 in 1667
4	1 in 1250
5	1 in 1000
10	1 in 500
20	1 in 250
25	1 in 200
50	1 in 100

Chronic exposure to arsenic through contaminated drinking water involves a relatively high individual risk of developing malignant tumors. Morbidity of malignant diseases, caused by the effect of large doses of drinking water arsenic, increases every year in the world, as well as mortality.

CONCLUSIONS AND IMPLICATIONS

This research showed that morbidity of malignant diseases in target organs, for both gender, were significantly higher in the exposed population compared to unexposed population in the observed period. It was expected that after the ban on the use of tap water for human use in 2004 in the City of Zrenjanin, number of malignancy will decrease. But, that was not the case. It was noticed an increase in malignancy in 2008 and 2009. In 2010 is observed the linear declining trend of newly observed malignancies in Zrenjanin area, as a result of the efforts of health services to timely register and eliminate modifiable risk factors. This only proves that the malignant diseases are multifactorial etiology, and that arsenic is only one of the possible risk factors. Incidence on malignant diseases for men was higher 9-13 (with the exception in 2007 with 24 times) times in exposed population in comparison to unexposed population. While for women incidence was higher 6-11 times (with the exception in 2008 with 24 times) in exposed population compared to unexposed population. To obtain a complete picture on individual exposure to arsenic from drinking water it is necessary to undertake further studies on level of inorganic arsenic in urine of exposed population.

REFERENCES

Agusa T., Fujihara J., Takeshita H., & Iwata H. 2011. Individual Variations in Inorganic Arsenic Metabolism Associated with AS3MT Genetic Polymorphisms. *Int J Mol Sci.* 12(4): 2351–2382.

Book of Regulations on the Hygienic Correctness of Drinking Water, in: Official Gazette SRJ, No. 42/98 and 44/99, Belgrade, 1999.

Celik I., Gallicchio L., Boyd K., Lam T.K., Matanoski G., Tao X., Shiels M., Hammond E., Chen L., Robinson K.A., Caulfield L.E., Herman J.G., Guallar E., & Alberg A.J. 2008. Arsenic in drinking water and lung cancer: a systematic review. *Environ Res.* 108(1): 48-55.

Christoforidou E.P., Riza E., Kales S.N., Hadjistavrou K., Stoltidi M., Kastania A.N., & Linos A. 2013. Bladder cancer and arsenic through drinking water: a systematic review of epidemiologic evidence. *J Environ Sci Health A Tox Hazard Subst Environ Eng*. 48(14): 1764-1775.

European Food Safety Authority (EFSA), Panel on Contaminants in the Food Chain, 2009. Scientific Opinion on Arsenic in Food. *EFSA Journal.* 7(10):1351.

Ghosh, N. C. & Singh, R.D. (2009). Groundwater Arsenic Contamination in India: Vulnerability and Scope for Remedy. *Tecnical Paper included in the special session on Ground water in the 5th Asian Regional Conference of INCID*, December 9-11, 2009 held at Vigyan Bhawan, New Delhi.

Kiurski-Milošević J., Vojinović Miloradov M., Jašin D., Šućurović A., & Ludajić G. 2013. Groundwater arsenic contamination in Zrenjanin area. *III International Conference "Ecology of Urban Areas" 2013*, Zrenjanin, 11th October 2013, pp. 243-251.

Lindberg A.L., Ekstrom E.C., Nermell B., Rahman M., Lonnerdal B., Persson L.A., & Vahter M., 2008. Gender and age differences in the metabolism of inorganic arsenic in a highly exposed population in Bangladesh. *Environ. Res.* 106: 110–120.

National Research Council (NRC), 1999. *Arsenic in Drinking Water*, Washington DC, National Academy Press, pp. 27–82.

Petrick J.S., Ayala-Fierro F., Cullen W.R., Carter D.E., & Aposhian H.V., 2000. Monomethylarsonous acid (MMA(III)) is more toxic than arsenite in Chang human hepatocytes. *Toxicol. Appl. Pharmacol*. 163, 203–207.

Petrick J.S., Ayala-Fierro F., Cullen W.R., Carter D.E., Vasken, & Aposhian H. 2000. Monomethylarsonous acid (MMAIII) is more toxic than arsenite in Chang human hepatocytes. *Toxicol. Appl. Pharmacol.* 163 (2):203–207.

Roy P. & Saha A. 2002. Metabolism and toxicity of arsenic: A human carcinogen. *Current Science* 82 (1): 38-45.

Saha J. C., Dikshita A. K., Bandyopadhyaya M., & Saha K. C. 1999. A Review of Arsenic Poisoning and its Effects on Human Health. *Critical Reviews in Environmental Science and Technology* 29(3): 281-313.

Saha, K. C. 1995. Chronic arsenical dermatoses from tube-well water in West Bengal during 1983-87. *Indian J. Dermatol.* 40(1): 1-12.

Styblo M., Del Razo L.M., Vega L., Germolec D.R., LeCluyse E.L., Hamilton G.A., Reed W., Wang C., Cullen W.R., & Thomas D.J. 2000. Comparative toxicity of trivalent and pentavalent inorganic and methylated arsenicals in rat and human cells. *Arch. Toxicol.* 74 (6):289–299.

Tseng C.H. 2007. Arsenic methylation, urinary arsenic metabolites and human diseases: current perspective. *J Environ Sci Health C Environ Carcinog Ecotoxicol Rev*, 25(1):1-22.

World Health Organization (WHO) 2011. *Guidelines for drinking-water quality, 4th edition,* Geneva, World Health Organization.

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THE EXAMINATION OF SEASONAL GEOTHERMAL EXCITATION POTENTIAL INFLUENCE ON OXYGEN DIFFUSION POTENTIAL IN URBAN RIVER WATER

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ABSTRACT

The prediction in this paper acc. to Eiring theory of transition state is that irradiated energy quant from the earth as black body correspond to vibration and rotation energy of active center in transition complex and in followed thermo-electric produced geothermal excitation potential efective in electrochemical and in phase transformation relaxation processes. This phenomene is examined in the case for urban river Begej, during one year, on the basis of a correlation between geothermal excitation potential and oxygen diffusion potential controled with it concentration. The monitoring data fit linear functional dependences ($R^2 \geq 0,93$) indicate to the constant sum of seasonal geothermal excitation potential with seasonal oxygen diffusion over-potential, and with crystallization or condensation water active center free enrgy, equal to exchanged molar heat of active centers, water crystallization latent heat and oxygen dissolution enthalpy. The detailed understanding of seasonal geothermal excitation potential influence on oxygen diffusion overpotential enable explanation of purifying efficiency seasonal change in aeration, flotation, oxidation and aggregation step in purifying plants, as well as optimization of purifying procedure.

Keawords: *Earth iradiated energy quant, Transition, Relaxation processes, Relative electric permitivity of excited plane,surface relative electric permitivity effective in excitation and relaxation processes.*

INTRODUCTION

According to Eiring theory of transition state, internal vibration and rotation energy levels of active centers correspond to energy quants iradiated from the earth as black body. Then followed relaxation processes keep minimal free energy state, by absorbed quant energy conversion in vibration and rotation thermal energy and in geothermal excitation potential by termo-electric conversion in intermetal contact surface followed by electro-chemical relaxation and phase transformation. In our paper this phenomene is examined in the case for urban river Begej, during one year, on the basis of a correlation between thermo-electric produuced geothermal excitation potential and calculated oxygen diffusion over-potential. River water contain metal particles and chemical deposit of industrial and communal wastewater, as a possible system which could generate material for storage of slow generated membrane fuel cell, without hydrogen heat storage (S. Sieniutycz, 2010, Nedjib Djilali, Dongming Lu, 2002). In river water minimal free energy state of couple between dissolved iron, ammoniac, oxygen and hydrogen control free energy of transition complex (Pavlović et al, 2013) and in aerated refinery waste water surface polarization of crystallization and condensation water active centers control affinity to electron of chemisorbed gases (N. Perišić Janjić, 2008) ($E_a(Cl+e=Cl^-) = -349$ kJ/mol), ($E_a(F+e=F^-) = -328$ kJ/mol), ($E_a(Br+e=Br^-)=-329$ kJ/mol), ($E_a(J+e=J^-)=-295$ kJ/mol), ($E_a(S+e=S^-) = -200$ kJ/mol), ($E_a(H+e=H^-) = - 73$ kJ/mol). Also in aeration of refinery wastewater through membrane diffuser surface polarization are controlled with oxygen affinity to electron $E_a(O^- +e=O^{2-}) = 782$ kJ/mol), ($E_a(O+2e=O^{2-}) = 641$ kJ/mol) balanced with spontaneous oxygen polarization ($E_a(O+e=O^-) = -141$ kJ/mol) (Stanojević, M., et al, 2013).

Electron energy in metal particles according to Fermi distribution control thermo-electron current, $j = A \cdot T^2 \cdot e^{-\frac{\Phi - \Delta\Phi}{k_B T}}$ depend on metal work functions, Φ (for alkali metals Φ= 1 V, for Cs 1,8 V, for the most metals 4-5 V and for Hg is 6,8 V which decrease the presence of C, Ba , V_f etc) , on modifying attractive force of produced electric field, E , $\Delta\Phi = -e(eE)^{1/2}$ and on Richardson measured constant , A= 6E-5, A/m^2K^2 (Perović B., 1971).

The seasonal irradiated quant energy from the earth in other phase , $hc/\lambda^{\#}$ can be calculated depending on equilibrium temperature of river water $T^{\#}=T_L$ or air $T^{\#} = T_{air}$, on the basis of Wien's low (Pavlović M. 2004):

$\lambda^{\#} = 2898$ E-6/ $T^{\#}$, (1)

Applying transition complex theory where $hc/\lambda^{\#}=k_BT$ (J.A.V. Batler, 1924, 1932) showed that transition period for change of beginning level e=2,7 times control electrical polarization equal to thermal energy.
That correspond to geothermal excitation potential :

$\eta_e{}^{\#}{}_w = hc/e\lambda^{\#} = k_BT/ e$ (2)

The combination Eq.1 and Eq.2 gives:

$\eta_e{}^{\#}{}_w = (hcT^{\#}/2898e\lambda)$E6, V (2a)

In free energy minimum state, the relative electric permittivity of chemisorbed dipole of transition complex $\varepsilon^{\#}$ and in contact surface with air, ε_0 the balance is achieved at equilibrium temperature of water and of air :

$e\eta_a{}^{\#}/\varepsilon^{*} = k_BT^{\#}/\varepsilon_0$

where: $\varepsilon_r{}^{*} = e\,\eta_e{}^{\#}{}_w/ k_BT_{air} = hc/e2898\, k_B = 4,981$ (3)

The working hypothesis of this work is that at the geothermal excitation potential, $\eta_e{}^{\#}{}_w$ enable catalytic thermal energy conversion in liquid and /or air temperature which control:

- water condensation nucleuses free energy change , $\Delta_{evap} G^{\theta} = 44000-119T_{air}$, J/mol (4)

- water crystallization nucleuses free energy change, $\Delta_{melt}G^{\theta} = 6010 - 22\, T_L$, J/mol (5)

- and oxygen diffusion over-potential in liquid phase (Ševaljević, M., et all. 2001)

$\eta_{dif}(O_2)_L = \eta_{dif}(O_2)_G - \Delta_{G/L}\mu^{\theta} = RT_L \ln c_{O2(L)}/F$, V (6)

The examined correlations between geothermal excitation potential with oxygen diffusion potential, as well as crystallization nucleuses free energy and its influence to condensation active centers free energy present the Table 1, Table 2 and Figures 2-5.

EXPERIMENTAL RESULTS

The monitoring of oxygen content and water and air temperature of urban river water Begej before input in the town Zrenjanin, performed Institute of the Public health in Zrenjanin 2009 and 2010., using the modified Winkler method analogous to EN 25813 (after oxygen oxidized manganese (II) to manganese (III) and in acidic solution form red complex with Titriplex for the photo-metricaly determination with WTW photometer and oxygen cell test, WTW 14694).

Figure 1. River Begej

Table 1: The monthly monitoring data for air and urban river water temperature before input in the town Zrenjanin, and the calculated parameters according zo theoretical consideration

The date	T_w K	T_{air} K	$\lambda^\#$, µm Eq. 1	$\eta^\#$,V Eq.2a	$\Delta_{melt}G^\theta$, Eq.5, kJ/mol	$\Delta_{evap}G^\theta$, Eq.4, k J/mol	$\eta_{dif}(O_2)_L$, V Eq.6
15.10.009	286,25	279,65	10,124	0,119	-0,27	10,72	-0,189
4.11.2009	281,35	276,75	10,300	0,117	-0,16	11,07	-0,188
2.12.2009	281,85	279,45	10,282	0,117	-0,17	10,75	-0,191
13.1.2010	278,55	276,45	10,404	0,115	-0,10	11,10	-0,204
3.2.2010	274,45	272,65	10,559	0,114	-0,01	11,55	-0,209
3.3.2010	281,15	280,05	10,308	0,116	-0,16	10,67	-0,221
29.4.2010	289,95	292,65	9,995	0,12	-0,35	9,17	-0,229
14.5.2010	291,65	292,45	9,937	0,121	-0,39	9,20	-0,222
6.6.2010	297,55	302,75	9,740	0,123	-0,52	7,97	-0,216
1.7.2010	297,75	302,85	9,733	0,123	-0,52	7,96	-0,202
19.8.2010	299,45	300,75	9,678	0,124	-0,56	8,21	-0,198
15.9.2011	296,45	294,95	9,776	0,123	-0,49	8,90	-0,196

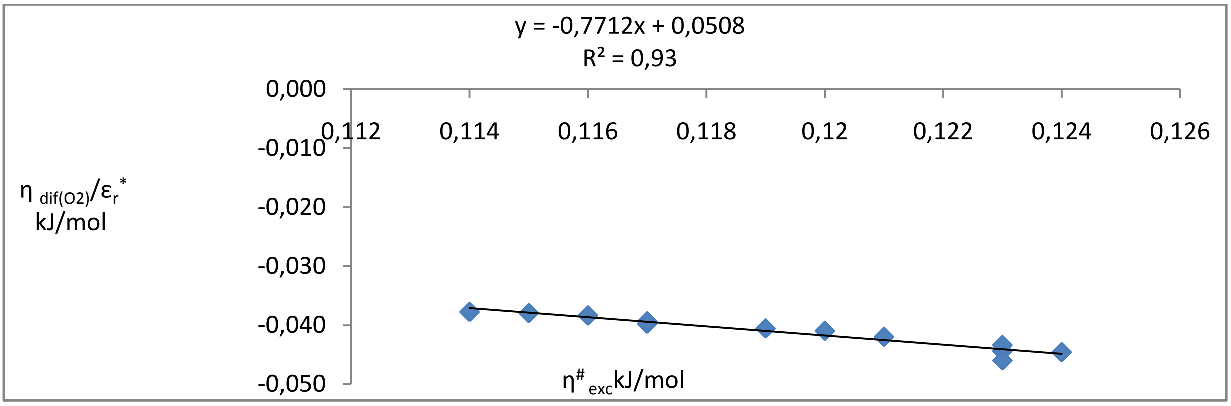

Figure 2. Linear functional dependence which fit the calculated monthly oxygen diffusion potential and geothermal excitation potential

Acc to Fig. 2 geothermal excitation potential fit the linear functional dependence on measured oxygen diffusion potential with strong correlation coefficient, $R^2 = 0{,}93$:

$$\eta_{dif\ O2}/\varepsilon^* = -\ 0{,}7712\eta^\# + 0{,}0508.$$

where: $\tan = -\ (\Delta\eta_{dif(O2}/\ \varepsilon_r^*)\ /\Delta\eta^\# = 0{,}7712 = 1/\ 1{,}296 = 1/\ \varepsilon_{r(H2).}$,

indicate to the balance between geothermal excitation potential change in surface controlled with relative electric permittivity of chemisorbed hydrogen, $\varepsilon_{r(H2)}$ with oxygen diffusion over potential change in contact surface of transition complex , ε_r^*:

$$\Delta\eta^\# /\varepsilon_{r\ (H2).}\ = -\ \eta_{\ dif(O2)}/\varepsilon_r^*$$

The constant *free therm in obtained function*, $F\eta_e = 0{,}0508\cdot 96{,}5$ kJ/mol = $-\ \Delta G^\theta_{\ ac.\ c.} = -\ C_{V,\ ac.\ ct}T_0$ in thermo-electrochemical equilibrium corresponds to the molar heat, C_V (Si) ≈ 17 J/molK.
The obtained function indicate to the active centers internal energy C_VT balance with the sum of geothermal excitation and oxygen diffusion energy controled with relative electric permitivity of transition complex, $\varepsilon_r{}^* = 4{,}89$:

$$C_{V,\ ac.\ ct}T = -(F\ \eta_{\ dif\ O2}/\ \varepsilon_r^*\ \ +\ \ F\eta^\#_{\ exc}/\varepsilon_{r\ H2}\ )$$

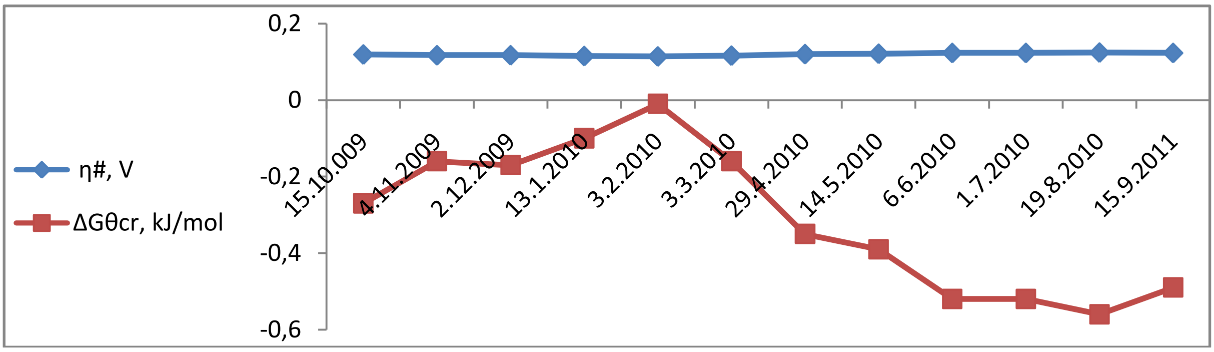

Figure 3. The monthly values of water crystallization nucleuses free energy, minimal in February and increased from January to October, as well as increased from March to September

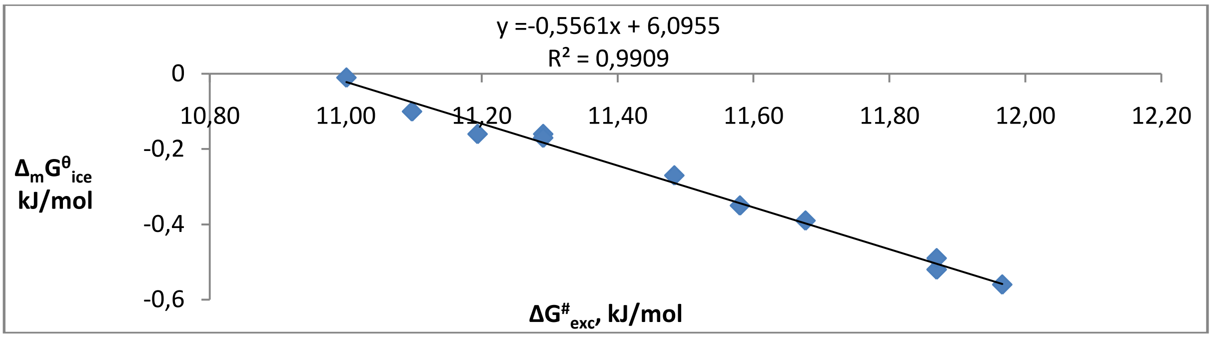

Figure 4. Linear functional dependence which fit the free energy of water crystallization centers and geothermal excitation free energy

Acc. to Fig. 4 geothermal excitation energy also fit linear functional dependence on free energy of water crystallization centers:

$$\Delta_m G^\theta{}_{ice} = -\,0{,}5561\Delta G^\#{}_{exc} + 6{,}0955\ .$$

where: $\tan = -\,d\Delta_{/m} G^\theta{}_{ice} / d\,\Delta G^\#{}_{exc} = 1/\,\varepsilon_{r\ ice} = 0{,}5561 = 1/\,1{,}79$

indicate to the balance between *geothermal excitation energychange in contact surface with oxygen* $(\varepsilon_r(O_2)=1{,}5$ *or* $\varepsilon_r(O_2)=1{,}7)$ *and* crystallization nucleuses free energy change in contact surface with air:

$$d\,\Delta G^\#{}_{exc} / \varepsilon_{r\ ice\ exc} = -\,d\Delta_m G^\theta{}_{ice}$$

The constant free therm in obtained function correspond to water crystalisation nucleuses molar latent heat, $\Delta_{melt} H^\theta{}_{ice}$ =273,15 (69,9-48)= 6010 J/molK .

The obtained function indicate to water crystallization latent heat conversion in geothermal excitation energy and oxygen diffusion transport energy :

$$\Delta_{melt} G^\theta{}_{(ice)} + \Delta G^\#{}_{exc} / \varepsilon_r = 6{,}0955$$

Equal geothermal excitation potential in the Fig 2 and Fig 4 gives:

$$-C_{V,\,ac.\,ct} T_0 .- F\,\eta_{\,dif\,O2} / \varepsilon_r^{\,*} = 6{,}0955 - \Delta_{cr/melt}\, G^\theta{}_{(H2O)}$$

$$\varepsilon_r^{\,exc} = (\Delta_m G^\theta{}_{ice} - (C_{V,\,ac.\,ct} T + 6{,}0955)) / F\eta_{\,dif\,O2}\ ,$$

enable the determination of relative electric permitivity effective in conversion of geothermal excitation potential (Table 2).

The re-arrangement:

$$F\,\eta_{\,dif\,O2} / \varepsilon_r^{\,exc} = \Delta_{cr/mel}\, G^\theta{}_{H2O} - (C_{V,\,ac.\,ct} T_0 + 6{,}0955)$$

$$F\,\eta_{\,dif\,O2} / \varepsilon_r^{\,exc} = -\,C_{V,\,ac.\,ct} T - (\Delta_{\,mel} H^\theta{}_{ice} - \Delta_{\,mel}\, G^\theta{}_{ice})$$

$$F\,\eta_{dif\,O2} / \varepsilon_r^{\,exc} = -T(C_{V,\,ac.\,ct} + \Delta_{\,ice/L} S^\theta{}_{H2O})$$

The obtained function indicate to the active centers internal energy, $C_V T$ balance with the sum of water entropy heat change in ice/water phase transition and oxygen diffusion energy, in plane with relative electric permitivity $\varepsilon_r^{\,exc}$ =1,02-1,25, corresponding to overcooled hydrogen:

$$C_V T = -\,(F\,\eta_{dif\,O2} / \varepsilon_r^{\,exc} + T\Delta_{\,ice/L} S^\theta{}_{H2O})$$

Table 2: The monthly values of relative electric permittivity, effective in energy conversion of geothermal excited active centers to oxygen diffusion transport

Month	X	XI	XII	I	II	III	IV	V	VI	VII	VIII	IX
$\varepsilon_r^{\,exc}$	1,24	1,25	1,23	1,15	1,12	1,06	1,02	1,06	1,09	1,16	1,18	1,20

Acc. to the results in Table 2 relative electric permitivity from minimal value $\varepsilon_r^{\,exc}$= 1,02 in April to maximal value $\varepsilon_r^{\,exc}$=1,25 in November enable energy convesion of active centers internal energy and water entropy heat change in phase transition in oxygen diffusion transport energy.

Also the monitoring data for water crystallization active centers free energy o*f*, $\Delta G^{\theta}{}_{cr.aq\ and}$ and water condensation active centers free energy fit the linear functional dependence (Figure 5), with strong correlation coefficient, $R^2 = 0{,}9409$, $\mathbf{\Delta G^{\theta}{}_{cond}} = 6{,}8804\Delta G^{\theta}{}_{cr} + 11{,}894$

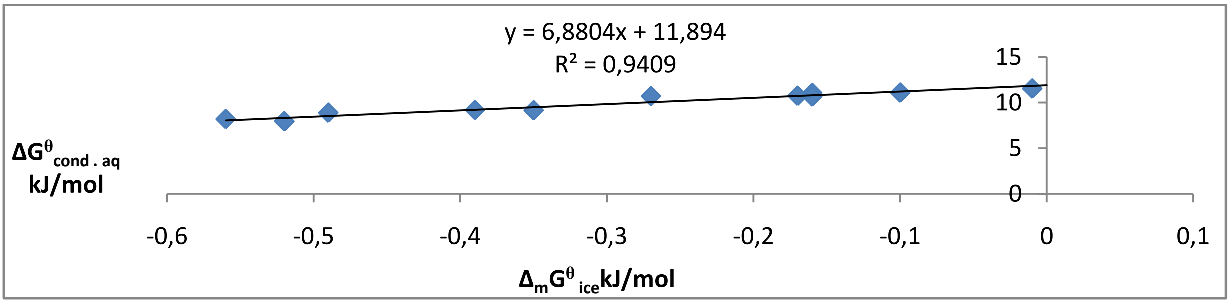

Figure 5. Linear functional dependence of the water condensation and crystallization active centers free energy

The free therm in obtained function corresponds to oxygen dissolution enthalpy $\Delta_{dissol.}H^{\theta}(O_2) = -11{,}7$ kJ/mol and the slope corresponds to relative electric permitivity near inner Helmholtz plane $\varepsilon_{rI,\ rel} \approx 6{,}9$. The obtained function:

$$6{,}8804\ \Delta_m G^{\theta}{}_{ice} - \mathbf{\Delta G^{\theta}{}_{cond}} = \Delta_{dissol.}H^{\theta}(O_2)$$

indicate at temperature $T_0 = 273{,}15$ K, where $\Delta_m G^{\theta}{}_{ice} = 6010 - 22T = 0$, water vapor condensation free energy, $\mathbf{\Delta G^{\theta}{}_{cond}}$ favor spontaneous oxygen dissolution and the slope indicate to relative electric permitivity of relaxation process plane effective in water condensation and oxygen dissolution $\Delta_{dissol.}H^{\theta}(O_2)/\ \Delta G^{\theta}{}_{cr} = \varepsilon_{r,\ rel}$.

CONCLUSIONS

The obtained results confirm transition complex in contact surface between earth with water and air, enable earth irradiated quant energy conversion in thermo-electric geothermal excitatation potential and followed relaxation phase transition couple processes with oxygen diffusion transport energy, depending on seasonal water and air temperatures.

The detailed understanding of seasonal geothermal excitation potential influence on oxygen diffusion overpotential enable explanation of purifying efficiency seasonal change in aeration, flotation, oxidation and aggregation step in purifying plants, as well as optimization of purifying procedure.

REFERENCES

J.A.V.Batler, Trans . Faraday Soc., 19.729 (1924), 19.734 (924), 28.379 (1932)

Pavlović M. (2004) , Ekological Engineering “ Technical Faculty “Mihajlo Pupin” inZrenjanin

Nedjib Djilali, Dongming Lu (2002) Influence of heat transfer on gas and water transport in fuell cell, Int. J. Therm. Sci., 41 p. 29-40

N. Perišić Janjić (2008), Chemistry, University in Novi Sad, PMF, Novi Sad

Perović B., (1971) Physic of ionised gases, Belgrade

S. Sieniutycz, (2010) Finite-rate thermodynamics of power production in thermal, chemical and electrochemical systems, International Journal of Heat and Mass Transfer 53 , p. 2864

Stanojevic Miroslav M Sevaljevic Mirjana M Simic Stojan N Ševaljevic Miladin (2013), Influence of the water height in aeration regimes with the same membrane diffuser on technical characteristics of aeration system, *Desalination and Water Treatment, vol. 51 br. 22-24, str.* 4271-4282

Ševaljević, M., Stanojević, M, Simić, S. and Pavlović, M. (2001**)**, *Thermodynamic study of aeration kinetic in treatment of refinery wastewater in bio-aeration tank*s, Desalination, 248 (2009) 941- 960

Pavlović M., Ševaljević V. M., Nikolin T and Ševaljević M.M (2013), Urban river water influence on seasonal pollutants free enrgy changes, *III International Conference Ecology of Urban Areas*, Zrenjanin, p. 273-278

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“ECOLOGY OF URBAN AREAS” 2014

THE EXAMINATION OF JOULE-THOMSON EFFECT INFLUENCE ON TECHNICAL AND THERMODYNAMIC PARAMETERS OF REFINERY WASTEWATER AERATION REGIME

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ABSTRACT

The diagnostic of Joule-Thomson coefficient, is applied in this paper , in aeration regimes of refinery wastewater with the same diffuser membrane, on the basis of the slope of the linear function $dT_{R/G} = f(dp)$*, with correlation coefficients,* $R^2 = 0{,}9299 - 0{,}9983$*. Aeration regime (c-h-q) define added oil content-c(0, 5 and 10 mg/l) water column height h(1 m and 2 m) and air flow, q(2, 6 and 10* m^3/h*). The negative value of the Joule –Thomson coefficient for aeration regimes without added waste motor oil, 0-2-q is obtained, but the positive values for the other regimes depending on waste motor oil content and water column height. Linear functional dependences fit its influence to measured oxygen saturation degree and oxygen volume transport coefficient decreasing. Also, the linear functions fit the dependence between added waste motor oil content and Joule-Thomson coefficient as well as with electron density, in aerated saturated gas bubbles. The applied method could be useful in the aeration devices optimization at minimal Joule -Thomson coefficient where intermolecular forces in gas bubble are negligible, for achieving minimal resistance to stimulated aeration velocity equal to the actual oxygen consumption velocity in a certain phase of the treatment process.*

Keywords: *Refinery wastewater aeration regime, Joule-Thomson coefficient, Electron density, Oxygen volume transport coefficient, Evaporation latent heat.*

INTRODUCTION

Efficiency of aerobic biological processes in wastewater depends on the amount of dissolved oxygen introduced by aeration system. When aeration systems are designed, it is necessary to use aeration devices with an actual oxygen introduction velocity higher or equal to the actual oxygen consumption velocity in a certain phase of the treatment process of wastewater. In various primary wastewater treatment combined with stimulated aeration, as well as in biology treatments of technological wastewater and communal waters, aeration by perforated membrane distributer fixed with a ring over disc of material ((PA GF30) with material EPDM (ethilen-propilen-dimer) “Gummy-Jaeger“ can be applied (Simic, N.S., 2006).,

In the previous paper the influence of oil content on achieved stationary oxygen content in the aerated refinery wastewater was examined (Pavlović M. et al, 2008).

Also electron density influence to hydrogen and oxygen polarization (Ševaljević M. et all, 2012) was examined and the influence of the water height in aeration regimes with the same membrane diffuser on technical characteristics of aeration system (Stanojević M. et al, 2013).

Adiabatic transport where, dH=0 at U+pV=const or $C_p dT+(dH/dp)_T dp=0$ and combining with

$$H=U+pV \quad C_p(dT/dp)_H = - (dU/dp)_T-(d(pV)/dp)_T$$

enable Joules -Thomson coefficient definition, $\mu_{J.T}$ (Dođević Đ.S, Dražić J.V., 1994):

$$\mu_{J.T} = (dT/dp)_H$$

a measure of Joule Thomson effect, i.e. adiabatic temperature change caused during over-pressure stimulated gas transition through membrane pores between two gas phases. In this present paper experimental data for over-pressure value before distributor when the first air bubble entered in the water and rounding air and gas bubble temperature difference are used for the determination of Jouele

–Thomson coefficient of gas bubble depending on aeration regime as a measure of inter-molecular forces type in gas bubbles and its relaxation processes .
The known value of Joule Thomson coefficient in combination with Clausius-Klapejron equation $n\Delta V^{\theta}dp/n\lambda^{\theta}_{evap}=dT/T$, enable the determination of a latent heat λ^{θ}_{evap} of gas effective in relaxation transport process after evaporation in Carnot cycle:

$$\lambda^{\theta}_{evap} = 101{,}321T_G\cdot\Delta V^{\theta}_G/\mu_{J.T}, \text{ kJ/mol}$$

The aim of this paper is deeper view in Joule-Thomson effect influence to thermodynamic parameters, molar evaporation heat of working gas depending on electron density, calculated in our previous paper (Mirjana. M. Ševaljević et all, 2012.), and its influence on oxygen volume transport coefficient deviation from the value corresponding to ideal gas state (Ševaljević. M., Stanojević, M, Simić, S. and Pavlović, M. 2009) .

EXPERIMENTAL RESULTS

Experimental work (Simić, :N.S. 2006) was performed at batch working conditions and varying air flow of 2 and 10 m ^{3}/h. The water level in the column was 1 and 2 m high and the total volume was 490 and 980 L. Water aeration with waste oil content of 5 and 10 mg/L was performed. Water aeration with the prepared real sample with added waste oil content of 5 and 10 mg/L of the viscous waste motor oil , SAE 15 W-40, with 132.0 mm^2/s viscosity index, with inflammation temperature, 231.0 ^{o}C, with 3.18 mg KOH/g TAN, as 9.73 mg KOH/g TBN, with content of 0.039 % Zn, 0.310 % Ca, 13.4 ppm Fe, 4.11 ppm Cu, 0.98 ppm Cr and 44.87 ppm Al. Densities of examined samples of refinery waste water were in range of 992 kg/ m ^{3} to 996 kg/m ^{3}, viscosity in range of $0.81\cdot10^{-6}$ to $0.99\cdot10^{-6}$ m ^{2}/s and surface tension coefficients were 76.2, 64.8 and 57.3 mN/m, respectively. Dissolved oxygen was previously removed using a chemical method. Air flow regulation is performed using a flow regulator and relieving valve until a set value for the adopted investigation regime is attained. Air flow is stabilized at over-pressure value before distributor when the first air bubble entered in the water. Water sampling from the column in equal time intervals starts ($\Delta\tau$ = 60 s) and the dissolved oxygen content, c $_s$ is measured until the same value is repeated three times with HANNA instrument with polarographic sensors (with accuracy 0.05 g/m^3) with aim to determine oxygen volume transport coefficient , k_La (Simic, N.S., 2006)

The described device with membrane air distributor for the water phase was used for the measuring of the volume coefficient of the oxygen transport, k_La (Simić, 2006, Pavlović et al, 2008.) based on the material balance, according to literature (Ashley, K., Hall, K., Mavinic, D.

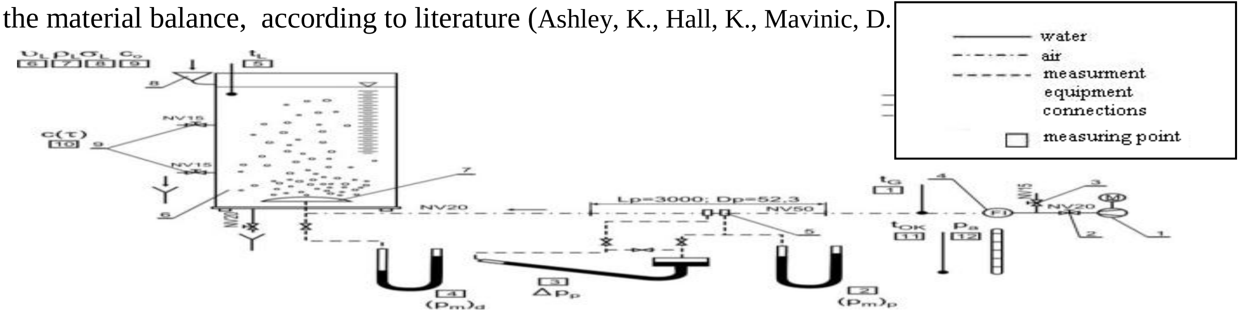

*Figure 1. The scheme of experimental installation (*Simic, N.S, , 2006)

1 – low pressure compressor (blower); 2 – valve on the air inflow pipe; 3 – relieving valve; 4 – air flow regulator; 5 – air flow measuring orifice plate; 6 – column with corresponding connections and framework; 7 – disk-shaped membrane air distributor; 8 – water supply; 9 – sampling connection.

The measured and calculated parameters for regimes c-h-q where: c-added waste motor oil in mg/l, h-water column height in m, and q-air flow in m^3/h, present the Table 1. The functional dependences between the examined parameters present Figures 2. to Figure 8.

Table 1: The measured and calculated parameter, Joule Thomson coefficient for water column 2m high

Regims c-h-q	p_{in}-p_a bar	t_R-t_G K	T_G K	$\mu_{J.T.}$ K/bar Fig (1)	k_La h^{-1}	$[e]_r$ $molm^{-6}$	λ^θ_{evap} kJ/mol	ΔG^θ in couple react,kJ/mol
0-2-2	0,2077	0,5	288,5	-40,689	2,51	59	-16,09	$\Delta_f G^\theta(NH_3)l = -\Delta_{diss} G^\theta(O_2)$
0-2-6	0,2342	-0,1	290,6	-40,689	2,66	57	-16,21	“
0-2-10	0,3344	-4,5	291,7	-40,689	4,68	73	-16,27	"
5-2-2	0,2199	-1	286,5	-0,5335	2,04	132	-1219	$\Delta_f G^\theta(Ca(NO_3)_2 2H_2O)c+3RT$ etc
5-2.-6	0,2492	0,9	287,3	-0,5335	2,03	130	-1222	“
5-2-10	0,0006	1,9	286,4	9,137	4,06	102	71,14	$E_{af}(H/H^-)$
10-2-2	0,2263	1	289,2	19,817	1,75	278	33,12	$\Delta_f G^\theta(S_2)_g=\Delta G^\theta(O_2/O_2^-)+RT/2$
10-2-6	0,2581	1,7	290,4	19,817	1,89	278	33,26	“
10-2-10	0,3165	2,8	288,5	19,817	2,293	360	33,04	“

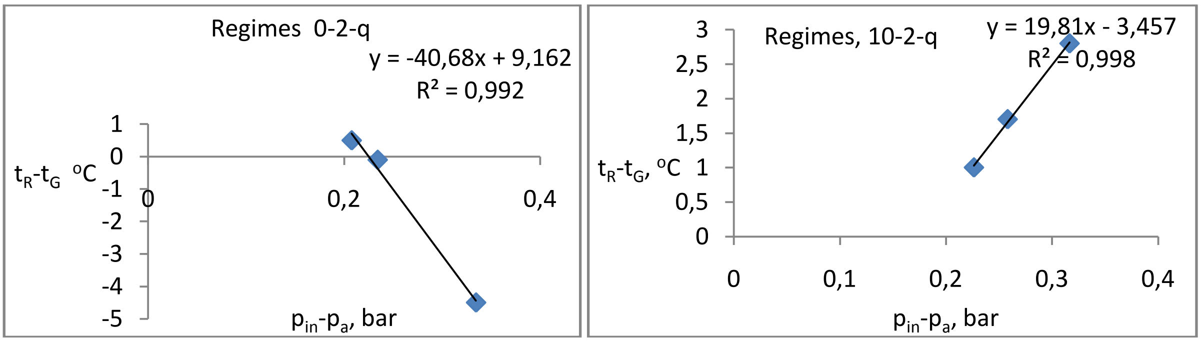

Figure. 2 Linear functional dependences witch fit the data for air pressure difference p_{in}-p_a and surrounding air and gas temperature difference, t_R-t_G for aeration regime c-2-q, excepting 5-2-q

Table 2: The measured and calculated parameters for water column 1m high

Regims	p_{in}-p_a bar	t_R-t_G= t_R-t_L K	T_G K	$\mu_{J.T.}$ $Kbar^{-1}$ Fig (1)	k_La h^{-1}	$[e]_r$ $molm^{-6}$	λ^θ_{evap} kJ/mol	ΔG^θ in couple reac,kJ/mol
5-1-2	0,1344	3,5	287,9	9,137	2,86	1925	71,51	$E_{af}(H/H^-)$
5-.1-6	0,1691	3,4	288,6	9,137	3,74	2100	71,69	“
5-1-10	0,2394	4,1	288,8	9,137	4,83	2083	71,74	“
10-1-2	0,1344	3,5	287,9	14,638	2,34	3111	44,64	$E_{af}(O_2/O_2^-)$
10-1-6	0,1664	4,4	287,8	14,638	3,11	3270	44,62	“
10-1-10	0,2434	5,2	287,9	14,638	3,95	3185	44,64	“

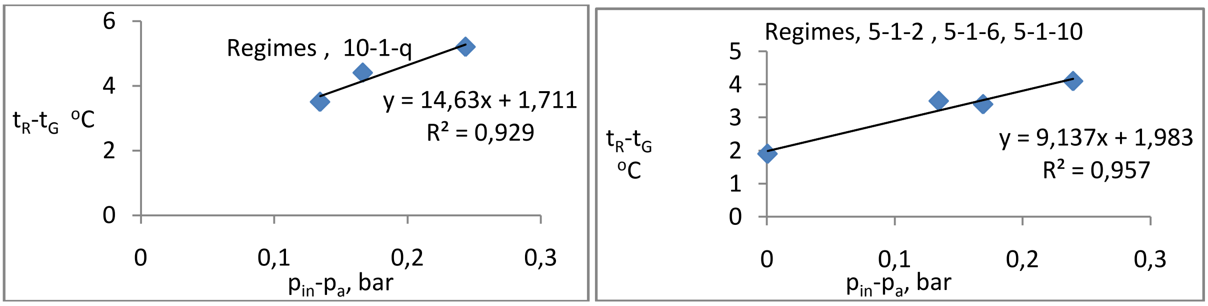

Figure. 3 Linear function which fit the data for surrounding air - gas temperature difference, t_R-t_G and air pressure p_{in}-p_a with the slope equal to Joule- Thomson coefficient, $\mu_{J.T}$ for water column h= 1 m

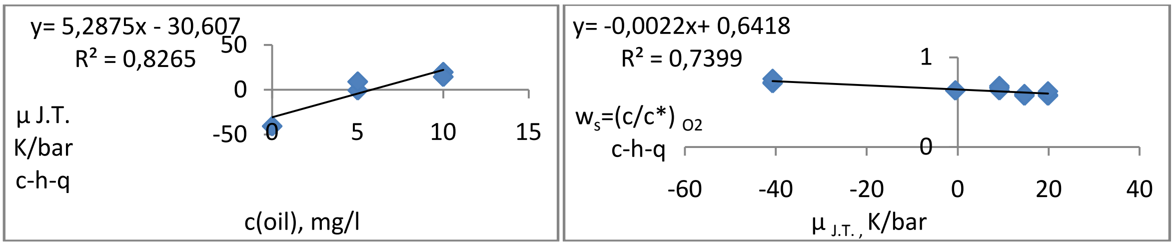

Figure 4. Wastemotor oil content, c influence on , $\mu_{J.T.}$, and $\mu_{J.T.}$, influence $_{on}$ oxygen saturation degree, w_s

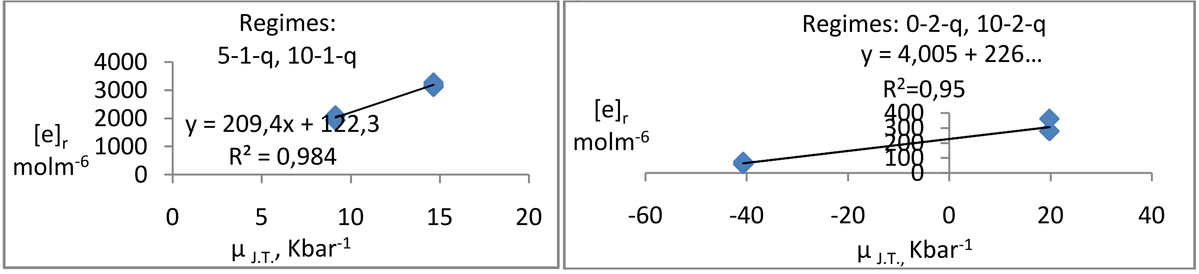

Figure 5. Linear functions which fit data for Joule-Thomson coefficient, $\mu_{J.T.}$, and electron density $[e]_r$

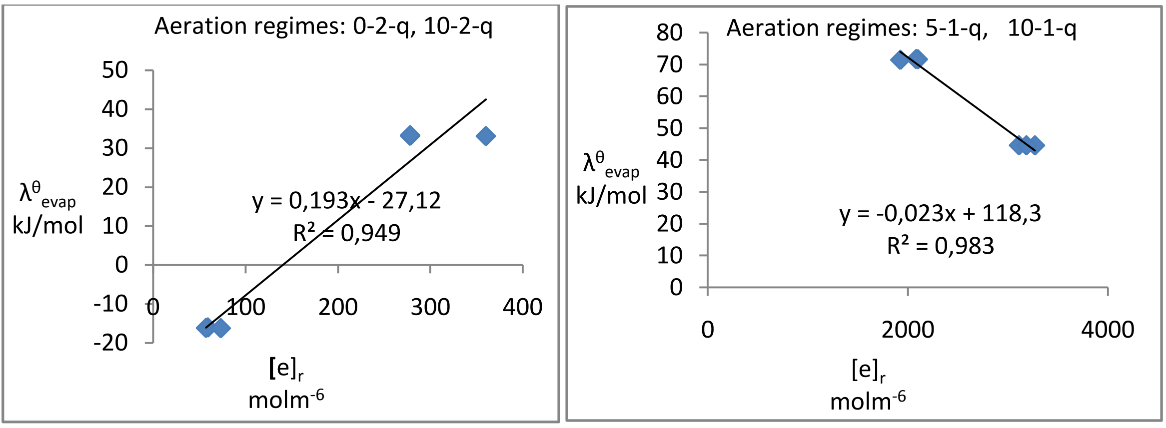

Figure 6. Linear functions which fit data for and electron density $[e]_r$ $_{and}$ evaporation latent heat, depending on aerationregime, , excepting 5-2-q

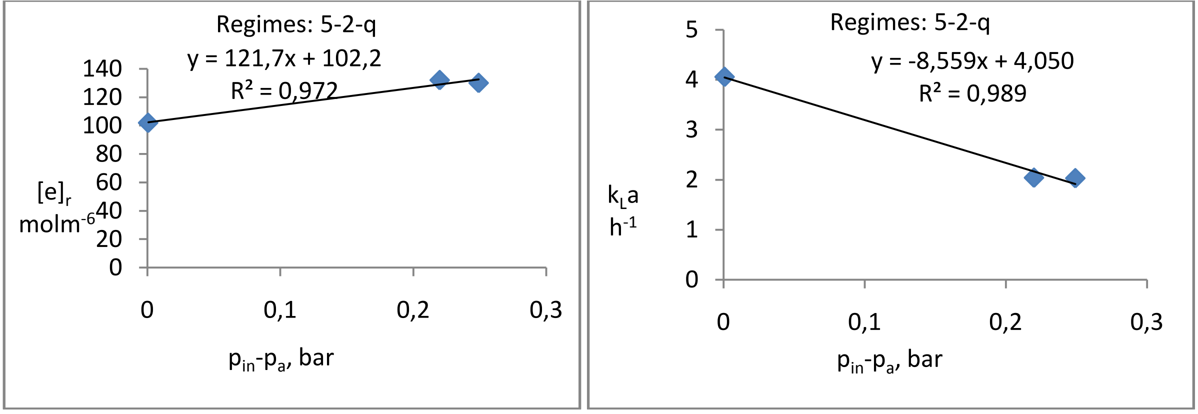

Figure 7. Linear functions which fit data for air over-pressure before distributor when the first air bubble entered in the water, p_{in}-p_a and electron density , or oxygen volume transport coefficient

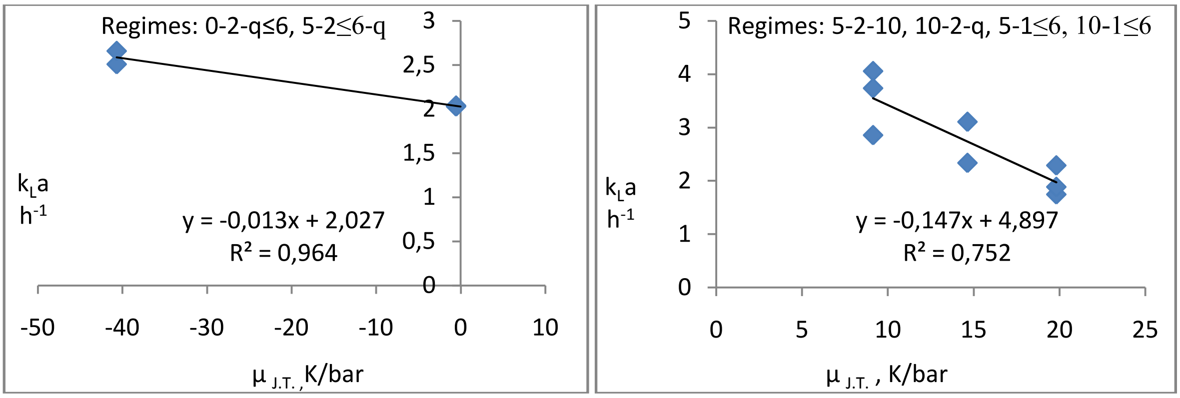

Figure 8. Linear functions which fit data for Joule –Thomson coefficient $\mu_{J.T.}$, and, oxygen volume transport coefficient, k_La

CONCLUSIONS

The conclusion remarks are as the follows:

- For aeration regime of refinery wastewater with the same diffuser membrane the diagnostics method of Joule-Thomson coefficient, $\mu_{J.T.}$ is applied, on the basis of the slope of the linear function $dT_{R/G} = f(dp)$, with correlation coefficients, $R^2 = 0{,}9299 - 0{,}9983$.
- The obtained results for the regimes without added waste motor oil, 0-2-q indicate to the negative slope i.e., the negative value of Joule-Thomson coefficient, $\mu_{J.T}=(dT/dp)_H$ due to decreasing intermolecular distance influence to temperature decreasing by potential energy increasing.
- The positive slopes, for the other regimes,10-h-q, as well as 5-1-q and 5-2-10 indicate to the increased temperature with over-pressure, due to increased attractive inter-molecular forces and inner pressure influence to oxygen potential energy decreasing.
- Added waste motor oil content increase Joule-Thomson coefficient linearly , $R^2 = 0{,}8265$, and Joule -Thomson coefficient decrease oxygen solubility degree, $R^2 = 0{,}74$, in the all examined regimes, c-h-q. The electron density increasing correlate to the evaporation latent heat increasing, R^2 (0-2-q, 10-2-q) = 0,9836 and to evaporation latent heat decreasing, R^2 (c-1-q) = 0,9836 .
- In aeration regimes (5-2-q) direct air over-pressure influence on electron density increasing and oxygen volume transport coefficient decreasing indicate to intermolecular forces negligible at minimal Joule–Thomson coefficient -0,5 $Kbar^{-1}$.
- Joule Thomson coefficient and oxygen volume transport coefficient, k_La fit the linear functions:
  - with the slope $dk_La/d\mu_{J.T}=-0{,}0137$, in regimes 0-2-q≤6, 5-2-≤6, $R^2 = 0{,}964$, where $\mu_{J.T}\leq 0$
  - and $k_La/d\mu_{J.T.}=- 0{,}1476$ in the regimes: 10-2-q, 5-1≤6, 10-1≤6, $R^2 = 0{,}7521$, where $\mu_{J.T}>0$
- The applied method for the determination of Joule-Thomson coefficient could be applied for identifying the aeration devices with gas bubble negligible intermolecular forces i.e. with minimal Joule -Thomson coefficient and minimal resistance to stimulated aeration velocity equal to the actual oxygen consumption velocity in a certain phase of the treatment process of wastewater.

REFERENCES

Ashley, K., Hall, K., Mavinic, D. (1991), Factors influencing oxygen transfer in fine pore diffused aeration, University of British Columbia, Water Research 25 pp. 1479-1486., Vancouver, Canada

Dudley, J.(1995) Mass transfer in bubble column-s comparison of correlations, Water Research, Swindon

Đođević Đ.S, DražićJ.V., (1994), Physical Chemistry, Technological- Metalurgy Faculty, Belgrade

Pavlovic Milan Stanojevic Miroslav M Sevaljevic Mirjana M Simic Stojan N (2008), Influence the wastewater oil concentration in water on the efficiency of the aeration process in refinery wastewater treatment,*Strojniški vestnik-Journal of mechanical Ingeneering* , vol. 54 br. 10, str. 675-684

Simic, N.S, (2006) Influence of Sistem of Aeration on The Efficiency of The Biologycal Treatment of TheRefinery Waste Water, *Ph.D. Thesis, Faculty oMechanical Engineering,* Belgrade, Serbia,

Stanojevic Miroslav M Sevaljevic Mirjana M Simic Stojan N Sevaljevic Miladin (2013), Influence of the water height in aeration regimes with the same membrane diffuser on technical characteristics of aeration system, *Desalination and Water Treatment , vol. 51 br. 22-24, str.* 4271-4282

Ševaljević M., Stojan N. Simić and Petar V. Ševaljević (2012) ”Thermodynamic diagnostic of electron densities in gas bubbles in aerated saturated refinery waste water”, *Deswater,* 42 Pages, 144-154

Ševaljević. M., Stanojević, M, Simić, S. and Pavlović, M. (2009) Thermodynamic study of aeration kinetic in treatment of refinery wastewater in bio-aeration tanks, Desalination, 248, p. 941- 960

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THE EXAMINATION OF WORKING FUNCTION DIFFERENCE IN WELLS WITH DIFFERENT DEPTH AND CORRELATION WITH POLLUTANT ADSORPTIVE FILTRATION EFFICIENCY

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ABSTRACT

The purification efficiency of ground water by adsorptive filtration of aluvial aquifers with different depths are examained in this paper, on the basis of monitoring data for water quality of aquifere depth about 50m (N ^{o}4) and about 100 m (N ^{o}3) . During four annual quartals the diffusion pollutant potential of dissolved components equal to electron working function was calculated, for the each of the two examined well. The obtained linear functional dependences of dipoles relative electric permittivity difference on the pollutants adsorptive filtration efficiency w_p *, %=100(c(N^{o}4)-c(N^{o}3))/c(N^{o}4) indicate to a direct water bonding between the two examined aquiferes. That confirm interphases contact surface free energy conversion into thermo-electro-chemical energy and pollutant mobilization transport work in hydrogen and oxygen striping relaxation processes.*

Keywords: *groundwater, aquifer different depths, pollutant adsorptive filtration, relaxation striping processes*.

INTRODUCTION

In the some regions (Bačka, Banat and a part of Srem) for drinking water people use a ground water from alluvial aquifer which is directly influenced with surface riverwater quality (National Strategy, 2012). The developing of methods of groundwater remediation s based on the understanding self-purifying effects of ground water of adsorptive filtration (Dimkić M.,2007) in wells with different depths (N., Kresić, S. Vujasinović, I. Matić, 2005) important in groundwater remediation procedures (Wiesner M.R.1996). The two class of solute relating to velocity of purification process are important due to the different velocities of contaminant infiltration in water and degradation and /or sorption in presence of suspended and colloidal particles:

A. class of the solute with “continuous” slow successive infiltration after the sorption or /and degradation

B. Class of the solute with “instant” (accidental), faster injection and percolation of parallel sorption or degradation (individually or collectively).

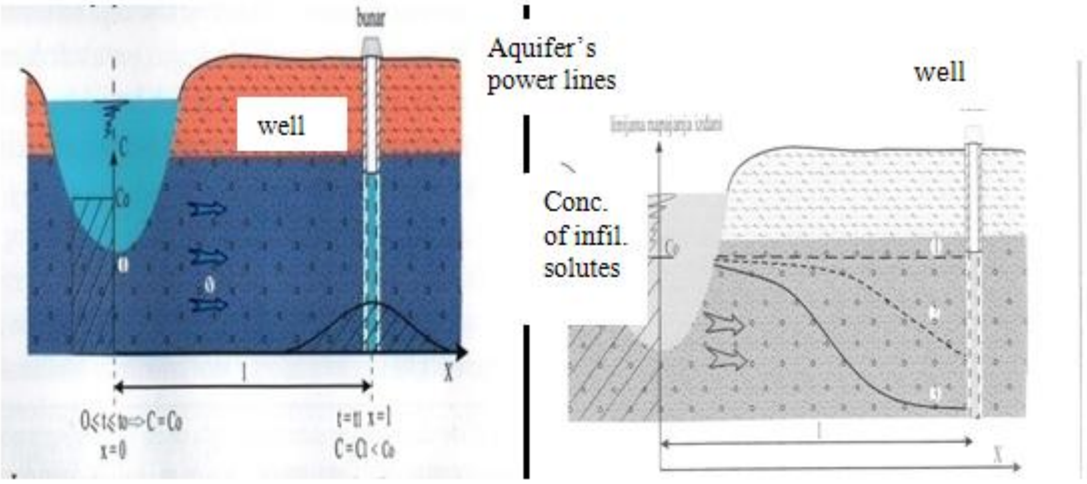

Figure 1. The scheme of water quality change impuls in well near a river, depending on well distance and well depth which indicate to influence of degradation and successive adsorption

In literature are investigated methods for adsorptive removal of manganese, arsenic and iron from groundwater (Buamah R., 2009). In this paper is examined the mechanism of adsorptive filtration in situ i.e. direct influence of different wells height to wellwater pollution or selfpurifying , according to method developed in our previous paper (Ševaljević M. M., Ionel I., Pavlović M., Vetres J., 2014). The theoretuical approach to monitoring results indicate to thermo-electrochemical energy conversion influence on pollution of gas and liquid phase, on the basis of the calculated parameters:

- working functions, i.e. free energy change of electron exit work from monoatomic layers in alloy intermetallic surface of one metal upon the othercontrolled with catalyst Volta potential $E_{i\ (ci=0)} = E^{\theta}_{j}$ on the basis of linear function between pollutant free energy and its concentration in the examined water applied previously in electric permitivity determination of of air pollutant efective in heat transport (Pavlović M. et al, 2013) which defines: $\Delta G^{\theta}{}_{c}(\gamma_p = 0) = FE^{\theta}{}_{(ci=0)}) = (F\varphi)_{catalyst}$
- depolarization surface reaction velocity of zero order is dominant in transport velocity, where:

- depolarization surface reaction velocity of zero order is dominant in transport velocity, where:

$$\frac{k_{A+}}{k_e} = \frac{m_e}{m_A}$$

- and dipole orientation work in the intermolecular bonds, where minimal free energy state is achieved for the state, where ΔG=0, according to Born equation :

$$\frac{FE^{\theta}{}_{W}}{\varepsilon_{dip}} = \frac{RT}{\varepsilon_0}$$

Hydrogen evolution rate constant in the fastest hydrogen relaxation-depolarization process control homogeneous catalytic reaction and the successive slovest hydrogen stripping of pollutant (Ševaljević et all, 2014) , where:

(a) $\gamma_p = \frac{k_{d.p}}{k_{H2}} + \gamma_{kdp=0}$,

(b) and $i_0 = C_f \eta_{H2} / d\tau_p$ acc to (Rotenberg, 1997) control hydrogen evolution overpotential in chemisoptions water layer on mineral particles produce thermo-electric current intensity change in electric double layer, where $\eta_{H2ech} = \frac{k_{A\cdot}}{k_e}\frac{E^{\theta}{}_{W}}{\varepsilon_r}$

The fastest excitation of a plasmon state, a successive relaxation in a closed contact surface control chemisorbed pollutant working function, according to electron impulses conservation law :

- $\frac{k_{A\cdot}}{k_e} = \frac{m_e}{m_A}$
- in contact surface between liqiuid and gas phase which controll hydrogen kinetic energy: $\eta_{H2,th} = \frac{k_{d,p} 3RT}{k_{H2} 2F}$,

Equal hydrogen over-potential in period of thermal and electric energy relaxation in successive striping processes control thermoelectrochemical impedance influence on relaxation period (Rotenberg, 1997), that give the functional dependence between indicator working function and its diffusion and hydrogen rate constant ratio (Ševaljević et all, 2014) :

$$\frac{k_{d.p}}{k_{H2}} = \frac{2}{3} \cdot \frac{1}{\varepsilon_r RT} \frac{m_e}{m_A} FE_w^\theta \tag{1}$$

$$tg = \frac{2}{3\varepsilon_r (m_A / m_e)\mathrm{RT}}$$

with the slope:

which enable the determination of dipole electric permittivity effective in water pollution mobilization work, after current breaking in hydrogen overpotential relaxation period:

$$\varepsilon_r RT = \frac{2}{3(m_A / m_e)tg} \tag{2}$$

The correlation between pollutant adsorptive filtration efficiency, w_p, % and orientation dipoles work difference, between shallow and depper well, $(\varepsilon_4-\varepsilon_3)$RT enable pollutant titration with hydrogen velocity which couple pollutant diffusion transport velocity change:

$\Delta k_H c_{pol} + \Delta k_d \cdot (c_4 - c_3) = 0$. (3)

After pollutant end titration point in shallow well its concentration keep stationary value $c_{pol}=c_4$. Then the combining with rearranged Eq. (1) give the linear functions between adsorptive filtration efficiency and working function of catalyst, $F\Delta E^\theta{}_w$ effective in relaxation work difference, $\Delta\varepsilon_r RT$ controlled with hydrogen and oxygen striping of water polutants:

$$\frac{c_4 - c_3}{c_4} = -\frac{3}{2} \cdot \frac{1}{F\Delta E^\theta{}_w} \frac{m_p}{m_e} \Delta\varepsilon_r RT \tag{4}$$

The prediction in this paper is that pollutant adsorptive filtration efficiency w_p , %$=100(c_4 - c_3)/c_4$ control surface planes water temperature on the blocked electrode in Galvanic and concentration cells, and relative electric permittivity of planes in double electric layer of active centers, effective in a de-blocking by relaxation work difference, $\Delta\varepsilon_r RT$ in hydrogen and oxygen striping processes.

EXPERIMENTAL RESULTS

The monitoring data are obtained in Institute for Public Health in Zrenjanin, and in „Waterwork ” in Zrenjanin.

Table 1: The monitoring data

Parameter	Well N°4 , Depth 36-61 m The dates. 27.X (2010),25.I, 27. IV. 25.VII (2011)	Well N°4 , Depth 98-118 The dates. 27.X (2010),25.I, 27. IV. 25.VII (2011)	*Ad, fil. effic,* w_p, *%*
T_{water} °C	14.3, 13.1, 15.2 16,6	15.8, 16.5, 17.7, 16.9	
T_{air} °C	4.7, -2.4, 21, 19.6	4.7, -2.4, 21, 19.6	
Turbidity, NTU	7.2, 4, 6.2, 6.3	0.6, 0.16, 0.41, 0.22	
pH	7.69, 7.72, 7.57, 7.63	7.97, 8.2, 8.12, 7,44	32,1(H^+)
POM, mg/l	41.23, 41.73, 34.68 39.13	37.16, 38.37 , 32.62, 36.79	7,55
Chloride ,Cl^-*, mg/l*	21.6, 22.6, 25.2, 22.8	5, <5, <5, 5.2	80,77
Elektric cond., κ, μS/cm (AVG)	1220, 1235, 1247, 1236 (1234,5±15)	1090, 1105, 1104, 1082(1090,25±15)	11,28
Iron, Fe^{2+}*, mg/l*	1.53, 1.55, 0.2, 1.07	0.22, 0.19, 0,01, 0,23	84,9
Manganese, Mn^{2+}*, mg/l*	0.050, 0.046, 0.37, 0.039	0,021, 0.021, 0.021, 0.021	5,29E+01
Na^+*, mg/l*	236.1, 212.5, 150, 312.5	315.8, 225, 168.8, 250	-4,41
K^+*, mg/l*	2.2, 2.6, 2.9, 2.9	0.6, 0.7, 0.8, 0.8	72,7
Mg^{2+}*, mg/l*	20.7, 23.7, 41.1, 21.8	15.6, 15.4, 12.1, 4.4	55,73
NH_4^+*, mg/l*	1.75, 1.69, 1.75, 1.74	1.46, 1.04, 1.17, 1.58	24,2
$P(PO_4^{2-})$*, mg/l*	0.36, 0.64, 0.05, 0.12	0.41, 0.43, 0.13, 0.24	-34,2
Ba^{2+}*, mg/l*	0.18, 0.25, 0.2, 0.1	0.01, 0.1, 0.2, 0.1	43,8
CO_2*, mg/l*	33.2, 28.8, 54.4, 44.4	15.4, 5.4, 11, 66.5	11,1
O_2*, mg/l*	1.1, 0.86, 0.8, 1	1.1, 1.32, 1.3, 1.2	-37,81
$(O_2)^*$, mg/l	10.34, 10.5, 10.1, 9.82	10.04, 9.65, 9.56, 9.73	10,46
Ca^{2+}	53.9, 57.4, 13.8, 57.1	14.3, 13, 14.9, 23.6	63,89
As, μg/l	5, 5, 7, 4	187, 170, 155, 102	-96,6
$c(O_2^*-O_2)$*, mg/l*	9.24, 9.64, 9.3, 8.82	8.94, 8.33, 8.26, 8.53	
NO_3^-	1.5, 0.8, 1.5, 0.8	1.8, 1.3, 1.3, 0.4	-12,9
$(t_{No3}-t_{No4})$, °C		1.5, 3.4, 2.5, 0.3	

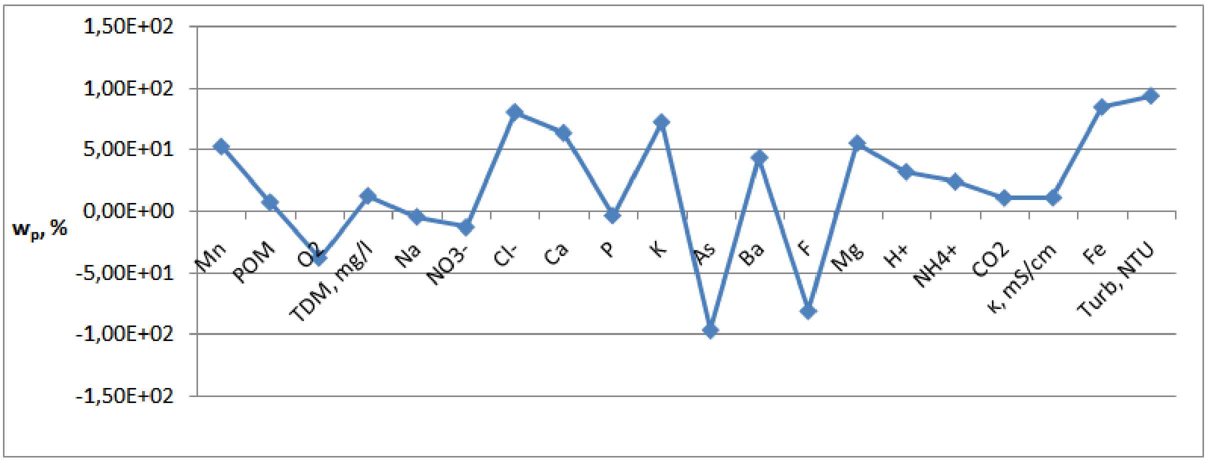

Figure 1. The calculated pollutant adsorptive filtration efficiency

Table 2: The linear functional dependences kd.p/kH2=f(ΔG4(c=0)) obtained with strong correlation coefficients, in well N o3 and N o 4 and the orientation dipoles work, εr 4RTw, effective in electrode surface de-blocking

	$k_{d.p}/k_{H2}=f(\Delta G_{4(c=0)})$ N°4	R^2 N°4	$\varepsilon_{r\,4}RT_w$ kJ/mol	k_e/k_A N°4	$k_{d.p}/k_{H2}=f(\Delta G_{4(c=0)})$ N°3	R^2 N°3	$\varepsilon_{r\,3}RT_w$ kJ/mol	k_e/k_A N°3	$\Delta\varepsilon_r RT$ kJ/mol
Mn	1E-08x + 2E-06	0,82	262,4	m_{Ba}/m_e	-0,0166x + 15,9	0,65	-39,6	$m_1/m_2\approx1$	302
POM	1E-05x + 0,0057	0,85	35,9	m_H/m_e	2E-06x + 0,0006	0,998	179,7	m_H/m_e	-143,8
O_2	0,0176x - 87,497	1	37,44	$m_1/m_2\approx1$	1E-06x - 0,0009	0,963	179,7	m_{H2}/m_e	-142,26
TDM	0,0393x + 8,4341	0,90	16,8	$m_1/m_2\approx1$	-0,0137x - 11,4	0,923	-48	$m_1/m_2\approx1$	64,8
Na	2E-07x - 7E-05	0,99	78,1	m_{Na}/m_e	-1E-07x - 0,0004	0,979	-64,5	m_{Fe}/m_e	142,6
NO_3^-	-4E-07x - 0,0003	1	-38,6	m_{Fe}/m_e	1E-06x - 0,0009	0,963	179,7	m_{H2}/m_e	-218,3
Cl^-	0,0393x + 8,4341	0,90	16,8	$m_1/m_2\approx1$	1E-06x - 0,0009	0,963	179,7	m_{H2}/m_e	-162,9
Ca	1E-05x + 0,0057	0,85	35,9	m_H/m_e	2E-06x + 0,0006	0,990	179,7	m_H/m_e	-143,8
P	1E-08x + 2E-06	0,82	262,4	m_{Ba}/m_e	2E-06x + 0,0006	0,990	179,7	m_H/m_e	82,7
K					-1E-07x - 0,0004	0,98	-64,5	m_{Fe}/m_e	64,5
As	2E-07x - 7E-05	0,99	78,1	m_{Na}/m_e	-0,0137x - 11,424	0,929	-48	$m_1/m_2\approx1$	126,1
Ba	1E-08x + 2E-06	0,82	62,4	m_{Ba}/m_e	-8E-10x - 5E-06		-44,88	m_H/m_e	107,28
F					-8E-10x - 5E-06		-44,88	m_H/m_e	44,88
Mg	1E-08x + 2E-06	0,82	262,4	m_{Ba}/m_e					262,4
H^+	1E-08x + 2E-06	0,82	262,4	m_{Ba}/m_e	-0,0137x - 11,424	0,923	-48	$m_1/m_2\approx1$	310,4
NH_4^+	1E-05x + 0,0057	0,85	35,9	m_H/m_e	-0,0166x + 15,933	0,654	-39,6	$m_1/m_2\approx1$	75,5
CO_2	2E-07x - 7E-05	0,99	78,1	m_{Na}/m_e	1E-06x - 0,0009	0,963	179,7	m_{H2}/m_e	-101,6
κ	0,0393x + 8,4341	0,90	16,8	$m_1/m_2\approx1$					16,8
Fe	y = -4E-07x - 0,0003	1	-38,6	m_{Fe}/m_e	-1E-07x - 0,0004	0,979	-64,5	m_{Fe}/m_e	25,9
Turb.	0,0176x - 87,497	1	37,44	$m_1/m_2\approx1$	-0,0166x + 15,933	0,654	-39,6	$m_1/m_2\approx1$	77,04

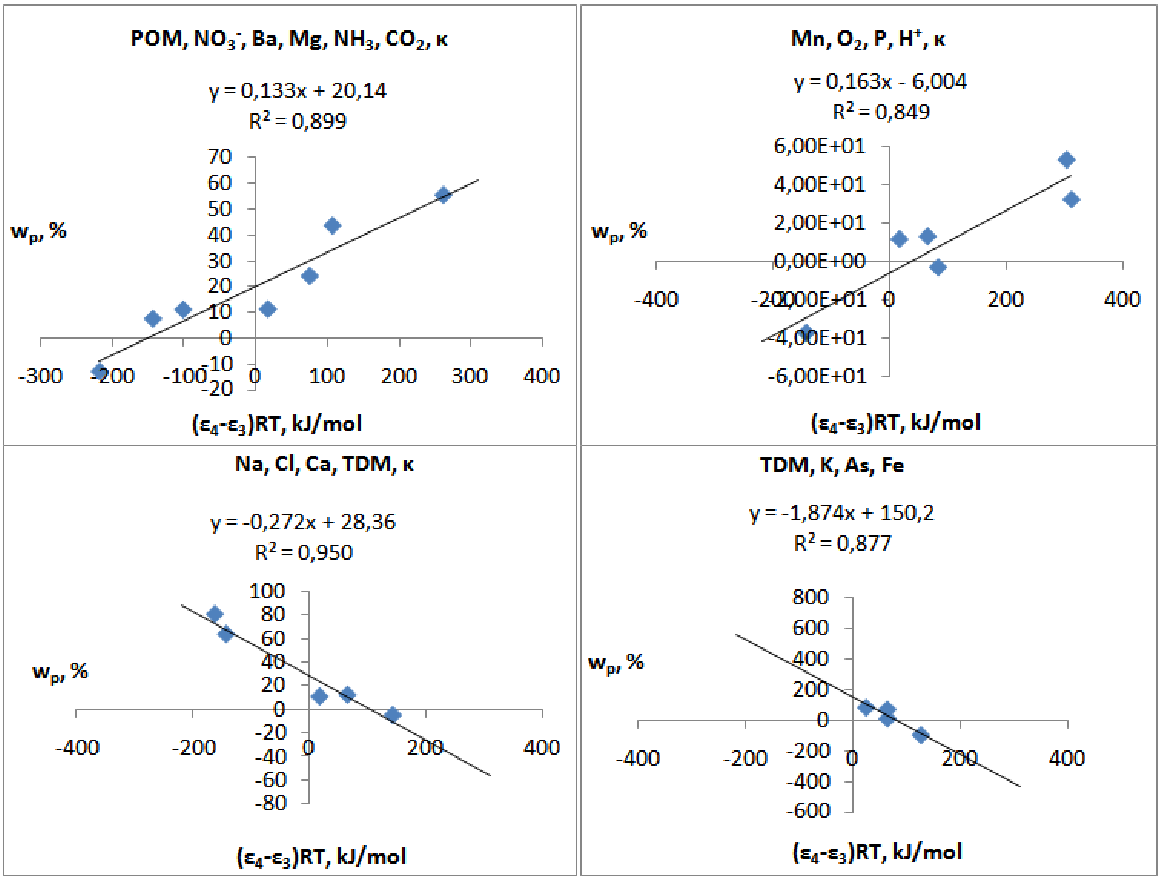

Figure 2. The correlation between pollutant adsorptive filtration efficience, w_p, % and orientation dipoles work difference between shallow and depper well, $(\varepsilon_4-\varepsilon_3)RT$

CONCLUSION

The conclusion remarks are as follows:

- The adsorptive filtration efficiency of examined pollutants, through alluvial earth layers, between shallow and deeper well, $w_p=(c_4-c_3)/c_4$, % vary depending on pollutant nature (Figure 1), from maximal positive values for adsorptive filtration efficiency of Turbidity, Fe, Cl, K, the decreased adsorptive filtration efficiency of NH_3, CO_2, H^+, POM up to negative values of As, P, Na, O_2, NO_2
- The obtained correlation between pollutant adsorptive filtration efficiency, w_p, % and orientation dipoles work difference between shallow and depper well, $(\varepsilon_4-\varepsilon_3)RT$ for the groups of pollutant, indicate to a successive hydrogen and oxygen relaxation striping processes and confirm the predicted functional dependences on anode and cathode working function influence on a pollutant diffusion and hydrogen stripping rate constant.

REFERENCE

Dimkić M., (2007) Self-purifying effects of ground water filtration, Beograd p.162, 168

Buamah R., 2009, Adsorptive removal from Mn, As and Fe from groundwater, Ph dissertation, Wageningen University, The Netherland

National Strategy of Sustainable Development and Using of Natural Resources,Sl. Glasnik RS., br 33/2012, Anex 6.1.3

N., Kresić, S. Vujasinović, I. Matić, (2005) Remediation of ground water and geologic media, Univerzity in Belgrade , Faculty of Mining and Geology, Belgrade

Pavlović M., Ionel I., Ševaljević M., N.S. Lontis[2], Đurić A.(2013) , Method for determination of electric permitivity of air pollutant efective in heat transport, published *on ICEEM07*, Wien

(Rotenberg, 1997) Z.A.Thermoelectrochemical impedance, Electrochemica Acta, 42(5), 793-799

Ševaljević M. M., Ionel I., Pavlović M., Vetres J., (2014), Termoelectrochemical surface energy conversion influence on air pollution, *Journal of Advances In Biotechnology, Vol 3, Nb. 3* Page 219-228

Wiesner M.R., M.C. Grant and C,R, Chutkins (1996), Reduced permeability in groundwtare remediation systems: Role of mobilized colloids and injected chemicals, *Environmental Science & Technology*30(11) p3184-3192

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BEGA CHANNEL WATER MONITORING

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ABTRACT

This paper represents results of Bega channel water monitoring which was done as part of the poject Romania-Republic of Serbia IPA Cross-border Cooperation Programme (Sustainable development of a research center in Banat region and Danube flow area through scientific research and environmental simulation tools to access and evaluate potential threats). Concerning the fact that one of the features of the Banat watercourses is that they all have their source in Romania, and confluence in Serbia, and that all rivers in Banat region belong to Danube basin, as well as that water courses in Banat are loaded with different type of pollutants concerning the fact that there are variety industry sectors, one of the defined activity of the IPA project was the monitoring of surface water quality in the region of Banat performed by both Serbia and Romania side. During the the sampling period, an action called "Bega in the the tube", was realized at the section of the Bega trought the city of Zrenjanin. During the action five samples of surface water were taken with active participation of students. Monitoring was performed in order to define the surface water quality as well as it's degradation by industrial, urban and other relevant pollution sources typical for this region. Parameters and location selection was performed according to standards and recommendations for surface water monitoring and it was based on detail analyses of the present point and diffuse sources, as well as the previous results of surface water monitoring. Results indicated pollution with nutrients, especially nitrites and phosphorus, which causes relatively low concentrations of dissolved oxygen.

Key words: *monitoring, water quality, surface water, Bega canel.*

INTRODUCTION

Water is an essential element that provides life on Earth. Importance of clean, healthy and safe water for each person, comunity, industry and other activities is priceless. In Banat region, next to the Danube and the Tisza, Bega is the largest tributary of the Tisza in our country as well as the most important river, and water source for diferent type of activities (agriculture and industry) . In Serbia, Bega consists of two parts: the Old Bega and Bega channel (or navigable Bega). The two parts flow into one another at Klek, forming Bega which further flows through Zrenjanin, next to Ečka, Lukino Selo, Stajićevo and Perlez, to the confluence in the Tisza. The confluence is on the tenth kilometer of the river Tisza, about 3 km upstream from Knićanin, in Titel at the opposite bank of the Tisza. From the source to the confluence length of the Bega is 244 km of which 67 km in Romania and 168 km in our country.

The Old Bega and the Channel Bega area is extremely agricultural (94.23 % consists of arable land and gardens). During the second half of 20th century industry on the river bank was higly developed as well. Today there are a lot of abandoned facilities, but some of the industry is still working. However, Bega pollutant register was made which have identified all significant point and diffuse sources of pollution of watercourses. (JVP „Vode Vojvodine“2010).

Table 1 gives a list of pollution sources on the river Bega.

Table 1: List of pollution sources on the river Bega

Pollution source	Location
Žitište	
Slaughter, "Agroživ"	N 45°28'394" E 20°33'344"
Zrenjanin	
Shipyard , D.o.o. Bomex 4M	N 45°14'249" , E 20°24'029"
Shipyard , Brodogradilište “Begej” ad.	45° 23’ 902’’ N, 20° 26’ 557’’ E
Sewage , JKP „Vodovod i kanalizacija“	N 45°21'263" E 20°24'403"
Edible oil production, "Dijamanat"	1. N 45°23'235" E 20°25'136" 2. N 45°23'230" E 20°25'171" 3. N 45°23'143" E 20°25'073" 4. N 45°23'109" E 20°24'592" 5. N 45°23'098" E 20°25'073"
Dairy , Mlekoprodukt	45° 23’ 312’’, 20° 25’ 367’’
Detergent production, Beohemija-inhem” d.o.o	45° 22’ 096’’, 20° 24’ 130’’
Power plant, Panonske Te-To” section Te-To	N 45° 21'24", E 20° 24'55"
Animal waste recycling, “Prekon” d.o.o	45° 21’ 839’’, 20° 25’ 101’’
Tinning of hides and skins, ”Dafar” d.o.o	45° 21’ 961’’, 20° 24’ 235’’
	N 45° 22'056", E 20° 26'029"
Foundry Industry, Radijator, ad	

MATHERIAL AND METHODS

Sampling sites

Selection of parameters and location for sampling was performed according to standards and recommendations for surface water monitoring and it was based on detail analyses of the present point and diffuse sources, as well as the previous results of surface water monitoring. Table 2 lists measurment sites location, and Figure 1. presents locations of water pollution sources and sampling points.

Table 2: Description and locations of Bega channel measurment site

Meaurment site	Description	Coordinates
	Before Zrenjanin/before dairy	N 45°23'16", E 20°24'34"
	After dairy	N 45°23'18", E 20°20' 7.13"
	After edible oil production	N 45°23'16", E 20°24'26.70"
	Before Aleksandrovački cannal	N 45°22'66", E 20°24'34"
	Before Aleksandrovački cannal	N 45°21'26", E 20°24'40.3'

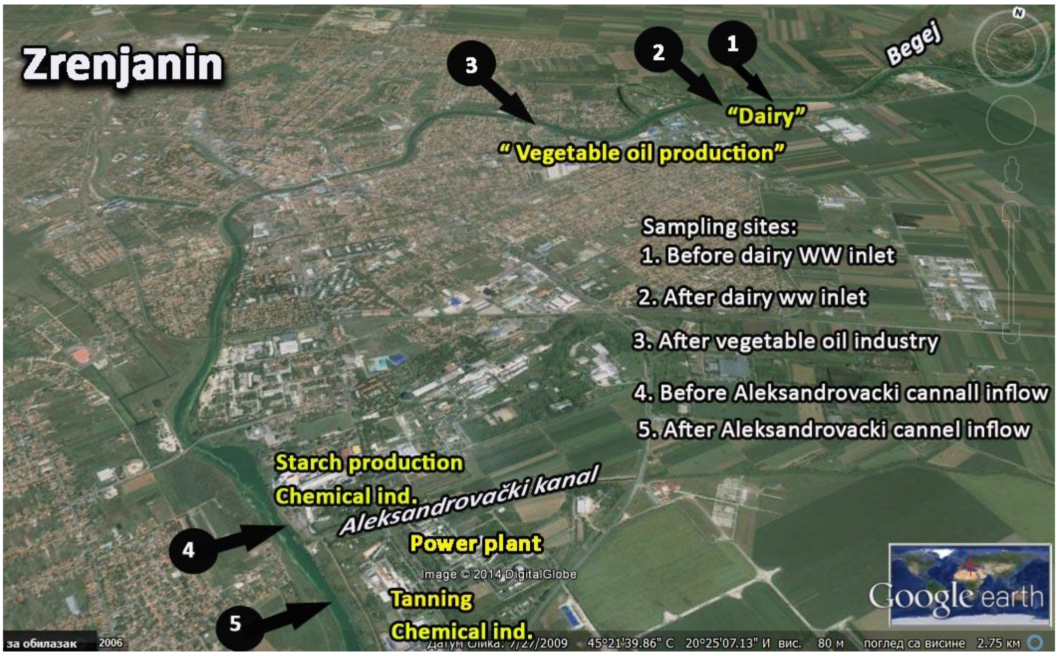


Figure 1. Surface water monitoring points and pollutant sources on Bega river in Zrenjanin

Parameters and analysis

After sampling organoleptic analysis, presence of visible matter water temperature, pH value and dissolved oxygen concentration were done on site. Concentrations of nitrate nitrogen, nitrite nitrogen, phosphorus, suspended soils, COD and BOD_5 were done in laboratory using spectrophotometry whithn the 48 hour from sampling time. Methods that were used in analysis of individual parameters are shown in Table 3.

Table 3: Methods used for analysis of water samples

Parameters	Methods
pH	Potenciometry
Dissolved oxygen	Voltametry
Suspended matter	Spektofotometry
BOD5	Manometry
COD	Dichromate method/ Spektofotometry
NO3-N [nitrates]	Spektofotometry
NO2-N [nitrites]	Spektofotometry
P [phosphorus]	Spektofotometry

Limit values of measured parameters

According to Bylaw on limit values of pollutants in surface and ground waters and sediments, and the deadlines for their achievement ("Official gazette RS" No 50/2012), Banat rivers are classified in following groups: Type 1 - large lowland rivers, the dominance of fine sediment (Bega, Tisza, Timis, Danube), Type 2- the great river, the dominance of the middle sediments (Nera), and Type 5- streams of the Pannonia basin (Karas)

Limit values for measured parameters prescribed in Rulebook on parameters of ecological chemical status of surface waters and parameters of ecological, chemical and quantitative status of ground waters ("Official gazette RS" No 74/2011) are shown in Table 4.

Table 4: Limit values for measured parameters in surface water

Parameters	Unit	Limit value				
		I class*	II class*	III class*	IV class*	V class*
pH (Type I, II and V)		6,5-8,5	6,5	8,5	6,5	>6,5 or >8,
Dissolved oxygen						
(Type I, II)	mgO2/l	8,5	7	5	4	>4
(Type V)		8	6	5	4	>4
Suspended matter (Type I, II and V)	mg/l	25	25	-	-	-
Nitrates						
(Type I)	mg/l	1	3	6	15	>15
(Type II and V)		1,5	3	6	15	>15
Nitrites	mg/l	0,01	0,03	0,12	0,3	>0,3
Total phosphorus						
(Type I and II)	mg/l	0,05	0,2	0,4	1	>1
(Type V)		0,15	0,3	0,4	1	>1
BOD5						
(Type I)	mgO2/l	2	5	7	25	>25
(Type II)		1,8	4,5	7	25	>25
(Type V)		2,5	5	7	25	>25
COD	mgO2/l	10	15	30	125	>125

**I class* - Water in this class corresponds to great ecological status. Surface water in this class, based on limit values of quality elements, provide conditions for functioning of ecosystems and survival and protection of fishes (salmonides and ciprinides) and it can be used in the following purposes: as a drinking water after pre-treatment that includes filtration and disinfection, for swimming and recreation, irrigation, industrial use (process and cooling water).

II class - Water in this class corresponds to good ecological status. Surface water in this class, based on limit values of quality elements, provide conditions for functioning of ecosystems and survival and protection of fishes (ciprinides) and it can be used in same purposes as I class water.

III class - Water in this class corresponds to moderate ecological status. Surface water in this class, based on limit values of quality elements, provide conditions for functioning of ecosystems and survival and protection of fishes (ciprinides) and it can be used in the following purposes: as a drinking water after pre-treatment with coagulation and flocculation, for swimming and recreation, irrigation, industrial use (process and cooling water).

IV class - Water in this class corresponds to poor ecological status. Surface water in this class, based on limit values of quality elements, can be used in the following purposes: as a drinking water after combination of treatments above and improved methods, irrigation, industrial use (process and cooling water).

V class - Water in this class corresponds to bad ecological status. Water in this class can not be use in an purpose.

RESULTS AND DISCUSSION

Visual analysis

Waters' turbidity - Turbidity presents suspended and colloidal matter in water. Turbidity is a reduction in water clarity because of the presence of suspended matter absorbing or scattering downwelling light, and water is considered turbid when the presence of suspended particles becomes conspicuous. Inorganic suspended materials, suspensoids or tripton, reduce light penetration, form adsorption and desorption surfaces, and are able to aggregate with dissolved substances, bacteria, and algae (Grobbelaar, 2013)

The adsorbed substances are available for bacteria, algae, and zooplankton. During water sampling it was found that water appearance on all points was the same, except at Aleksandrovački channel, where some of the green particles could be seen clearly (Figure 2a) as well as foam at inflow of Aleksandrovački channel in the Bega river (Figure 2b). Samples from other location on Bega shown low levels of turbidity.

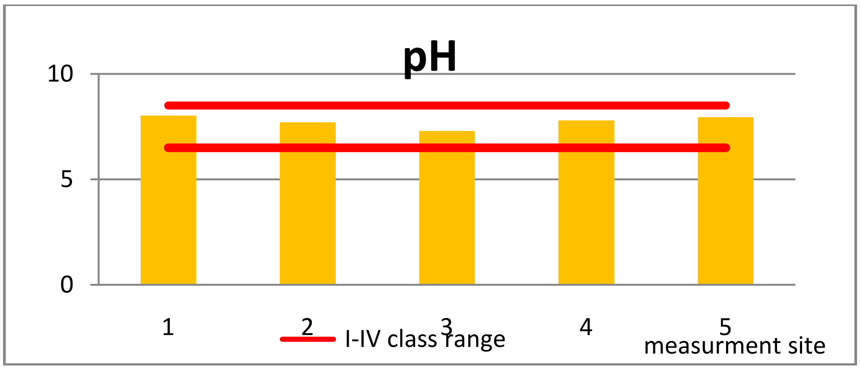
Figure 2. - Visible matter (a) and foam (b) at Bega

Organoleptic analysis

The smell of the water can indicate on a potential pollution. The oil and grease contained in the wastewater aggregates foul the sewer system and generate an unpleasant odor (Zhao et al., 2014). Also products of some algae and bacteria can cause different types of smell. Biological degradation can be followed by production of gas or formation of simple organic compounds which cause the unpleasant smells. Samples which were taken from the Bega watercourses had no smell.

Chemical analysis

pH value of aquatic ecosystems which are not under anthropogenic influence is on the range from 6.2 to 8 (Maletić, 2012). The pH value of the water which the most of organic organisms can survive in has the range from 4.5 to 9. Acidity and alkalinity of water depend on geomophological characteristics of soil, but also on human activities. Major anthropogenic influence on pH of aquatic system is discharge of nutrients (fertilizers) which leads to rapid growth of algae and increase of pH value. During the analysis of surface water samples the pH values were from 7.3 to 8.4. Such values are defined for I and II class of water and are considered as having a great and good ecological status, respectively (Graph 1).



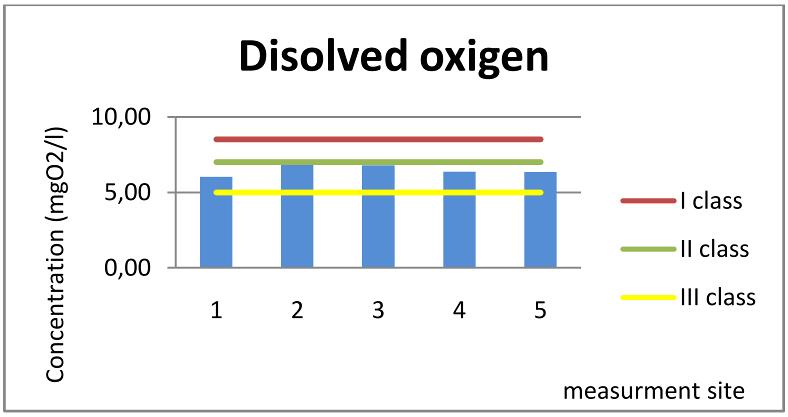
Graph 1. pH values in surface water of Bega channel

Suspended matter

Suspended soils in surface water usually arrive by soil’s washing away, erosion or sediment resuspenzion (Bečelić and Tamaš, 2004). Chemical composition may vary and it is one of it’s most undesired characteristics that can have a bad impact on surface water. In taken samples the concentration of suspended soils was in range from 3 to 9 mg/l which is classifies these samples in I and II class (25mg/l).

Dissolved oxygen

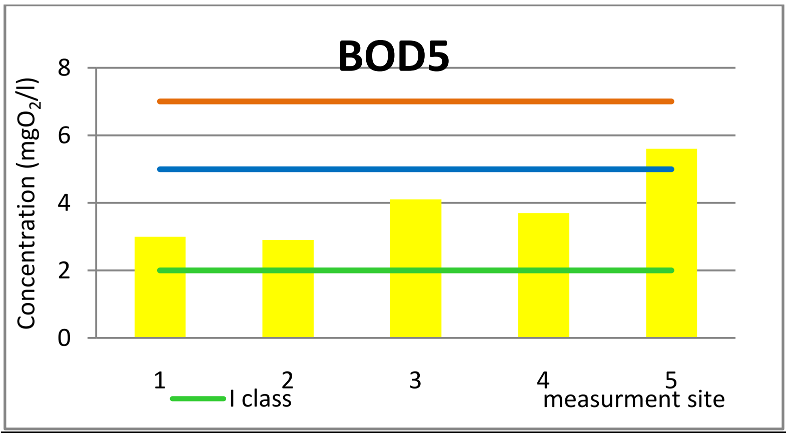
Dissolved oxygen is one of the most significant features of all aquatic ecosystems because it is essential for the existence of all aquatic organisms. Problems associated with inadequate dissolved oxygen concentration, which can be brought about by consumption of introduced solid or dissolved organic matter (e.g., sewage waste) by decomposer organisms, include mortality of aquatic organisms and the overall decrease in stream esthetics (e.g., odor, taste) (Bailey and Ahmadi, 2014). If the concentration of dissolved oxygen is higher, water quality is better (minimal concentration for I class is 8,5 mgO2/l). Turbulence of the watercours, temperature, number of organisms that use and produce oxygen are some of natural factors that affect the concentration of dissolved oxygen in water. The concentration is also affected by compounds which "consume" oxygen. Largest group of them is group of organic compounds. Organic compounds belong to pollutants that are degradable in aerobic conditions, therefore in the presence of oxygen. Measured concentrations show values in range from 6,04 to 7,07 mgO2/l. Most of the samples can be classified as III class which could be desribed as water with modetare ecological status (Graph 2).



Graph 2. Dissolved oxygen (mgO2/l) in surface water samples

Biological oxygen demand (BOD)

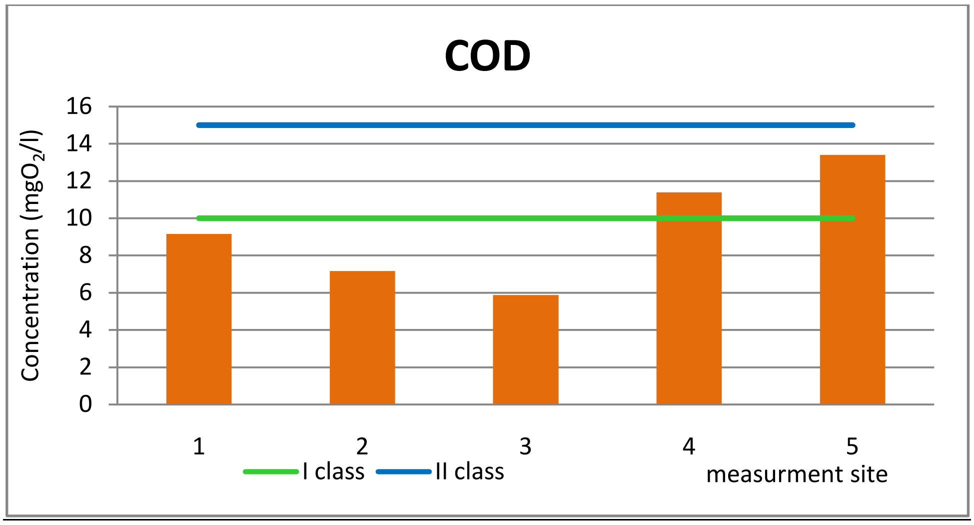
BOD is an important parameter for usage conditions of surface waters. It is an approximate measure of the amount of biochemical degradable organic matter present in a water sample. It is defined by the amount of oxygen required for the aerobic microorganisms by the amount of oxygen required for the aerobic microorganisms (Dogan et al., 2009). Values for BOD_5 were in the range from 3.00 to 5.6 mg O2/l. Obtained results showed that, according to 4 samples, the Bega river may be classified as II class (good ecological status). However, sample taken after inlet of Aleksandrovački channel shows values that classify it as III class (moderate ecological status), which confirmed that strong influence of this channel on the quality of the Bega water (Graph 3).



Graph 3. BOD (mgO2/l) in samples from Bega channel

Chemical oxygen demand (COD)

COD presents the necessary level of oxygen for oxidation of both organic and inorganic matters and it is expressed in mg O2/l. This indicator, as well as others, can be used for water pollution assessment, especially for industrial wastewater (Sawyer et al., 2003). COD values are always higher then BOD for the same sample. According to COD values for water samples number 1, 2 and 3 belonged to I class, while samples number 4 and 5 belonged to II class of water (Graph 4) .



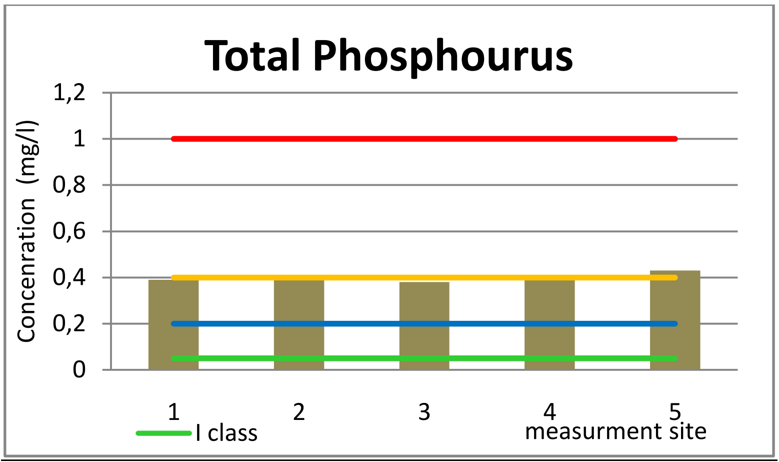
Graph 4. COD (mgO2/l) in water samples

Nutrients

Nitrogen (in form of nitrite and nitrate) and phosphorus, are chemical elements that are essential for growth of plants and animals. High concentrations of nutrients can cause a rapid growth of algae, which can reduce the concentration of oxygen in water, as well as occurrence of unpleasant smell and taste. This rapid growth of plants induced by the high concentration of nutrients is called eutrofication (Badruzzaman et al., 2012).

A lot of groceries contain phosphorus and its loss leads to increase of its concentration in water. Phosphorus is also part of hygiene products used in food industry. One of the greatest sources of phosphorus as an environmental pollutant are industrial wastewater. High concentration of phosphorus in aquatic ecosystems may cause rapid growth of algae, eutrofication and reduction of oxygen concentration in water and thereby negatively affect aquatic organisms.

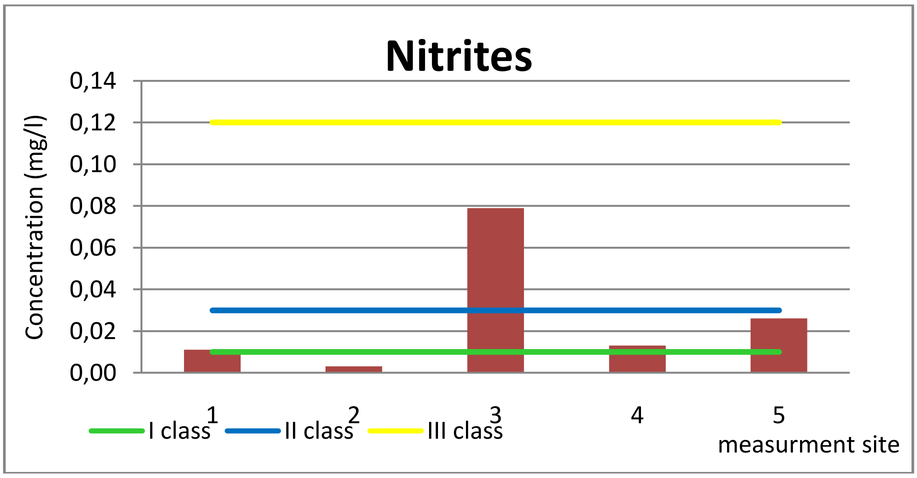
The concentration of total phosphorus in taken samples were in the range from 0,39 to 0,43 mg/l. Concentrations of phosphorus in some samples (1,3 and 4) reaches values that classify the samples as III class (poor ecological status), while samples 2 and 5 can be classified as IV class (Graph 5).



Graph 5. Phosphorus concentration (mg/l) in water samples

Concentration of nitrates is always higher than concentration of nitrites. Elevated concentrations of nitrate in surface and ground waters, as a result of firstly, excessive use of nitrogenous fertilisers, and secondly, disposal of untreated municipal and industrial wastes, are a serious global environmental problem (Loganathan et al., 2013). Nitrites can indicate relative fresh pollution, especially fecal type, while nitrates are final product of organic matter degradation and it is characteristic to detect them over long distances away from pollution source.

In samples of Bega river registrted concentrations of nitrites were in range from 0,003 (sample number 2) to 0,79 mg/l (sample number 3). According to nitrite content sample number 2 belong to I, samples 1, 4 i 5 belong to II and sample number 3 belong to III class of water (Graph 6).



Graph 6. - Nitrite concentration (mg/l) in water samples

Measured concentrations of nitrate were in the range from 0,7 - 1 mg/l. According to these results watercourses belong to I and II class.

CONCLUSION

The aim of the action "Bega in the test tube" was determination of water quality in Bega river. Samples were taken at five crucial localities, near wastewater inlets, that can potentionaly affect water quality. Analysis as organoleptic analysis, detection of visable waste matter, as well as meassuring of temperature, pH value and dissolved oxygen concentration were done on site, while parameters as concentration of nitrite, nitrate, phosphorus, suspended soils, COD and BOD were done in laboratory by spectrofotomery.

Results of analysis indicated that all samples were slightly turbid, without smell. Meassured pH values and concentrations of suspended solids were in range defined for I and II class of water, that are considered as great and good ecological status, respectively. Concentrations of dissolved oxygen in all samples are in range from 6 to 7 mgO2/l, so according to this parameter water of Bega belongs to III class, that presents moderate ecological status. Meassured values for BOD in samples 1, 2, 3 and 4 indicate that Bega river belongs to II class. However, in sample taken after inlet of Aleksandrovački channel (sample number 5) meassured value classify water of Bega river as III class, which confirm stong influence of this inlet. High concentrations of phosphorus were meassured and in some samples they reach values that calsify water as IV class (poor ecological status). Surface water that belong to this class can not be used in any purpose.

Analysis of water generally showed that water samples from selected localities at Bega channel are loaded with nutrients, especially nitrites and phosphorus, which causes relatively low concentrations of dissolved oxygen.

With the aim of comprehensive understanding of surface water in Banat, it is necessary to implement analysis of water and sediment at more localities with the expand the scope of parameters that, beside chemical analysis, would include biological analysis of representative and sensitive species.

Also, one of the measures which is very important for improvement of water quality in rivers is treatment of industrial wastewater, stricter control of diffuse sources, such as landfills, agricultural areas, farms, but also raising of the public awareness about importance of water ecosystems in the entire environmental.

REFERENCES

Badruzzaman M., Pinzon J., Oppenheimer J., Jacangelo J.G., *Sources of nutrients impacting surface waters in Florida: A review*, Journal of Environmental Management 109 (2012), Pages 80 – 92

Bailey R. T., Ahmadi M., *Spatial and temporal variability of in-stream water quality parameter influence on dissolved oxygen and nitrate within a regional stream network*, Ecological Modeling 277 (2014), Pages: 87-96

Bečelić M., Tamaš Z, *Analysis and controlof physico-chemical parameters*. At: Water analysis - quality control, results interpretation (Editors: Dalmacija B, Ivančev-Tumbas I.), University of Novi Sad, Faculty of Sciences, Department of Chemistry, Pages 51-79

Bylaw on limit values of pollutants in surface and ground waters and sediments, and deadlines for and the deadlines for their achievement ("Official gazette RS" No 50/2012)

Clair N. Sawyer. Perry L. McCarty, Gene F. Parkin, *Chemistry for Environmental engineering and science* (5th edition), ISBN 0-07-246066-1

Dogan B., Sengorur B., Koklu R., *Modeling biological oxygen demand of the Melen River in Turkey usingan artificial neural network technique*, Journal of Environmental Management 90 (2009), Pages: 1229–1235

Limit values for measured parameters prescribed with same Regulation as well as Rulebook on parameters do ecological, chemical status of surface waters and parameters do ecological, chemical and quantitative status do ground waters ("Official gazette RS" No 74/2011)

Loganathan P., Vigneswaran S., Kandasamy J., *Enhanced removal of nitrate from water using surface modification of adsorbentse - A review*, Journal of Environmental Management 131 (2013), Pages: 363 - 374

Maletić S., *Importance of some parameters in water quality standards*. At: Water quality parameters (imission standard), editor Božo Dalmacija, University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Novi Sad, Page: 211

J.U. Grobbelaar, *Reference Module in Earth Systems and Environmental Sciences*, from Encyclopedia of Inland Waters, 2009, Pages 699-704, Current as of 19 March 2013.

JVP „Vode Vojvodine“: *Analiza otpadnih voda zagađivača na Teritoriji JVP „Vode Vojvodine“, u cilju proširenja i ažuriranja baze podataka i Identifikacije vodećih sila i značajnih Pritisaka na odabranim vodotocima,* Departman za hemiju, biohemiju i zaštitu životne Sredine,Katedra za hemijsku tehnologiju i zaštitu životne sredine,Novi Sad 2010

Zhao S., Huang G., Cheng G., Wang Y., Fu H., Hardness, COD and turbidity removals from produced water by electrocoagulation pretreatment prior to Reverse Osmosis membranes, Desalination 344 (2014), Pages: 454–462

IV International Conference
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OPIMIZATATION OF SEASONAL EFFICIENCY OF OIL AND FATS REMOVAL BY PRIMARY PURIFAYING, ON THE BASIS OF MONITORING DATA

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ABSTRACT

In the period of time from 2007.-2011., the measured values for oil and fat removal efficiency were: $\eta_{IV\ quartal}$ *=0,96-50,8 % and* $\eta_{I\ quartal}$ *= 5,06-95,97 %* $\eta_{II\ quartal}$ *=3,93-82,86 % and* $\eta_{III\ quartal}$ *=6,82-71,51 %. The monitoring data indicate to statistical significant influence with strong correlation coefficient between removal efficiency of oil and fat and suspended matter with water and air temperature difference, Tw-Tair in I quartal, and in IV quartal, as well as between air temperature in II and III. In second quartal the air temperature dominant influence on oil and fat removal efficiency is found and in third quartal. The obtained functional dependence between oil and fats removal maximal seasonal efficiency and oxygen solubility degree indicate to the dominant influence of spontaneous oxygen saturation in equalization and coagulation part and of stimulated aeration in flotation part.*

Key words: *Monitoring of wastewater purifying efficiency, Oil and fats, Oxygen solubility degree, Suspended matter and COD removal efficiency, Water and air temperature.*

INTRODUCTION

Wastewater influence on surface and ground water contamination, depending on technological process and because it must to be purified before exit in recipient, canalization, river water etc. *Technological wastewater from edible oil industry contains suspended matter, colloids, emulsion,* and dissolved substances which can be removed by primary purifying. The dominant seasonal influences on suspended matter, COD, oil content are examined (Ševaljević at al., 2007, Protić at all, 2011) (Ševaljević, Minić, 2011), (Ševaljević, M. Jovanović L Nikolin T) indicate to decreased and increased removal efficiencies of oil and fats depending on seasonal water temperature influence on destabilizations of colloid particles.

The working hypothesis in this paper is that correlations between monitoring parameters enable the determination of dominant parameter for achieving oil and fats maximal removal seasonal efficiency.

EXPERIMENTAL RESULTS

In the industry of edible oil AD “Dijamant” Zrenjanin, wastewater after primary purifying exit in canalization. The monitoring results obtained in Institute for public health from 2007. up to 2011., by standard methods enable the examination of parameter dominant in the process optimization with the aim to achieve maximal removal efficiency of oil and fats at the same procedure Nikolin T., 2000. and Nikolin T., Ševaljević, M.)):

$$\eta=100\ (c_{in}-c_{out})/c_{in},\ \%,$$

The correlations obtained with the strong correlation coefficients on the basis of monitoring data present the Figures 1. to 5.

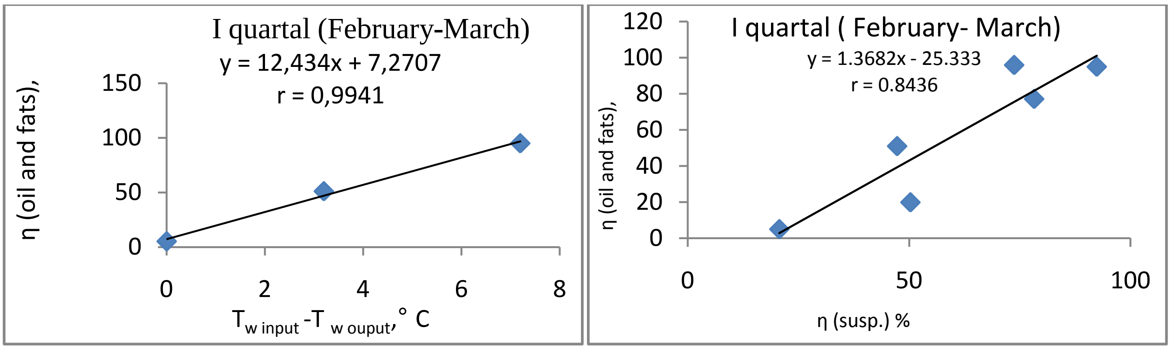

Figure 1. The functional dependences obtained with significant correlation coefficients between water temperature difference and removal efficiency I quartal (Nikolin Tatjana, 2014)

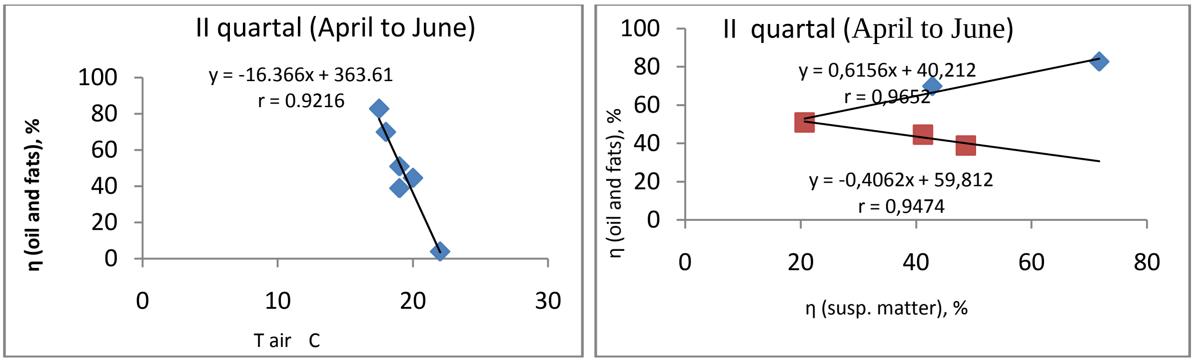

Figure 2. The functional dependences obtained with significant correlation coefficients between water temperature difference and removal efficiency II and III quartal (Nikolin Tatjana, 2014)

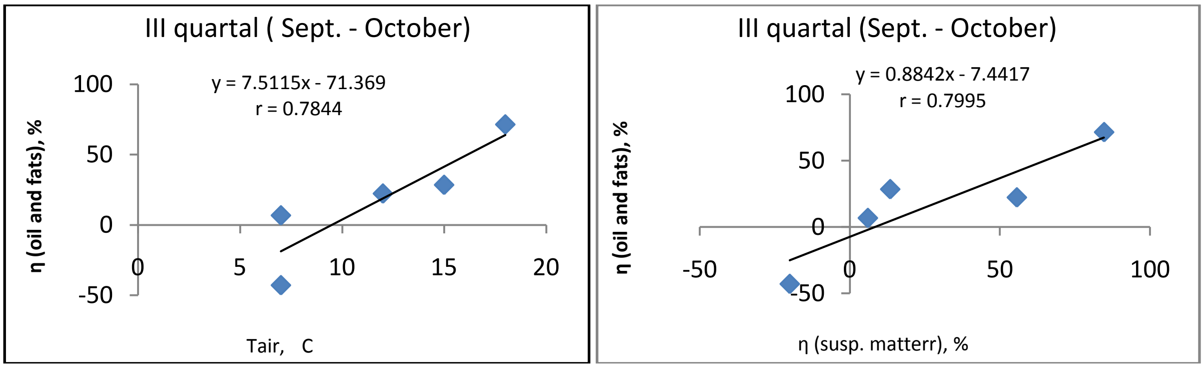

Figure 3. The functional dependences obtained with significant correlation coefficients oil and fats removal efficiency and IV quartal with air temperature, and with suspended matter removal efficiency (Nikolin Tatjana, 2014)

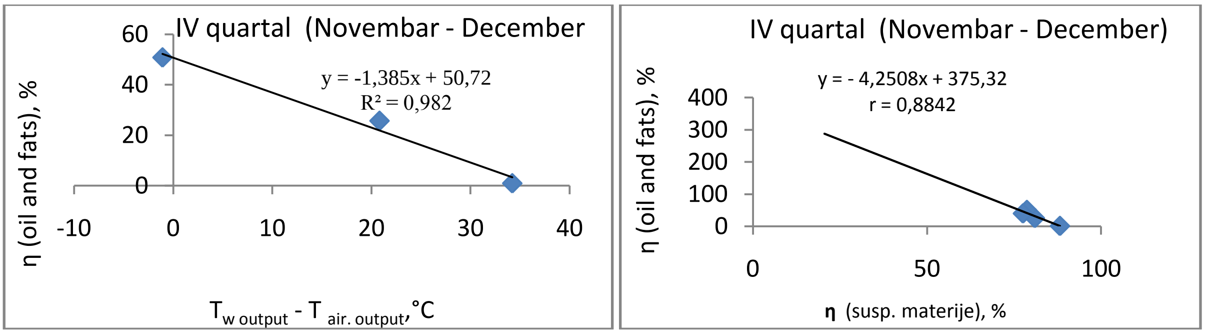

Figure 4. The functional dependences obtained with significant correlation coefficients between oil and fats removal efficiency and IV quartal with water /air temperature difference on plant output, and with suspended matter removal efficiency (Nikolin Tatjana, 2014)

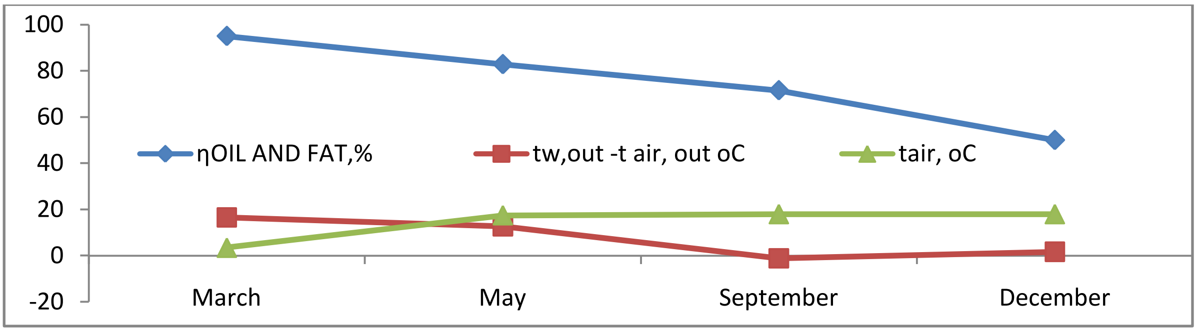

Figure 5. Optimal parameters in achieving oil and fats removal maximal seaonal efficiency

CONCLUSIONS

The conclusion remarks are as follows:

1. The measured quartal values oil and fats removal efficiency in period of time from 2007.-2011. vary : $\eta_{IV\ quartal}$ = from 0,96 to 50,8 %, $\eta_{I\ quartal}$ = from 5,06 to 95,97 % , $\eta_{II\ quartal}$ = from 3,93 to 82,86 % and η III quartal = from 6,82 to 71,51 %. The monitoring data indicate to satatistical significant influence with strong correlation coefficient, of oil of fats removal efficiency in the dependence on the suspended matter removal efficiency, as well as on $T_{air,\ out}$ on plant output and with water/air temperature difference, T_w-T_{air} .
2. Optimal parameter enable maximal efficiency of oil and fats removal to be achieved:
   - in I quartal, η MAX, I quartal = 95,03 %, in March, where also maximal suspended matter removal efficiency, 92,39 % is achieved, the dominant controlling parameter is positive value of temeprature difference Tw input -T w ouput= 7,2 °C
   - in II quartal, η MAX , IIquartal = 82,86 % in May, where, where also maximal suspended matter removal efficiency 71,7 % , the dominant controlling paraameters are air temperature t air= 17,5 o C and (tw-tair)out= 15,8 o C .
   - in III quartal, η MAX , III quartal = 71,51 % in September where also maximal suspended matter removal efficiency, 84,66 % is achieved, the dominant controlling paraameters are t air= 18 o C, and (tw-tair)out = 8 o C
   - and in IV quartal η MAX, I Vquartal = 50,08 % , in December where maximal suspended matter removal efficiency 78,7 % is achieved, the dominant controlling paraameters are he efficiency in the slowest successive step control water /air temperature difference on plant exit tair=18 ^{o}C, $(t_w\text{-}t_{air})_{out}$ = -1,1 ^{o}C and $T_{w\ input}$ -$T_{w\ ouput}$= -3,8 °C

The theoretical consideration of the obtained linear functional dependences between varying measured oil and fats removal efficiency and dominant controlling parameter, could help in the developing of optimized seasonal procedure which enable achieving of maximal values.

REFERENCES

Nikolin Tatjana , Primary purifying of oiled wastewater with the aim of environment protecting, *Mag . work , 2000 Faculty of Environment Protecting , Univerzity in Novi Sad*

Nikolin Tatjana , Testing parameters that interfere with the removal of fats and oils in the primary treatment of oily wastewater, *Ph. D. dissertation , 2014 Edukons Univerzity, Sremska Kamenica*

Nikolin T., Sevaljević M. (*2014),* The examination of the seasonal influence on the efficiency in oil and fats removal through primary treatment from the wastewater of edible oil industry *Hemijska industrija, On Line-First (00):89-89* KB) DOI:10.2298/HEMIND130906089N

Ševaljević M, Pavlović M, Velimirović M.Tošić D. (2007), Seasonal temperature variation and the water self-cleaning in the lake systemBegejs loop, Zrenjanin, *Proceedings of the International Conference onEnvironmental Management Engineering, Skiathos*, pages 1081-1086

Protić I., M. Ševaljević, Aćin N., Novaković M., Nikolin T., Velković Z. (2012), The influence of seasonal temperature change rate on relqaxation processes in the raw and chlorinated water in Zrenjanin urban Waterwork, *II International Conference “Ecology in Urban Areas”,* in Zrenjanin, Pages 220-225

Ševaljević M., Minić M. (2011), Seasonal kinetic aspect of of purification of urban atmospheric wateri n petrochemical refinery , *I International Conference "Ecology in Urban Areas"in Zrernjanin ,* Pages 224-229

Ševaljević, M. Jovanović L Nikolin T, (2011) Correlation analysis of oil wastewater treatmentand mechanism of puirification , *International Scientific Conference on Sutainable Development in the Function of Environment Protection, Beograd* Pages 18-20

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SCREENING OF ORGANIC POLUTANTS OF URBAN SURFACE WATER OF EUROPE

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ABSTRACT

Quality of surface water depends on many factors. One of very significant groupe of contaminants is group of organic pollutants (xenobiotics). Xenobiotics in surface water present contamination caused by human activities. For analysis of this tipe of pollution it is ussaly used some of chromatografic techniques (GC-MS or LC-MS). For sample preparation it is ussaly used SPE extraction. The most significant groups that are detected in urban surface water in Europe are pesticides, PAHs, PCB, pharmaceutics etc. These compounds are mostly difficult for biodegradation (persistent), so they can reach a long distance from their source, what present a further risk. That can explain the fact that some pollutants that are characteristic for rural areas, as pesticides, are found in urban water.

Key words: *organic pollutants, screening, surface water, water pollution*.

INTRODUCTION

The quality of river water across Europe has improved significantly thanks to a range of EU environmental directives since the 1970s. However, pressures from agriculture, urbanisation, tourism and climate change suggest that guaranteeing water quality will continue to be a critical European environmental issue. Water quality is a complicated issue underlined by the influence of various pressures and multi-cause/multi-effect relationships.

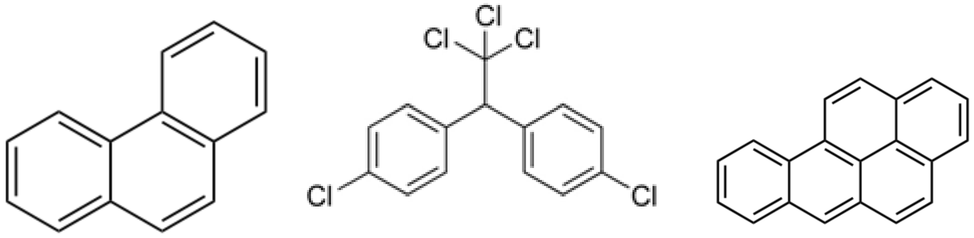
One of problems are organic pollutants, xenobiotics. There are more than 100 000 xenobiotics on market of EU. About 30 000 are chemicals that are used every day, that are used in tons every year.70 000 xenobiotics may have harmful impact on human health an environmental *(Ivančev-Tumbas, 2009).* The most widespread contamination of the aquatic environment is from pesticides and pesticide residues (EEA). Origin of xenobiotics are antropogenic activities: emission of insufficient treated wastewater, emission of xenobiotics to atmosphere and it's precipitation to surface water and runoff from soil *(Đurić and Petrović, 1996*. These compounds are mostly difficult for biodegradation (persistent), so they can reach a long distance from their source, what present a further risk. Persistent pollutants usually have hydrophobic character, so they can be easily adsorbed on sediment or in lipid fraction of biota, what can lead to biomagnification (*Ivančev-Tumbas, 2009*).

Weather preliminary known which poluutant will be analyzed, there are target and non-target analysis. Screening can be target if analyzed that are analyzed completely defined. If pollutants are not defined and only qualitative analysis is performed it is non-target analysis. Their identification may be performed using special softwares for comparing with commercial bases of spectra (technique of identification). If full scan analysis is applied it is posibel to identify al large number of various compounds, which can narrow scope of target analysis, that should be done for the sake of correct concentrations of contaminants. That is one of the biggest advantage of screening analysis relative to single ion monitoring (SIM) or tandem-mass-spectrometry (MS/MS). On the other hand, the biggest disadvantage of this type of analysis is reduced sensitivity. This disadvantage may be mitigated by using newer generation of CG analyser.

DISSCUSION

In one of the studys (*Hernandez et al., 2014*) samples of surface water were taken from Mediterranean part of Spain. Organic pollutatnts that dominated were pesticides and their metabolites, UV filters, musks and pharmaceutics. Among pesticides that occupy 69% dominate fungicydes and herbycides (29%), herbicides TPS (21%) and isecticides (20%). Concentrations of pesticides are between 0.02 and 0.1 µg/l. Identified compounds also were: dichlorodiphenyltrichloroethane (DDT) and it's metabolites, dichlorodiphenyldichloroethylene (DDE) i dichlorodiphenyldichloroethane (DDD) concentrations 0,02 µg/l. Significant pollutatnts that were identyfied were also polyciclic aromatic hidrocarbons (PAHs) and polychlorated bipheniles (PCBs), concentrations between 0,02 and 0,1µg/l.

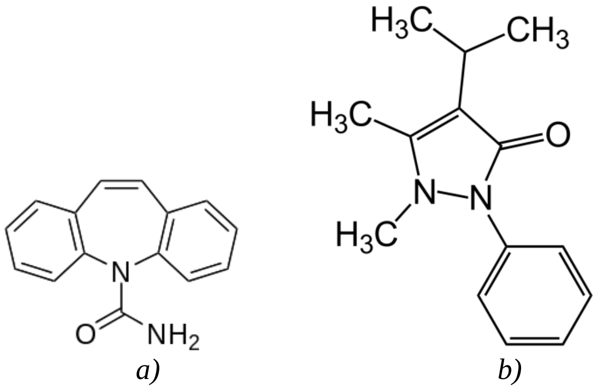
Also, during analysis of micropolutants in surface water of Valencia area (Spain) (*Pitarch et al., 2007*) the majority of analytes detected were pesticides, as a consequence of the wide use of these compounds in this area,where citric crops are predominant. The herbicides simazineand terbutylazine were detected in all the seven samples, atconcentration levels in the range 25–8100 ng/l. The other triazine herbicide monitored, atrazine, was only detected in surface and urban waste water at 40–400 ng/l. Among the rest of compounds investigated, lindane, some PAHs (acenaphthylene, phenanthrene and pyrene), alachlor and chlorfenvinphos were occasionally detected, but always at concentrations below 25 ng /l. The same situation as atrazine was observed for the insecticide chlorpyrifos, although it was found at concentrations lower than 100 ng/l (between 25 and 82 ng/l). 4-t-Octylphenol was detected in five samples, but it was quantified in only one surface water (30 ng/l).



a) *b)* *c)*

Picture 1. Structures of some of identifyed compounds: a) Phenantrene, b) Dichlorodiphenyltrichloroethane (DDT), c) Benzo(a)pyrene

During analysis of low-molecular weight pollutants in area of Lipe River (Germany) (*Dsikowitzky et al., 2004*) compounds that belong to various groups were identifyed. Some of most significant groups were PAHs (phenantrene, naphtalene, fluorene), phenoles, chlorinated organic compounds, physiologicly active compounds, compounds that contain phosphorus etc.



a) *b)*

Picture 2. Structuresof some compounds identyfied in German : a) Carbamazepine, b) Propyphenazone

Physiologicly active compounds, as pharmaceutics, in urban surface water arive very easily through emition of domestic wastewater. Most samples from the course of the Lippe River contained the pharmaceutics carbamazepine, propyphenazone and clofibric acid. Carbamazepine and propyphenazone are drugs that has beeen identified in German water (*Andreozzi et al.,2003; Tixier et al., 2003, Heberer et al., 1998, 2002*).

Most of the identified compounds could be attributed to anthropogenic input. Amongst them are components of household products (e.g. plasticizers, flame retardants, synthetic fragrances), by-products of industrial synthesis and pharmaceutical drugs. Some of the organic compounds which were frequently detected in Lippe River water were also present in the effluent of a municipal sewage treatment plant and in Lippe River tributaries. These compounds are obviously typical sewage derived contaminants which suggests their use as markers. Further quantitative analyses are underway to examine the persistence of these compounds, which is the condition for their general use as anthropogenic markers (*Dsikowitzky et al., 2004*).

In another research samples were taken from canal network in Spain. Sampling was carried out at four sites on a canal network (Prise au Rhone, Pichegu, Mas Soulet and Mejanelle), for irrigation and drinking water treatment . The canals are fed by the Rhone river. In these canals were detected very large number of organic compounds (139). Alcohols, phenols, aldehyde, ketones, acids, esters, ethers , aromatic hydrocarbons and derivatives, anilines and pesticides are predominant. A methodological approach was used for water quality measurement and pointed out firstly the importance of each chemical family with the preponderance of natural compounds (aldehydes and ketones, acids, esters and ethers) and secondly the low total concentration of anthropogenic families (total concentration < 400 rig/l). The proposed pollution indices are therefore water quality measurement tools to detect occasional water pollution (*Deroux et al., 1997*).

Also in Spain, in province of Jaén, were taken 19 samples of surface water. Analysis of selected priority and emerging contaminants was done. Technics used for analysis were GC-MS and LC-MS. Some of most significant organic polutants were analyzed: pesticides, PAHs, drogs of abuse, and pharmaceuticals. The concentrations of priority compounds were below the limits established by the Directive 2013/39/EU in mostly all cases, except for one sample that exceeded the maximum allowable concentration of hexachlorobenzene in Guadalquivir River and for the concentration of chlorpyrifos in one sample of Guadalimar River. Therefore, it can be conclude that the quality of the surface waters is good, on the basis of the concentration levels of studied priority compounds, because only two samples presented concentration slightly over the limits established by the European WFD for hexachlorobenzene and chlorpyrifos-ethyl in the Guadalquivir and Guadalimar Rivers, respectively. Characteristic for this area is pesticide terbuthylazine, so it was found in all samples. Drogs and pharmaceuticals are found in nanogram levels, which can not cause the damage in the environmantal (*Robles-Molina et al., 2014*).

Samples taken in Netherlands at the river Rhine, river Meuse and the river Scheldt. In one study, some 150 compounds were found in a series of surface water samples covering the major river systems of the Netherlands. Their concentrations were in the low-ng/l to low-mg/l range. Pesticides, fragrances, PAHs, plasticizers, phenols and anilines were among theclasses of compounds most frequently detected (Van Stee et al., 2002).

In central Europe one of importane rivers is Danube river. Screening of organic polutants were done in 2012 (*Paunović, 2013*.). Analysis was done by gas chromatography with mass detector (GC/MS). Samples were taken in March and May in Novi Sad, after inlet of comunal wastewater (GC – 2). There were identified 20 organic pollutants in this water taken in March and 19 in sample taken in May. Largest groups are organic acids and esters. Beside that, groups of PAHs, phenoles and phtalates were also identified.

CONCLUSION

Organic pollution is present in all surface water. Some of pollutants can not be found in natural water, and their presence proves strong antropogenic impact. In urban areas it is expected to detect a lot of organic pollutants because human impact is very strong since there are inlets of wastewater (industrial and domestic). Concentrations of organic polutants in surface water is usally in ng/l and µg/l. Characteristic pollutants found in all areas are PAHs and pesticides. PAHs are formed during combustion of organic matter as fosil fuels. In urban areas sources of PAHs are traffic and incdustry, as well as households during heating season. In surface water these pollutants arive by flushing from surfaces. Pesticides are characteristic for agricultural areas, but they ar, as well as PAHs, very persistant and can be found far away from the source, so they arive to urban areas. Some of other groups that are identfified mostly are some pharmaceuticals and domestic chemicals, that are expected for urban areas. It is very important to control sources of these pollutants as much as it is possible. It is also important to do monitoring of these compounds, because they have very strong impact on environmental and aquatic ecosistems.

REFERENCES

Andreozzi, R., Raffaele, M., Paxe´us, N., (2003), Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment, *Chemosphere* 50, Pages: 1319–1330

Deroux J.M., Gonzalez C., Le Cloirec P., Roumagnac A., (1997), Long-term extractable compounds screening in surface water to prevent accidental organic pollution, *The Science of the Total Environment*, 203 Pages: 261-274

Dsikowitzky, L., Schwarzbauer, J., Kronimus A., Littke, R. (2004) The anthropogenic contribution to the organic load of the Lippe River (Germany). Part I: qualitative characterisation of low-molecular weight organic compounds, *Chemosphere* 57, Pages 1275–1288

Đurić D. B, Petrović Lj. J., (1996)., *Environmental polution and humen health – ecotoxicology*, Velarta, Beograd

Heberer, T., Schmidt-Ba¨umler, K., Stan, H.-J., (1998), Occurrence and distribution of organic contaminants in the aquatic system in Berlin. Part 1: Drug residues and other polar contaminants in Berlin surface and ground water, *Acta Hydrochim. Hydrobiol.* 26, Pages: 272–278

Heberer, Th., Reddersen, K., Mechlinski, (2002) A., From municipal sewage to drinking water: fate and removal of pharmaceutical residues in the aquatic environment in urban areas, *Water Sci. Technol.* 46, Pages: 81–88

Hernandez F., Ibanez M., Portoles T., Cervera M.I., Sancho J.V., Lopez F.J., (2014), Advancing towards universal screening for organic pollutants in waters, *Journal of Hazardous Materials*

Ivančev-Tumbas I., 2002., *Natural organic matters in water*, editors Ivančev-Tumbas I. i Dalmacija B., Faculty of Science, Novi Sad, Pages: 26-31

Paunović, O. (2013) GC-MS screening of organic pollutants and characterisation of NOM present in Danube, Conference paper, *III International conference ecology of urban areas 2013*

Pitarch E., Medina C., Portoles T., Lopez F.J., Hernandez F., (2007), Determination of priority organic micro-pollutants in water by gas chromatography coupled to triple quadrupole mass spectrometry, *Analytica Chimica Acta* 583, Pages: 246–258

Robles-Molina, J., Gilbert-López B., García-Reyes, J. F., Molina-Díaz, A., (2014), Monitoring of selected priority and emerging contaminants in the Guadalquivir River and other related surface waters in the province of Jaén, South East Spain, Science of the *Total Environment* 479–480, Pages: 247–257

Tixier, C., Singer, H.P., Oellers, S., Mu¨ller, S.R., (2003), Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters, *Environ. Sci. Technol.* 37, Pages: 1061–1068

Van Stee, L., Leonards, P., Van Loon, W., Hendriks, J., Maas, J., Struijs, J., Brinkman, U., (2002), Use of semi-permeable membrane devices and solid-phase extraction for the wide-range screening of microcontaminants in surface water by GC-AED/MS *Water Research* 36, Pages: 4455–4470

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MEASUREMENTS ESTIMATION OR CHARACTERISTICS CHANGE OF MATERIALS, OBJECTS AND PROCESSES AND ENVIRONMENT DIAGNOSTICS

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ABSTRACT

Contemporary measuring methods, estimating laser influence to inorganic and organic materials, including biosphere as well as electronic waste are subject of the numerous areas. Diagnostic methods, using some of the implemented laser techniques are in constant development. Regardless of the extend of the problems involved, several directions of development for measurement and interactions impose, showing a priori defined problems in interpreting results. Tremendous number of laser techniques based on scattering and diffraction are solved in parallel with other techniques and spectroscopy. Concerning biomaterials and bio-objects, a lot of unknown parameters occurs. Those values should objectively characterize object, environment and process. Wider approach is observation in general of the electromagnetic radiation in different parts of the spectrum and its influence on the same chosen objects (materials). Part of this paper deals with theoretical problems based on reference data and processing of this data, from which conclusions are drawn. Second part of this paper refer to experimental descriptions of optical characteristics of materials (plants, materials used during plant growth and creation of artificial conditions mimicking necessary climate, etc.) in order to use natural and artificial sources with the best possible efficiency. For the use of lasers in bio-stimulation and bio-modulation it is necessary to have coefficients of reflections, absorption or intermediate data correlating with these constants. Concerning methods, contemporary spectroscopy devices will be discussed and (compared) with anticipating others that are useful but not easily available. The FTIR, measurement of coefficient of reflection, angular distribution, ellipsometry, will be included in discussion.

Key words: *laser scattering, plants, optical characteristics, lidar, green house*

INTRODUCTION

Optical performances of leaves and optical plant constants of interest

Optical properties of leaves include several constants. These are: absorption coefficient k, reflection coefficient, i.e. infinite reflectance R_{∞}, scattering coefficients. In the references they are tabulated for some characteristics wavelength given in Table 1. One of the principal differences between optical constants of leaves and some other materials is that their values depend on the side of measurement. Investigations of transmittance/reflectance curves were numerous. One of them includes the influence of sun versus growing period. The others are at the moment involving lasers in: recognition of particular types, influence of various wavelengths in bio-stimulation purposes, and the new issues are inclusion of nonlinear phenomena. Some results from the references include: transmittance and reflectance dependences vs. wavelengths, their investigation in the natural environment previously of interest for solar radiation influence to plants. Solar radiation depends on geographic location where plants grow in either natural or laboratory or artificial environments (plastic covering), so optical constants are also of importance. Including biostimulation effects optical characteristics grow in importance for point of view for specific plants or seed spectral sensitivity [Wooley 1971, Srećković 2014, Jevtić 2014,Yoon 1993, 1998]. In general spectral absorptions and reflection from molecular to tissue levels have to be obtained. The most investigated examples were taken by spectrophotometric measurements for wavelengths in 0.45 (0.34) -2.7 μm for front and rear side of leaves and for stacked leaves of many plant species. Many data should be acquired depending on the geographic location (i.e. from the country). Next step is comparison of leaf curves through exact mathematical criteria with correlation function of higher order to leaves extracts, potato tuber tissue, glass beads in water, frozen leaves and fruits. Sometimes leaves are infiltrated with liquids of different refractive indices. In Table 2. some examples of the most characteristic maximum and minimum values for chosen plant species are presented [Allen 1970,Gausman,1973,1952]

Table 1: Some characteristic leaves performances

Wavelength [nm]	550	650	850	1450	1650	1950	2200
description of the color	green reflectance peak	chlorophyll absorption	infrared reflectance plateau	water absorption band	reflectance peak for water absorption band at 1450 nm	water absorption band	reflectance peak for water absorption band at 1950 nm

Table 2: Max and minimal value for plant species

λ [nm]	350	650	850	1450	1650	1950	2200
max	1.007 oleander	1.051 Orange	1.476 Oleander	0.956 Orange	1.129 Oleander	0.689 Crinum	0.834 Bean
min	0.407 onion	0.449 Onion	0.716 Corn	0.342 Begonia	0.446 Lettuce	0.313 Pigweed	0.378 Onion
mean ~	0.705watermelone	0.770 hyacinth	1.166 Wheat	0.655 Avocado	0.811 Ocra	0.498 Tomato	0.610 Sorghum

Modeling leaf optical properties

Depending on the geographic location, internal leaf structures have to be included. They are determined by ecological convergences in similar ecosystems. As primary photosynthesizing organs, leaves significantly affect planetary bio-geochemical cycles. The mechanisms in leaf life exactly are not completely understood in spite that the problems were studied for 150 years (Jackemoud 2009). Lasers give new possibilities due to coherence radiation and narrow lines. It could be of interest for more exact modelling as well as for plant recognition. The optical observation of plant leaves should be started with absorbance and observation how the state influence to it (frash, dry, powder, etc.). Plate models, compact spherical particle model, and flux, radiative transfer equation, stochastic approach, raytracing model etc. The models are presented by adequate convergence series (Ostojić, 2014.) of reflection and transmission part in the cases of one plate or multiple case. Some of illustration of models are presented in Figure 1 are also very complex (monocotiledon, with model multiple reflections), where R and T should be summed by adequate series. Dicotiledon leaf is obtained by multiple reflections Fig. 1 and the summing is presented by two fractions of reflected and transmitted.

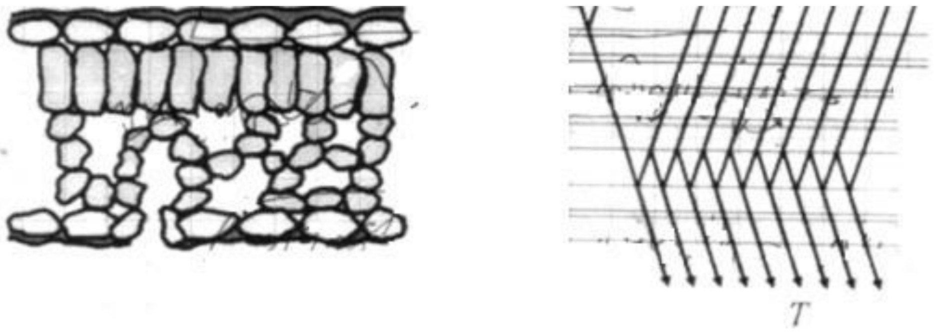


*Figure 1 Dicotyledon leaf and multiple reflections presentations by a set of N=m+n plates (*Jackemoud 2009*).*

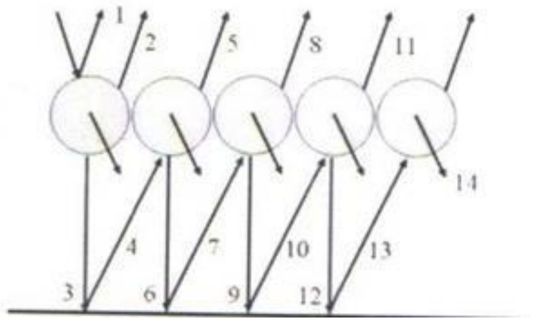


Figure 2. Scattering of light by a leaf.

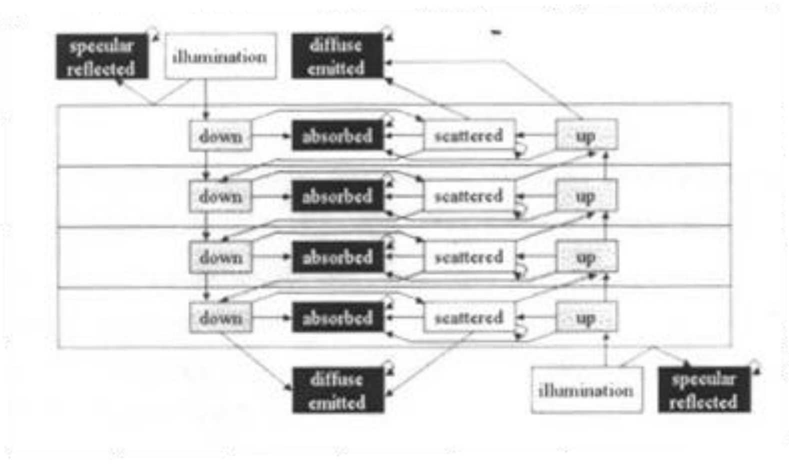


*Figure 3. Typical dicotyledon leaf in SLOP presentations with different photon states. (*Jackemoud *2009)*

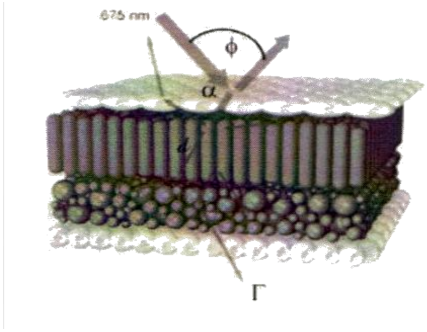


*Figure 4. Virtual bifacial dicotyledon leaf exposed to 675nm ( ). 300x300x170mm. (*Jackemoud *2009)*

Ray tracing diagram for light refraction by leaf epidermal cells is also performed (Jackemoud 2009) .Coupled differential equations are included in theory, and different program packages for adequate presentation. Radiative characteristics of plant leaves are studied using concepts. Based on new models spectra in 400-800nm are simulated (calculated) in various relative concentrations of light absorbing pig-ments (chlorophyll a, b, and carotenes) and various leaf thicknesses (Monte Carlo Method). (Krekov G.M.) Different measuring methods can be used for measurement of leaf characteristics; some of them are invented for paper, chemical, food industries. Plant leaf motion estimation using a 5D affine optical flow model (Schuchert 2010) is of interest for high accuracy motion analysis of plant leaf (plant physio-logy), estimation of orientation, temporal and spatial growth maps. Optical parameters of 30 species show the great difference for wavelength,but inclusion FTIR, measurement of coefficient of reflection, angular distribution, ellipsometry, should be included in comparisons.

Laser radar point of view of optical characteristics

Modern techniques of remote detections based on electromagnetic and acoustics beams, or detections based on own radiations of plants and other objects deserves particular analyses of the applicability and precision of chosen physical process [Srećković 2010, Srećković 2014. Sensing by mm waves, radar observations, and IR multisensors use, have to be compared also, Table 3. In Fig.5 some of existing algorithms will be presented. Millimeter wave and IR multisensory design and signal detection theories.

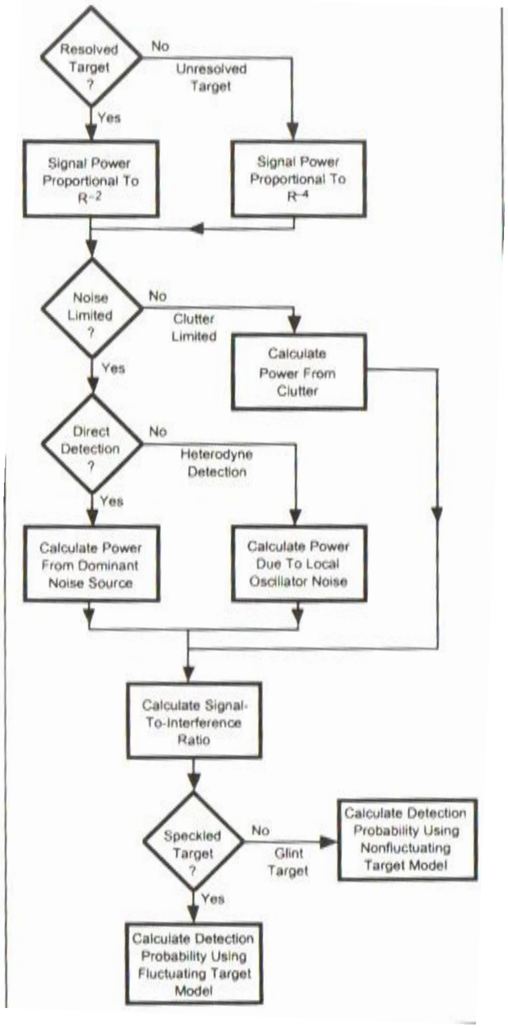


Figure 5. Detection probability calculation process for laser radar

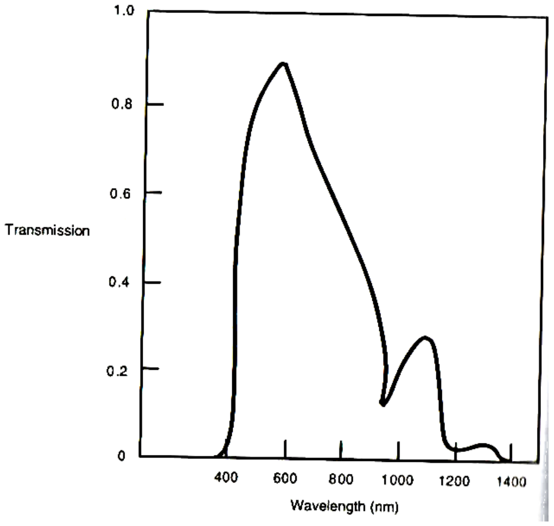


Figure 6. Transmission of human eye.

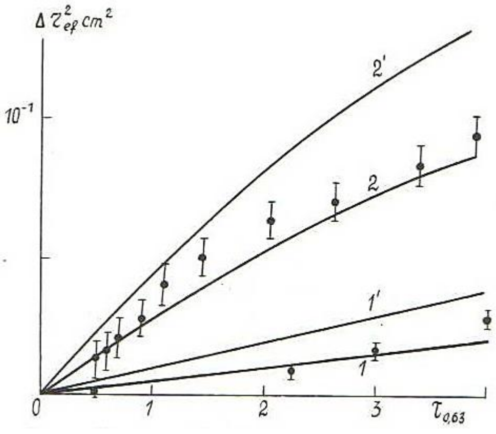


Figure 7. Influence of aerosol to CO_2 laser beam radius.

Table 3: Comparison of Milimeter-wave and IR signal detections (Klein 1997) processing

Millimeter-Wave	Infrared
Heterodyne or homodyne sensors (use a mixer)	Direct detection , passive sensors and GaAs laser radar Heterodyne, homodyne detection as with CO2 laser radar
Targets are fluctuating or unfluctuating ones	Targets: fluctuating to laser radars and passive sensors, unfluctuation to laser radar when glint targets are observed and to passive sensors
Noise statistics Gaussian Electronic noise is dominant interference for air-to air applications Ground clutter statistics vary from Rayleigh to log - normal. It is dominant when searching ground -based targets Detection probability for passive and active sensors is calculated (derived) from the same theory.	Dominant noise source is a function of detection process (direct, heterodyne and photon limited) Ground clutter statistics has to evaluated for operating scenario (factors: wavelength and angle) Detection probability for passive sensors ids function of noise statistics (white or quantum). For active ones correspond to MMW radar theory
processing is incoherent (as with radiometers, radars) or coherent with other radars	Processing is incoherent with passive sensors and GaAs laser radar Coherent with CO_2 laser radar

Target designator, range finder, target detection and object classification in civil and military applications of laser radar are simplified by semiconductor laser implementation. The reasons are: small sizes, ragged-ness and output characteristics. Wavelength of 1.4 μm are preferable for lidar (laser radar) devices to avoid accidents linked to human eyes,Fig. 6. Therefore, the irasers in solid state are developed.

Romanian wine study was performed using IR spectroscopy in comparisons with H1-HNR.[Todasca 2007] As we mentioned before, the same methods as in monitoring of environment (fire) are based on spectroscopy techniques including lasers which are used in food processing industry, waste treatments, Tab.4. The aerosols affect the CO_2 laser beams, Fig. *7*. The same hold for volcanic eruptions and dust as well as aerosol monitoring,coral relijef ,fish, clouds, atmospheric turbulence ,etc. Figures 8, 9,[Hedley ,2002, Jevtić, 2014 a,b,Mellin, 2009,Mazin,1983,Palagin,1986]

Table 4: E-Waste components, Process, Potential Hazard, Possible Techniques of Detection

E waste	**Process used**	**Potential Environmental Hazard**	**Lidar detections based on scattering, fluorescence and reflectance**
Cathode ray tubes (TV, monitors, ATM, video cameras	Breaking and removal of yoke, then dumping	Pb, Ba and other heavy metals leaching in the ground water and re lease of toxic phosphor	+
Printed circuit board (image behind table, thin plate with chips and other electronic components	desoldering and removal of computer chips, open burning, acid baths to re-move metals after chips removing	Air emission , discharge in rivers of glass dust, tin, Pb, Br. Di, Be,Hg	+
Chips and other Au plated components. Plastic	Chemical stripping using nitric and hydrochloric acid and burning of chips	HC, heavy metals, brominated substances discharged in the rivers acidifying fish and flora, Sn and Pb contamination of surface and ground-water, air emissions of BrDi, heavy metals and HC	+
Plastic from printers,	Shredding and low	Emissions of BrDi, heavy	+

keyboards, monitors,	temp. melting to be reused	metals, HC	
Computer wires	open burning and stripping to remove Cu	HD ashes in air, water, soil	+

BrDi brominated dioxins. Hydrocarbons HD

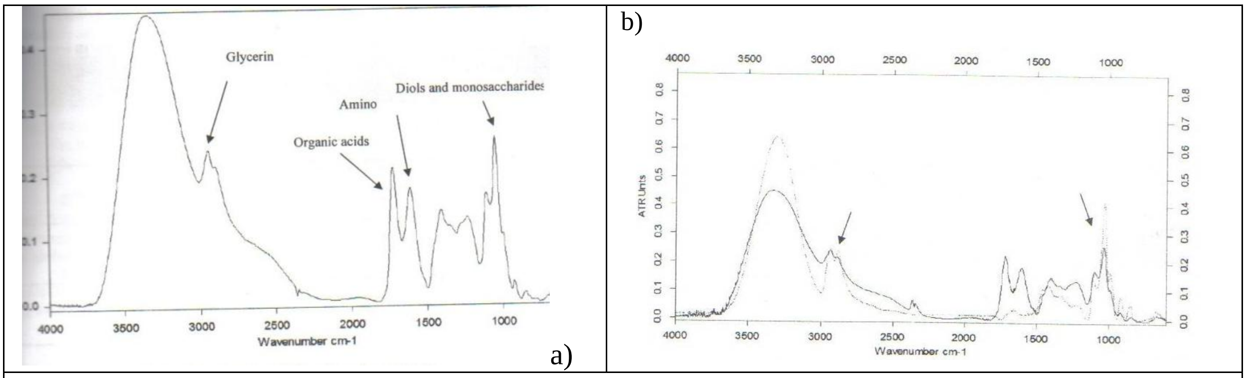


Figure 8. a). IR Spectrum of a red CS variety wine evaporate and b) IR spectrum of a red wine evaporate cw line , overlapped with glycerin (dot line).

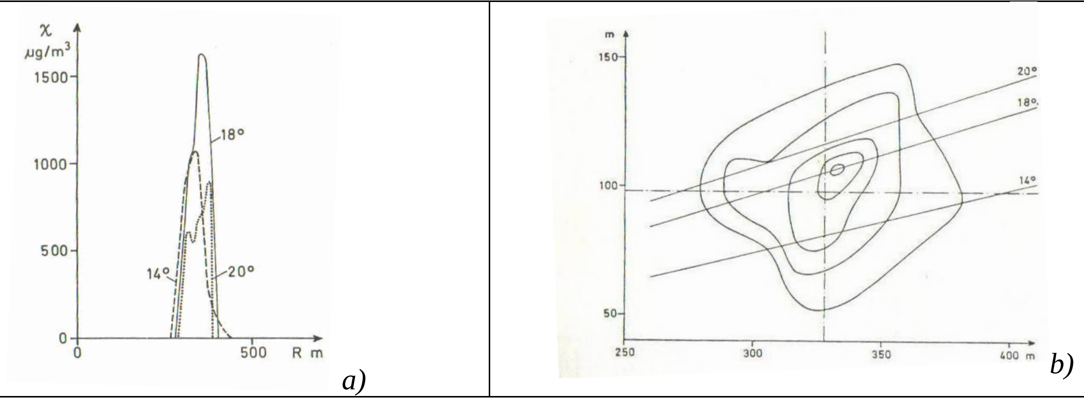
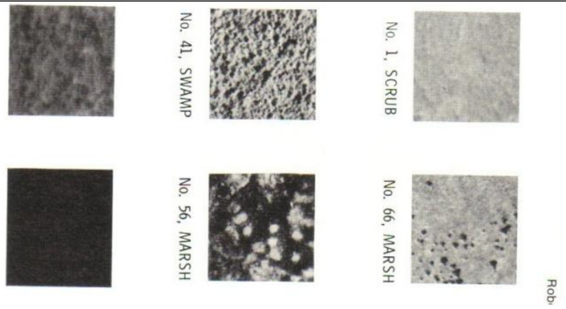


Figure 9. a) Concentrations profile versus height and b) the cross sections of concentrations profile. (Waidlich

Pattern recognition. Statistical Image Texture Analysis

It includes analysis of: Autocorrelation function and texture relation, Orthogonal transformation, Gray tone coccurance, mathematical morphology, gradient analysis, relative extreme density, shape from texture, Markov random fields (discrete), and Random mosaic models, texture segmentation.

Figure 10.a,b negative images of the influence of same kind of lava can have a different texture coarses ⁅Young1986⁆

	
Figure 11.a Texture influence to land use categories in panchromatic aerial photography	*Figure 11.b Size and spacing of vegetation case texture to change from fine to coarses [Young1986]*

EXPERIMENTS (Methods and Materials)

The absorption spectrophotometer Hach Lange (Fig. 12) model 3900 is used in the range of 320-1100*nm*, for determining spectral coefficient of transmittance. The positioning of wavelength was 1nm with repea-tability 0.1*nm* by resolutions of 1*nm*. The scanning rate was 8 nm/s with 1 nm steps and spectral width 5 nm. Photometric range of transmittance/absorption spectrophotometer was 0.1T do 100%T -the transpare-ncy i.e. 0-3 Abs for absorbance value. Photometric linearity of the instrument was lower than 0.5 % (for 100%T.). Stray light radiations was lower than 0.10 %T at 340 nm (a and b).

System calibrations were performed, initial device alignments for various wavelengths as well as all needed measuring procedures. Part of the procedures are presented in Table 5 and referent environmental conditions in Table 6.

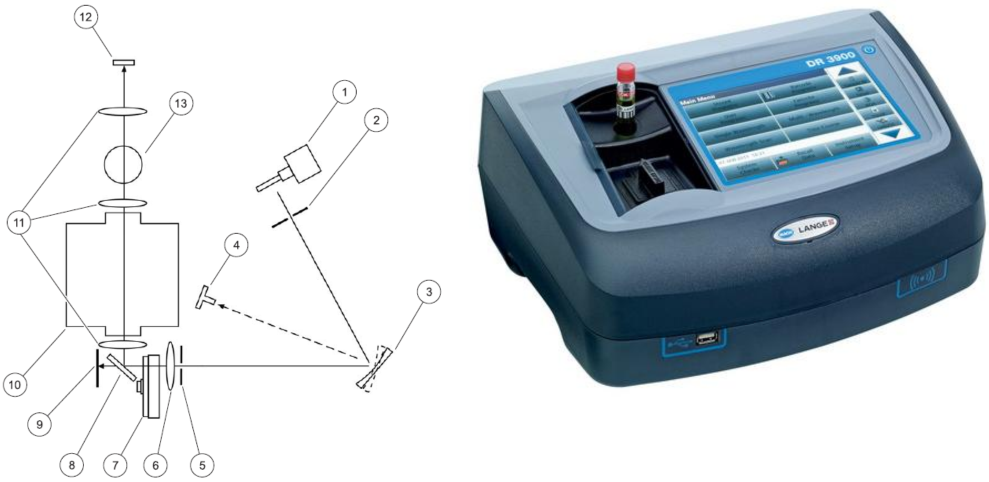


Figure 12. Absorption spectrophotometer: 1- Source of optical radiation (halogen bulb);2,- Input ,output slits; 3-Diffraction grating, 4-Angular indicator, 6, 11- lenses, 7-holder with filters (filter wheel), 8-Beam splitter mirror, 9-Referent detector, 10- Cell holder (square basis), 12 ,13- Holders of cylindrical cell.

Table 5: Measuring equipment (a part)

Description of standard	No of certificate	Identification designation
Reference etalon of Holmium oxide filter as wavelength standard Thermo Fisher Scientific	393-2/2-01-2010/1	06
Reference etalon filter for absorption coefficients (filter) Thermo Fisher Scientific	393-2/2-01-2009/1	A858-1

5 standards have to be included with similar details

Table 6: Environmental conditions

Temperature	22.1 – 22.2 °C	temperature of filters 22.1 – 22.2 °C. Filters are positioned at working room temperature (without temperature corrections)
Humidity %RH	31.5 – 31.9	

Measuring method. Method is based on relative measurements of spectral coefficients of transmission for various types of transparent plastics in specific measuring geometry. The calibration UV/VIS absorption spectrophotometer is perfomed by direct methods of the transmissiion of the value of spectral absorption coefficients. The wavelength was calibrated also in same method. The procedure of calibration of absorption spectrophotometetrs in UV/VIS in Laboratory for calibration and validation, Analysis d.o.o *Nr. proc. PR.17025.03*). It is supported directly to standard methods **-** *R 135:2004, Spectrophotometers for medical laboratories* and **NIST -** *Special Publication 2260-166, 1994.*The calibration (standard refe-rent material) of spectral coefficients of transmitance and wavelength, which are used by calibration of absorption spectrophotometers, have direct links to National metrological Institute of Republic Serbian (Direction for measurements and precious metals) performed through the Certifications of calibration Nr. 393-2/2-01-2009/1, 393-2/2-01-2010/1 and Nr. 393-2/2-01-5024/1.

RESULTS OF PERFORMED CALIBRATION AND MEASUREMENT

The result of calibration and measurement of reflectances (transmitances are presented in table 7 and 8 and figs. 13, 14, 15 and 16 including detector sensitivity Fig. 14.

Table 7: Results of calibration by determinations of spectral coefficients of transmittance for various wavelengths

Values of transmittance standards for 405nm wavelength	Obtained values on measuring instrument for coefficients of transmittance	Absolute deviation	Relative deviation %	Total uncertainty of measuring %
0.71149	0.7078	0.00369	0.52	1.54%
0.28215	0.2776	0.00455	1.61	0.57%
0.02184	0.0207	0.00114	5.22	0.11%
0.41423	0.4102	0.00403	0.97	0.84%
0.12285	0.1200	0.00285	2.32	0.24%

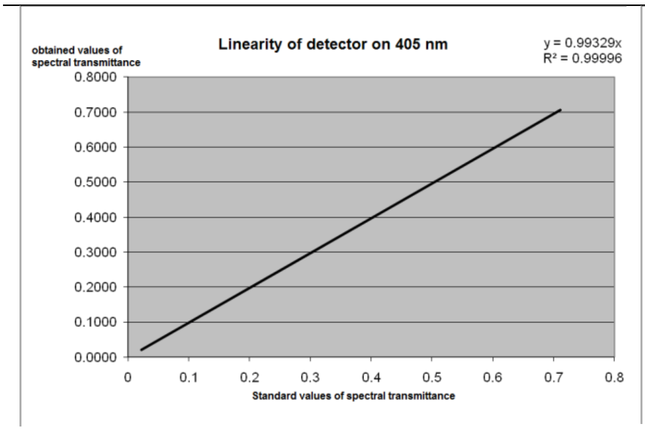


Figure 13a.

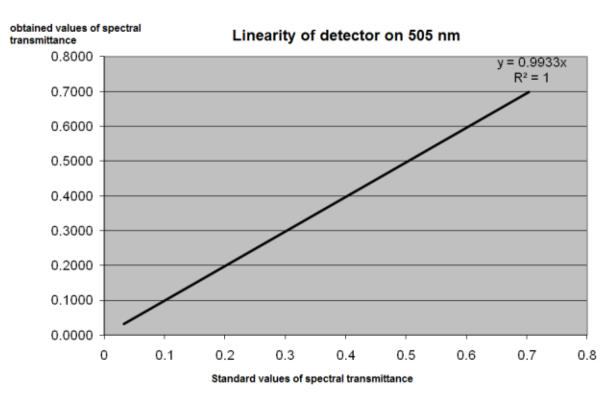


Figure 13b.

Table 8: Determine the accuracy and measurement uncertainty of the monochromator

Indication reference for wavelength	Indication of measuring instrument for wavelength	Absolute deviation	Total uncertainty of measuring
418.80 nm	418 nm	0.80	0.30
445.60 nm	446 nm	-0.40	0.30
536.30 nm	537 nm	-0.70	0.30
636.30 nm	637 nm	-0.70	0.30

The reported expanded measurement uncertainty is based on a standard uncertainty multiplied by a coverage factor k = 2, providing a level of confidence of approximately 95%.

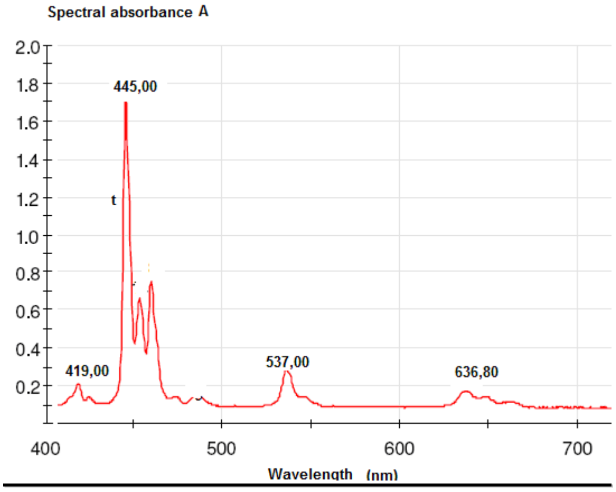


Figure 14.

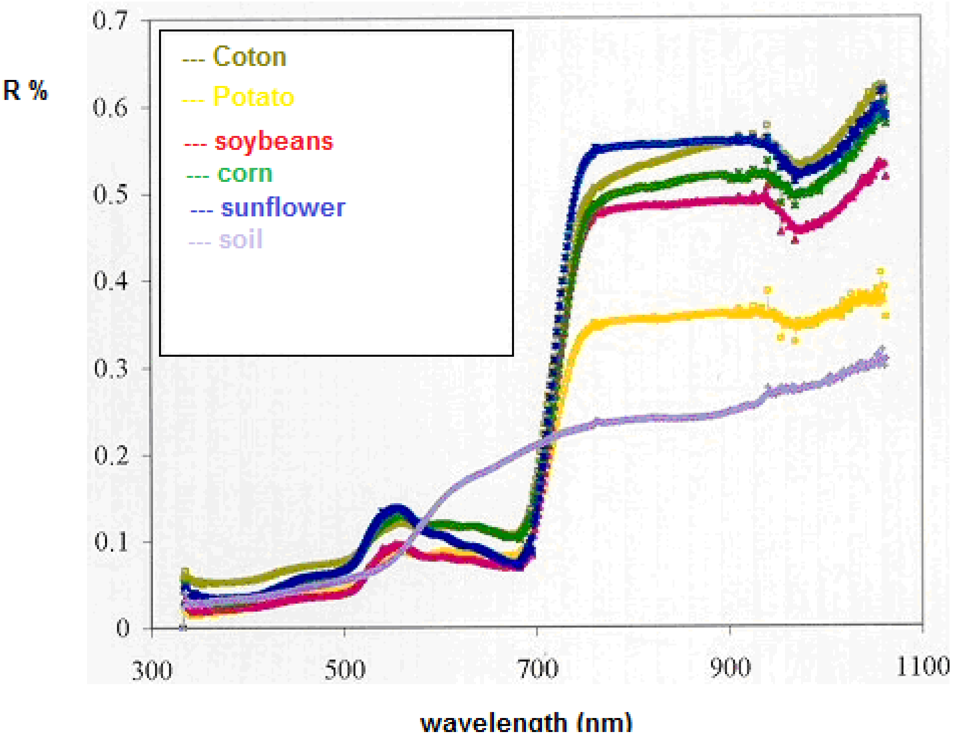


Figure 15. Spectral characteristics diffuse spectral reflectance (in %) for chosen material: cotton, soyabeans, corn, soil

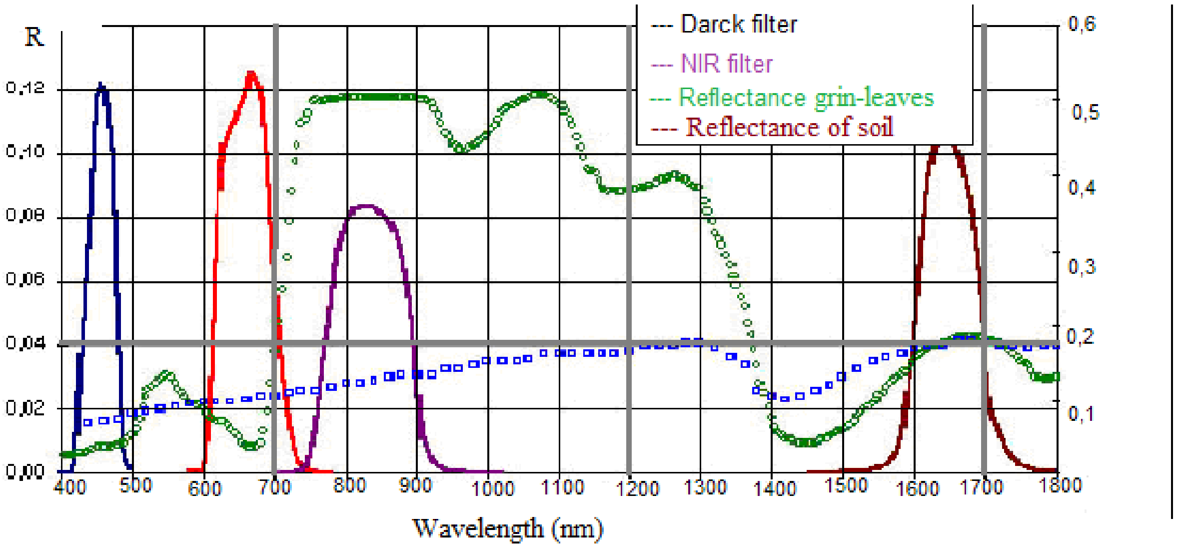


Figure 16. Spectral characteristics different filters which used in different measurement technics.

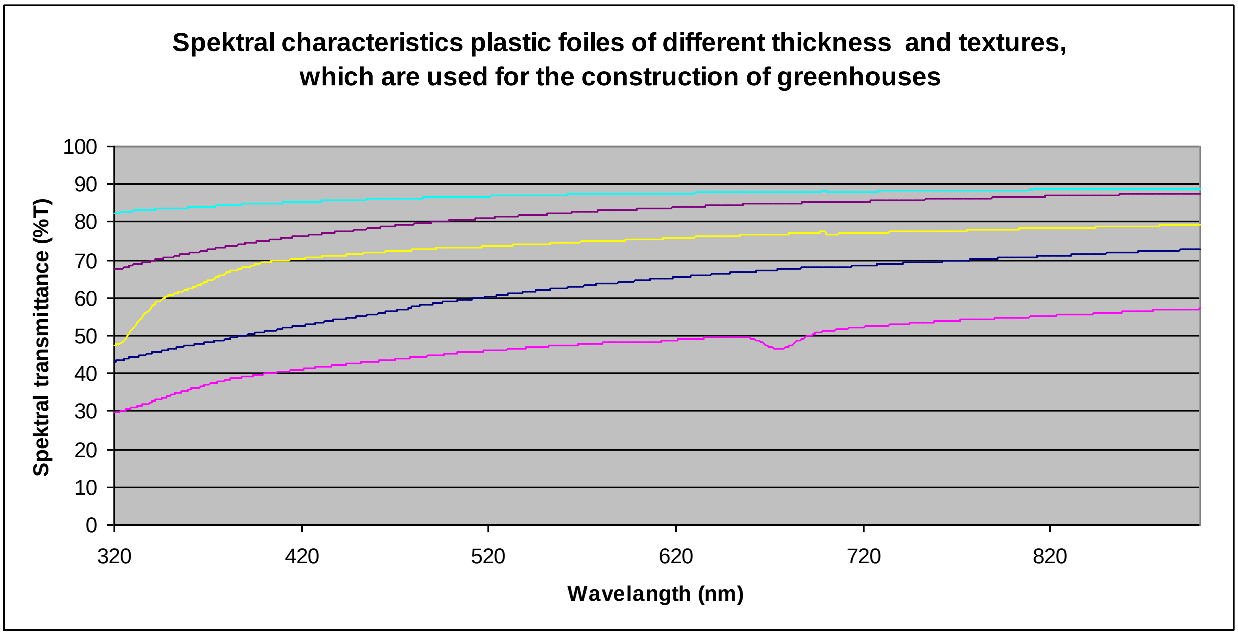


Figure 17. Spectral characteristics of plastic follies and textures which are in use versus wavelength (nm)1-5 various materials for greenhouses

CONCLUSION

Despite of large investigations, there is many unsolved tasks in the area of possibilities of techniques, understanding of processes in respect to plant growing, lidar detection, correlations between various growth periods and optical characteristics. The same hold for modeling processes. The multidisciplinary approach should be performed, and theories from various scientific disciplines. In references are found differences between the values even for calibration standards concerning measurements performed with spontaneous sources and laser ones. (One of the reasons is the line widths). On the other hand in biostimulations experiments there is not enough details for repetition and some experiments. The techniques for pattern recognition and remore controls in civil and military application need to be expanded with particular date based on optical characteristics plant and other monitor object. Considering influence green house and biostimulation by laser both optical characteristics of seed, leaves, fruits should be known. For farther analysis of measured object powder, different granularity etc. Despite decades of research, optical properties of leaves deserves further investigations. Next optical models should include more of leaves anatomy and adaptations to different environmental conditions. Impro-vement in optical characterization (complex refractive index of more biochemical compounds should be expanded to the range of detection limits. It is not possible to identify and quantify specific leaf pigments separately (chlorophyll a,b) anthocyanin, oxygen-free carotenes and xantophiles. It would be significant-ly improve possibility of the biological control of photosynthesis, and chlorophyll fluorescence.

REFERENCES

Allen, W. A., Gausman, H. W., Richardson, A. J., & Wiegand, C. L., (1970) Mean Optical effective constants of thirteen kinds of plant leaves, *Appl.Opt.* , 9 (iss.11) .2573-7,

Gausman, H. W., Allen, W. A., Cardenas R., Richardson A.J., (1970)Relation of light reflectance to histological and physical evaluation of cotton leaf maturity, *Appl. Opt.,* 9(3) 545-52,

Gausman, H.W, Ramser, J.H., Dungan, G.H. Earle, F.R. 1952.),MacMasters, M.M Hall. & H.H. Baird, P.D Drying of Corn Grain, Some Effects of Artificial Drying of Corn Grain, Plant *Phys.* 27, (4), 794-802.

Gausman, H. W. & Allen,W.A., (1973) Optical Parameters of Leaves of 30 Plant Species, *Plant Physl*. 52(1), 57-62.

Hedley, J. D., & Mumby, P. J., (2002.), Biological and remote sensing perspectives of pigmentation in coral reef organisms, *Adv. Mar. Biol.*, 43, 277-317.

Jacquemoud, S. and Ustin, S. L, Modeling Leaf Optical Properties, www.photobiology.info/Jacq_Ustin.html, acc. 30.9.2014.

Jevtić S.D., Srećković M. Ž., Pelemiš S. S., Konstantinović Lj. M., Jovanić P.B., Petrović L. D., Dukić M. M , Laser influence to biosystems,Chemical Industry, doi broj DOI:10.2298/HEMIND140415059J doiSerbia

Jevtić, S., Srećković, M. and Radovanović R., Lidar Methods in early detection, monitoring and estimation fire processes,NBP, to be publ

Klein L.A. (1997), Millimeter wave and ir multisensor design and signal processing, Artech house, Norwood,

Krekov, G. M., Krekova, M. M., Lisenko, A. A., Sukhanov, Y. Ya (2009), Radiative Characteristics of Plant Leaf, *Atmos. and Ocean. Opt.*, 22 (2), 241-356.

Mazin, I. P., (1983) Oblaka stroenie i fizika obrazovaniya, *Gidrometeoizdat*, Leningrad.

Mellin C.,Yndrefouet, S., Kulbicki,M., Dalleau,M. &Vigiola,L.(2009) Remote sensing and fish-habitat relationship in coral reef exosystems:review and pathways for multi-scale hierarchical research,*Mar.Poll. Bull*.,58 (1)11-9)

Ostojić,S.,Srećković M, et al., (2014.) This conference

Palagin Yu, I., Fedotov S.V., Shalygin, A.S, (1986),Probability simulation of the atmosphere turbulence and the sea waves fields while investigating complex systems, *Radiot. elect.*, 31(4), 721-729.

Peynado, A., Gausman, H. W., Escobar, D. E., Rodriguez, R. R., & Garza, M. V., Evidence of Cell Membrane Injury Detected by Reflectance Measurements, *Cryobiology*,(19769).16, 63-68.

Schuchert, . T. (2010) Plant Leaf Motion Estimation Using a 5D Affine Optical Flow Model,V57, Schriften des Forschungszentrum ,Jülich, Disertation

Seksistov V.N., (1986)Primenenie metoda etalonnih uravnenii momentov issledovaniya statističeskih momentov polya korotkih voln, rasprostranyayuščihsya v srede sa gaussovskimi silnimi slučajnim neodnorodnostyami, *Radiot. i electron.* 31(4), T., 684-688

Srećković, M., Vasić, R., Dukić, M. Jevtić, S. Jovanić, P. (2014) *J.Agricult- Sci. and Technol.*, A end B,4,(3B

Todasca M-C,Chira N.,Deleanu C.,Rosca S.,(2007) Romanian wine study using IR spectroscopy in Comarison with ^{1}H-NMR,U.P.B.,*Sci.Bull.*, B,69(4)3-10

Young Y T., Fu K.S.,Eds. (1986)Eds. Handbook of Pattern Recognition and Image Processing, Orlando,Prent. Hall.

Yoon, G., Prahl S.A., Welch J.A., (1989) Accurace of the diffusion approximation and its similarity relations for laser irradiated biological media, *Appl. Opt.*, 28, (12), 2250-2255

Yoon, G.,Ghosh R.D.N, Straight R.C.,(1993) Coherent backscattering in biological media:measurement and estimation of optical properties, *Appl.Opt*. 32(4) ,580-585

Waidlich Ed.,(1982)Optoelektronik in der Technik, Berlin:Springer

Wooley, J. T (1971), Reflectance and Transmittance of Light by Leaves, *Plant Physiol*., 47, 656-662.

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PHYSICAL APPROXIMATIONS USED IN APPLIED ESTIMATIONS OF ENVIRONMENTAL PARAMETERS

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ABSTRACT

Using various techniques for estimation of material characteristics in microscopic and macroscopic levels, different issues arise during interpretation of obtained values. Some of these differences are connected to fundamental, basic reasons and some are caused by approximations, which are a part of measurement techniques, sometimes not obtained consistently and mathematically correct. Mentioned problems are related to optical methods in laboratory and remote control of the environment that are consequences of non-performed mathematical evaluations and checkups, that would confirm the justification of neglected higher order terms of the established series, substitution of the line shape, signal processing approximations, statistics of obtained measured results and good sampling during measurement. Estimation results of certain parameters depend on chosen process statistics, and on the specific dynamic, that is studied, also. There are problems of dimension estimation, distribution determination (Gaussian, logarithmic, Log-Normal, etc.)…done in laboratories or industrial processes, or remotely taken using developed theories from quadratic or asymmetrical matrices. In this paper we chose several of those approaches. Correct mathematical analysis is discussed and some cases how to search for other more correct approaches are shown. That means where and how to: cut the series, prove the series convergence, or perform necessary summations, etc.

Key words: *laser scattering, series convergence, particle shape, aspherycity, line shape, multi-layer .*

INTRODUCTION

From the Tyndal's and Rayleigh's days, theory and experiment are in continuously development. The analytic tasks are supported by numeric calculation which inspite of computer capacity sometimes last many days. The problem is by following high power laser propagation what is the project between several scientific groups of different countries. Some results in confirmation of the prediction for one measuring point last by months. Those processes appear by calculation of laser beam fragmentation. Some tasks of scattering theory are to explain the processes in biology, too.

The accuracy of the diffusion approximation should be compared with more accurate solutions for describing light interaction with biological tissues. It underestimates the light distribution in the surface region, and, for high albedos, it significantly underestimates the fluence rate. This difference is only a few percent for albedos of less than 0.5 due to the dominance of collimated light. As the anisotropy of scattering increases, deviations increase. Fluxes can be computed more accurately with the diffusion approximation than fluence rates. For anisotropic scattering, better results can be obtained by simple transforms of optical coefficients using the similarity relations. They improve flux calculations, but computed fluence rates have substantial errors for high albedo and the large index of refraction differences at the surface (Yoon G., 1989).

The modern problems in regard to laser scattering contain many unsolved tasks. Exact mathematical procedures by deriving exact needed formulas, could be proved. Some examples of tasks for further adjustments in experimental and theory are:

- The summing of the series with regular geometrical shape of scattering centre,
- The choice of distribution function of definite ensemble,
- Problems of the number of the terms in series,
- Multi-layers scattering center manipulation in theory,
- Multiple scattering calculation,
- Irregular shape of scattering centre,
- Boundary conditions,
- Problems with asphericity connection and particles shape asphericity.

Od interest are also, the inclusion of asphericity of particles, multi-layers, shell structures, etc (Barber, 1975, Block, 2010, Ilić, 2001). Some approximations in selected formula for modeling light (laser) scattering phenomena of ecology are the object of our paper.

Numerical-analytical analysis of coherent electromagnetic radiation scattering in optical portion

Many approaches exist to the electromagnetic scattering. The scattering appears in everyday life (and we do not often think of it). Applications include measuring techniques, which are implemented in various commercial and sophisticated uses, from medicine, food industry, to nanomaterial analysis. The interpretation is possible only through applied classic and quantum statistical methods (statistical mechanics and physics). Depending on the material chosen, adequate physics of solid state and gases is implemented. There are many theoretical predictions, which remain to be experimentally confirmed, perhaps due to poor experimental equipment or erroneous theoretical approach. All these should be observed critically and with special attention. Not all polarized components appeared in experiments, which were expected from the Raman scattering predictions.

One approach to the scattering is statistical one, while there are others as well: statistical physics with thermodynamics, quantum-mechanics or classical presentations of electrical field associated to the laser beam (i.e. spontaneous or coherent source). The relations connecting wavelengths of the incident beam, the size of scattering centre and the angle of scattering, are the principal physical properties, already determined by the theory. Other physical parameters considered include momentums, vector calculus, etc. Introducing matrices is more elegant way of expressing detailed descriptions of the center of scattering. Note that the starting point could be the Kirchoff general diffraction formula (Born 1973.). The development of the measuring devices was very fast after lasers became implemented as sources. After static scattering devices with natural light and gas-discharge lamp sources, lasers have given the possibility of dynamic light scattering, from the 60's of the 20th century. Cylindrical geometry has been used. In paper presented, we have analyzed tasks which are recognized in the application of various results (resulting from different theories) with the laser implementations which deserve further discussion. The discussion includes exact mathematical formulation and solutions, such as: matrix calculus, series summations, Fourier transforms, data processing, etc. In the consideration of coherent light scattering, the case described by following characteristics is used. In the generalized case, the scattering with the geometry, Figure 1, could be analyzed. The linear polarized light and cylindrical geometry are selected.

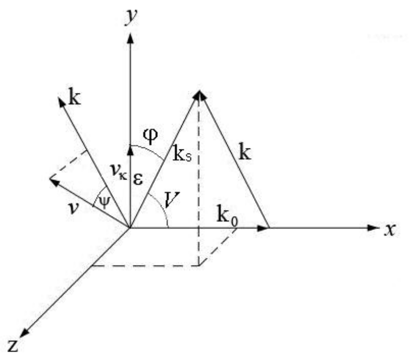


Figure 1. Scattering geometry in generalized approach.

Mechanism of problem interpretation

The starting expression is the identity electromagnetic scattering on homogenous cylindrical shape for incident radiation normal to cylinder's axis (Ostojić, 2000., 2002., Bohren, 1998.)

$$I = \frac{\lambda}{\pi^2 r}\left| b_0 + 2\sum_{m=1}^{\infty} b_m \;\cos m\psi \right|^2 ,$$

where is , 1

$$b_m = \frac{\det M_1}{\det M_2},$$

λ -wavelength of incident laser beam, r-distance of scattering center and detector, ψ-scattering angle. (Note that Fig. 1 for spatial treatment is depicted; our calculation is in 2D presentation.). For the case of homogeneous dielectric cylinder and polarization plane normal to the cylinder axis, matrices for M_1 i M_2 are:

$$M_1 = \begin{pmatrix} n_0 J_m \;\; \rho_0 & n_1 J_m \;\; \rho_1 \\ H'_m \;\; \rho_0 & J_m{}' \;\; \rho_1 \end{pmatrix} ,$$

2

$$M_2 = \begin{pmatrix} n_0 J_m \;\; \rho_0 & n_1 J_m \;\; \rho_1 \\ H'_m \;\; \rho_0 & J_m{}' \;\; \rho_1 \end{pmatrix}$$

where J_m-(z) Bessel functions of first order and expression $H_m(z)=J_m(z)-iN_m(z)$ - Hankel functions of the second order, $N_m(z)$ -Bessel function of the second order. Arguments of the functions are $\rho_i=n_i$ ka, where n_i- refraction index of the material (n_1) and of the environment (n_0), k= 2π/λ-wavenumber and a-radius of the cylinder.

$$B_m \;\; z = \frac{J_m \;\; z}{N_m \;\; z}, \quad \text{3a}$$

$$F_m \;\; z = \frac{J_{m+1} \;\; z}{J_m \;\; z}, \quad \text{3b}$$

$$D_m \;\; z = \frac{N_{m+1} \;\; z}{N_m \;\; z}, \quad \text{3c}$$

After respective analytic transformation, we get coefficient b_m in the form

$$b_m = P/Q \qquad 4$$

$$P=B_m \; \rho_0 \left[m\left(\frac{n_0}{\rho_1}-\frac{n_1}{\rho_o}\right)+F_m \;\rho_0 \;-F_m \;\rho_1 \right]+in_1\left[\frac{m}{\rho_o}-D_m \;\rho_o \right] \qquad 5$$

$$Q = B_m \frac{\rho_0 \left[m\left(\frac{n_0}{\rho_1}-\frac{n_1}{\rho_o}\right)+F_m \;\rho_0 \;-F_m \;\rho_1 \right]-im\left[\left(\frac{n_0}{\rho_1}-\frac{n_1}{\rho_0}\right)+F_m \;\rho_o \;-F_m \;\rho_1 \right]-}{-i\left[m\left(\frac{n_0}{\rho_1}-\frac{n_1}{\rho_o}\right)+n_1D_m \;\rho_0 \;-n_0F_m \;\rho_1 \right]} \qquad 6$$

$$n\lim_{n\to\infty} b_m = \frac{-\frac{n_1}{n_0}}{\frac{n_0}{n_1}-\frac{n_1}{n_0}}$$

More detailed derivations were reported in (Ostojić, 2002). Applicability of those derivations is in fiber theory and measuring methods in fiber and wire technology, as well as in fabrics technology in descriptions of radius and shape of drawing products. This way the task appears to follow the nature and convergence of the sum of order (series). The proof that series given are convergent appears as the principal task, as well as that the expression given could be applied to the modeling of the scattering cases of the electromagnetic radiation, in particular in the optical spectrum range. The analyses of the expression with computer support application usually starts from (1) where special functions are included if necessary. Finally, approach like this has a problem with proving the convergence of series in both classical as well as general viewpoint.

From the mathematical point of view, it should be proved that the expression is summable i.e. that it could be described by the finite sum. Various convergence criteria should be considered in analyzing the behavior of the series suggested (Ostojić, 2000, 2002.).This paper consider the case of the trigonometric series expression. It could be accommodated to suit the possibility of application of the trigonometric series in complex i.e. Euler's form. This formula is considered for the case of scatterers with cylinder shape, which could be used for the control of the diameter during process of wires extruding. It could be of interest in the multyfunctional uses in fiber optics in general, in textile industry, etc. The shape of the curve showing partial sum dependence of *m* is quasi-periodical. The quasi-periodicity tends towards the ideal periodicity, for the very large *m* (Fig. 2). The frequency of extrema in partial sums is increased with the rise of the angle ψ. The magnitude of *m* for which the dependence becomes ideally periodic increases with decreasing the angle ψ. Periodicity does not exist for $\psi = 0$.

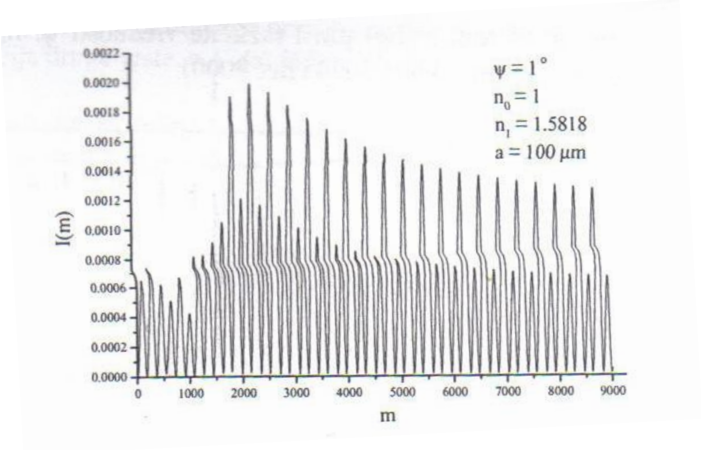


Figure 2. Partial summations for m≤3000 and m≤9000, for He Ne laser wavelength, radius of scattering centre a= 100μm.

Let us consider the problem of the series convergency which often used in scattering problems. Starting point is the characteristic term

$$\sum_{m=1}^{\infty} b_m \cos m\psi = -\sum_{m=1}^{\infty}\left(b - \operatorname{Re} b_m\right)\cos m\psi + \sum_{m=1}^{\infty} b\cos m\psi + i\sum_{m=1}^{\infty} \operatorname{Im} b_m \cos m\psi$$

$$\lim \operatorname{Re} b_m = b \ \text{ and } \ \lim \operatorname{Im} b_m = 0 \qquad 7$$

The series Im b_m linearly decreases. On the basis of series convergence theory (Ostojić 2002), that it can be concluded the first and the third series on the write side of (7) converge in Causchy's sense. The sum of the series

$$\sum_{m=1}^{\infty} b\cos\ m\psi = b\sum_{m=1}^{\infty}\cos\ m\psi\ , \qquad 8$$

can be calculated by Cesare's procedure,

$$\sum_{k=1}^{\infty}\exp\ \ im\psi\ \ = \sum_{m=1}^{\infty}\exp\ \ i\psi\ \ ^{m}\ ,$$

$$s_k = \frac{\exp\ \ i\psi\ \ \ 1-\exp\ \ ik\psi}{1-\exp\ \ i\psi} \qquad 9$$

For r=1,

$$S_n^{(1)} = \sum_{k=1}^{n} s_k = \frac{e^{i\psi}}{1-e^{i\psi}}\sum_{k=1}^{n}\left(1-e^{ik\psi}\right)$$

$$c_n^{(1)} = \frac{S_n^{(1)}}{\binom{n+1}{1}} = \frac{e^{i\psi}}{1-e^{i\psi}}\sum_{k=1}^{n}\frac{1-e^{ik\psi}}{n+1} \qquad 10$$

It should be proved that

$$\lim c_n^{1}\ = \frac{\exp\ \ i\psi}{1-\exp\ \ i\psi} \qquad 11$$

Based on (4) it could be concluded that the series $\sum_{m=1}^{\infty} b\cos m\psi \quad C,1$ summable.

$$\sum_{m=1}^{\infty}\cos m\psi = \mathrm{Re}\left(\sum_{m=1}^{\infty} e^{im\psi}\right) = \mathrm{Re}\frac{e^{i\psi}}{1-e^{i\psi}} = -\frac{1}{2}$$

$$\sum_{m=1}^{\infty} b_m \cos m\psi = A + iB - \frac{b}{2}, \quad A,\ B \in R$$

$$A = \sum_{m=1}^{\infty}\left(b - \mathrm{Re}\, b_m\right)\cos m\psi \quad \text{i} \quad B = \sum_{m=1}^{\infty}\mathrm{Im}\, b_m \cos m\psi$$

$$I = \frac{\lambda}{\pi^2 r}\left|b_0 + b_m \cos m\psi\right|^2 = \frac{\lambda}{\pi^2 r}\left|b_0 + 2(A+iB) - b\right|^2 \qquad 12$$

It could be find the relations betweeen Cesare's and Toeplitz's criteria.

The formula (10) is transformed in

$$c_n^{(r)} = \frac{S_n^{(r)}}{\binom{n+r}{r}} = \frac{\sum_{k=1}^{n} S_k^{(r-1)}}{\binom{n+r}{r}} = \frac{S_1^{(r-1)} + S_2^{(r-1)} + \cdots + S_n^{(r-1)}}{\binom{n+r}{r}} \qquad 13$$

It is taken into account that $s_k^{(r-1)}$, k=1,2,…n could be presented with s_k, where s_k is partial summation. The idea is that

$c_n = b_n$.

The link between $s_k^{(r-1)}$ and s_k is

$$S_n^{(r)} = \binom{n+r-2}{r-1}s_1 + \binom{n+r-3}{r-1}s_2 + \cdots + \binom{n+r-k-1}{r-1}s_k + \binom{n+r-k-2}{r-1}s_{k+1} + \cdots + s_n \qquad 14$$

Finally, after transformation it can be expressed as

$c_n^r = \alpha_{n1}s_1 + \alpha_{n2}s_2 ... + \alpha_{nn}s_n$,

where

$$\alpha_{ni} = \frac{\binom{n+r-1-i}{r-1}}{\binom{n+r}{r}}, \qquad i = 1,2,3,\ldots,n \qquad 15$$

another form (analog forme in matrix presentations)

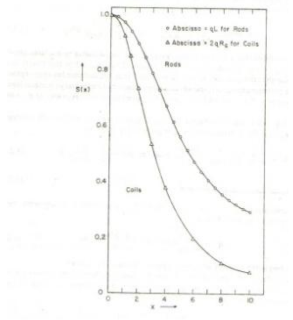
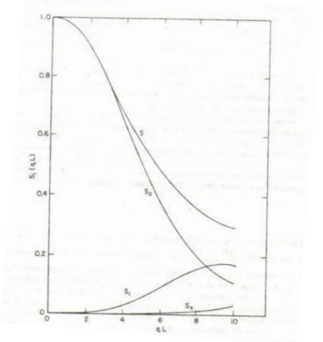
$$\begin{Vmatrix} c_1^{(r)} \\ c_2^{(r)} \\ c_3^{(r)} \\ \vdots \\ c_n^{(r)} \end{Vmatrix} = \begin{Vmatrix} \alpha_{11} & 0 & 0 & \cdots & 0 \\ \alpha_{21} & \alpha_{22} & 0 & \cdots & 0 \\ \alpha_{31} & \alpha_{32} & \alpha_{33} & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \alpha_{n1} & \alpha_{n2} & \alpha_{n3} & \cdots & \alpha_{nn} \end{Vmatrix} \times \begin{Vmatrix} s_1 \\ s_2 \\ s_3 \\ \vdots \\ s_n \end{Vmatrix} \qquad 16$$

It could be concluded that $b_n = c_n^{(r)}$

i.e. that $\sum_{m=1}^{\infty} b \cos m\psi$ A-summable.

Polydispersity effect, various approaches, structure factor role and approximations

It is the part of topics for very large particles. Angular distributions for scattering intensities differ for various particles shape, starting from regular geometrical one and finishing with very irregular shapes. Among them are often characteristic cases of Gaussian coils, rigid rods and spheres. By introducing structure factors and developing scattering theory, many problems are presented. Polydiseprsity is very important parameter in macromolecule treating, including biomolecules and their transformations in micellar formation. Figures 3 and 4 represent structure factors calculated for rigid rods and random coils. Note that R_G (radius of gyration) could be find directly by plotting Zimm's diagrams from static scattering (Berne, B. J., Pecora, R. (1976), Pecora R. 1982, Utyama, 1964, Zimm, 1945, Perepechko, 1978, Srećković, 2014). Here should be of course mentioned the links between cummulants and moments application.

	is also plotted in Fig. ... 
Figure 3. The structure factor S(x) of rigid rods and coils as a functions of the dimensionless variable x where for rods x=qL, for coils 2qRG. L is the rod length and R_G is the radius of gyration of the coils.	*Figure 4. Relative integrated intensities of light scat-tered from isotropic rigid rods. S-the total relative in-tegrated intensity, S_0-the intensity of pure translational part ,S_1-the first nonzero term whose spectral width contains the rotational diffusion coefficients and S_h-the sum of intensities of all other terms.*

Autocorrelation function (Cummins, 1978, Gardner, 1978) is known only in finite number of measuring points. Therefore, scattering study based on many points is needed. The interpretation of dynamic light scattering depends on the data that should be obtained from the measurements. In general, intensity of light scattering presented through static or dynamic issues contains coefficients of diffusion of various nature (for single molecules up to *effective* coefficient for micellar solution), molecular mass, radius of gyratation, dynamics of the scatterer ensamble (recognition of molecular interaction, directed stream beside thermal random motion, etc.). Of special interest is obtaining internal potential, for macromolecules, biomolecules as well as for micellar, colloid ensambles, etc (Berne&Pecora, 1976, Pecora,1985, Srećković, 1999).

Methods and experimental

The equipment for dynamic laser scattering has to include laser with enough power, photomultiplier or adequate detector, electronic subsystem for amplifications and correlator or spectral analyzator. The laser could be in CW or in pulse regime. Modern devices, for data processing, specific data processing programming packages are equipped which enable spectral linewidths Γ_1. For the case of polydisperse solutions Γ_1, Γ_2 and higher Γ could be directly obtained.

For each set up, calibration should be performed with standard powder (polystyrene spheres 0.5 μm)
One measurement series was with DTAB, with surface active molecules which can form micellar milieu (Ostojić, 2000, Srećković, 1999). Directly purified powder was prepared directly in the scattering cell. Strong concentrations were obtained, higher than 0.227M.
The ensamble of our solution contains: monomer, dimmer, micelles and sometime salts of small molecules (KBr). Considering measured data, those depend on the concentrations and resolution power of the equipment. For micellar ensamble, exist the possibilitiy for obtaining micellar charge and radius, as well as other data of interest.
In the presented analysis. we will evaluated the influence of number of measuring points included in linewidth evaluations, or, validity of experimental points. In here given measurements, we choose micellar solution without salt. (Salt addition stabilized solution performances.)

Experimental data for the solutions DTAB+H_2O were limited for the choice of polynomial order which should be used in data processing, for each concentration of measured solutions. It should be paid attention that $\Gamma\tau_{max} \leq 1.5$. Based on this assumption, polynomial of third order (or higher) should not be used, i.e. second order polynomial should be used. (Method of least square is applied)

Polidispersity and autocorrelation function

Let us remember that linewidth represent the polydispersity of the solution. Needed theory as follow.

Normalized autocorrelation function of the scattered associated field for the case of monodisperse scaterrers is

$$\left|g^{(1)}(\tau)\right| = \exp(-\Gamma\tau) \qquad (17)$$

where

$$\Gamma = Dq^2. \qquad (18)$$

For the case of poly disperse scattering centra, which shape is ideal (spherical) and solutions (weak or strong) hold in generalised case

$$\left|g^{(1)}(\tau)\right| = \int_0^\infty F(\Gamma)\exp(-\Gamma\tau)\,d\Gamma \qquad (19)$$

Distribution function F(Γ) is determined from the conditions that F(Γ)dΓ presents a part of the total scattering intensity from molecules for which the value Dq^2 is interval Γ i Γ+dΓ. F(Γ) and it is function F(Γ) should be normalized

$$\int_0^\infty F(\Gamma)\,d\Gamma = 1. \qquad (20)$$

Polydispersity is very important parameter and its description for almost all distributions is needed. One approach to it is obtained by calculations of inverse La Place transform of the experimental determined time correlation functions of the scattered beam with associated electric field $\left|g^{(1)}(\tau)\right|$.
There from F(Γ) as discrete or cw value case can be followed. In the generalized case, for the

obtaining of reasonable level of precision, experimental curve should be measured with high precision. It means many experimental points what is really impossible. Due to that fact, method of development of the exponential function exp (F(Γτ)) in $\left(\Gamma - \bar{\Gamma}\right)$ where $\bar{\Gamma} = \int \Gamma F \;\; \Gamma \; d\Gamma$.

It means that the degree of number of terms in series determine the level of uncertainty.

$$\begin{aligned} \exp\,(-\Gamma\tau) &= \exp\left(-\bar{\Gamma}\tau\right)\exp\left(-(\Gamma-\bar{\Gamma})\tau\right) \\ &= \exp\left(-\bar{\Gamma}\tau\right)\left[1-\left(\Gamma-\bar{\Gamma}\right)\tau+\frac{\left(\Gamma-\bar{\Gamma}\right)^{2}\tau^{2}}{2!}+\dots\right] \end{aligned} \tag{21}$$

After transformation and using mathematical derivations, is proved that

$$\ln a\left|g^{1} \;\; \tau\right| = \ln a - \bar{\Gamma}\tau + \frac{1}{2!}\frac{\mu_2}{\bar{\Gamma}^2}\left(\bar{\Gamma}\tau\right)^2 - \frac{1}{3!}\frac{\mu_3}{\bar{\Gamma}^3}\left(\bar{\Gamma}\tau\right)^3 + \dots \tag{22}$$

where,

$$\frac{\mu_n}{\bar{\Gamma}^n} = \frac{1}{\bar{\Gamma}^n}\int\left(\Gamma-\bar{\Gamma}\right)^n F \;\; \Gamma \;\; d\Gamma \tag{23}$$

is the n-th moment.

The approach with cumulants could be used for effective coefficients of diffusion. The comparisons of the methods by choosing cumulant or moments can be find in (Cummins, 1978) For the analyzing polydispersity, method of cumulant and moments were implemented in scattering theory and experiment for dynamical scattering. Autocorelation functions obtained by follwing development

$$\ln g^{(t)}\,(\tau) = 1 - k_1\tau + (k_2\,/2)\tau^2. \tag{24}$$

Many relations are derived for the correlations functions of higher and lower order. Time correlations functions, spectral distributions are investigated for the cases of: rigid large particles, Gaussian coil, anisotropic scattering, applications depolarized bacscattering and many other cases.

Evaluation of the influence of parasite measurements (*wrong* measurements) to the polydispersity

The evaluation is performed for the measurements of micellar solution of Dodecyltrimethylammonium bromide DTAB in aqua without additions of small molecules of respective salt molecules, how we mentioned before. The dynamic light scattering measurements are performed and presented in Fig. 5. Manipulations of data and results are presented in Figs. 6 and 7. By eliminating large errors, (*as we think*) we calculated the new cross-sections on the ordinate which should be used for the estimation of the first cumulant or further coefficient of diffusion (effective).

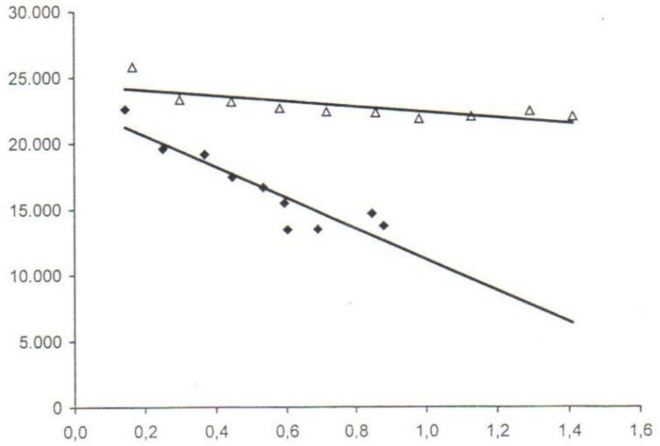


Figure 5. Determination of first cummulant k_1 by extrapolation of mean values of Γ_1 and Γ_2 to zero, of the products $\Gamma\tau$ with the inclusions of all measured points.

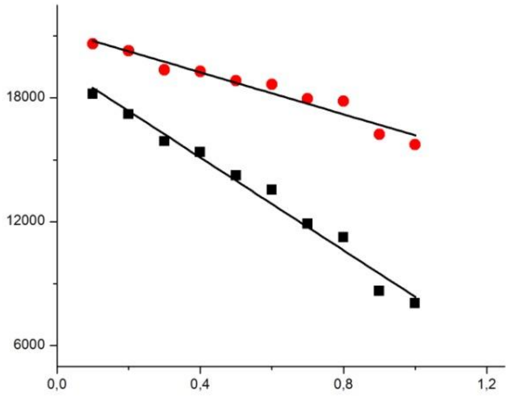


Figure 6. Determination of first cummulant k_1 by extrapolation of mean values of Γ_1 and Γ_2 to zero, of the products $\Gamma\tau$ without the "wrong " (first step) measured points.

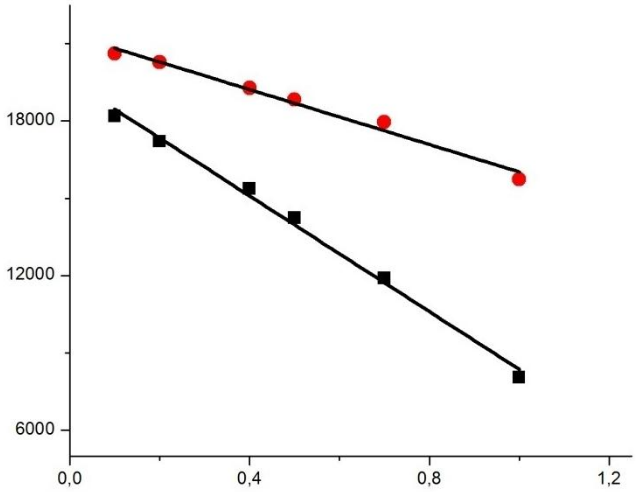


Figure 7. Determination of first cummulant k_1 by extrapolation of mean values of Γ_1 and Γ_2 to zero, of the products $\Gamma\tau$ without wrong (II step) measured points.

CONCLUSION

Intensity of laser scattering beam of cylindric objects is presented by the expression which contain trigonometric series. It is not convergent in classic (Cauchy sense) but it is generally convergent. Toeplitz's criterion of generally convergence enable to find associated number which can be treated as real value of intensity of scattering light. The evaluations of the first cumulant (i.e. coefficient of difusion effective) is performed by omitting wrong points and the deplacement of the cross-sections could be evaluated for some per cente.

REFERENCES

Barber, P., Yeh, C. (1975). Scattering of Electromagnetic Waves by Arbitraryly Shaped Dielectric Body, *Appl. Optics*, *Vol.14*, 286.

Berne, B. J., Pecora, R. (1976). Dynamic Light Scattering,Wiley-Interscience,:New York

Block, I.; Scheffold, F. (2010). Modulated 3D cross-correlation light scattering: Improving turbid sample characterization". *Rev. Sci. Instruments* **81** (12): 123107

Bohren,C.F.,Huffman D.R., (1998) Absorption and Scattering of Light by Small Particles, Wiley-VCH, New York, on line 29.dec. 2007.

Born, M., Wolf, E. (1973). Optical Principles, Moskva: Nauka.

Cummins H. Z., Pike R.E., eds, (1978) Corrrelation techniques in dynamic Light Scattering, Moscow :Mir.

Gardner, W. A. (1988). Statistical Spectral Analyses (Nonprobabilistic theory), New Jersey: Prentice Hall.

Ilić, J. ,Ristić, S., Srećković, M., (2001) The Detection Angle Choice in Characterisation ofAerosols and Hydrosols by LDA, Proceedings of Lasers Mc Lean,SoQuE, 620-627.

Ostojić, . S., Bundaleski, N., Srećković, M.,(2000)On the Convergence of Series in the Calculation of the Laser Beam Intensity Scattered by Cylinder, *Balkan Physics Letters*, BPL.10 (1) 17-24.

Ostojić, S., Bundaleski, J., Slavković, N., Tomić, Ž., Mamula,D., Mlinar, V. (2002). Analytical and Numerical progaming in Laser Scattering Phenomena and Experimental Techniques. Corcoran W.J and Corcoran T.A. (Eds.), *Lasers 2001,* Quebeck: Mc Lean, 351-358.

Pecora, R. (1982). Dynamic Light Scattering, Application of Photon Correlation Spectroscopy, Pecora R. (Eds.), New York:Plenum Press.

Perepechko, I. I. (1978). *Introduction in Physics of Polymers*. Moscow: Khimiya.

SrećkovićM.,Drifford,Ostojić S., Dalbiez J.P., (1999) Dynamic Scattering of Coherent LIght Estimation of Characteristics of the Centres of Scattering and Their Interactions, ATTI fondazione Ronchi. LIV,(5)

Utiyama, U., Kurata, M. (1964) Light Scattering from Dilute Solutions of Flewxible Chain Characteristic. Bull. I of Chemical Research, Kjoto: Univer.

Yoon, G., Prahl, S. A., Welch, A. J. (1989) Accuracies of the diffusion approximation and its similarity relations for laser irradiated biological media. *Appl. Opt., 28 (12)*, 2250-2255.

Zimm B.H.,(1945) Molecular therory of the scattering of Light in Fluids, J.Chem Phys.13(4),141

SOIL AND DEGRADATION OF SOIL

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EFFECT OF SLUDGE-CONTAMINATED SOIL ON MICROBIAL POPULATION SIZE IN THE RHIZOSPHERE OF HORSE BEAN AND SPRING WHEAT PLANTS

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ABSTRACT

In this study, Pot experiment were conducted with different levels of sludge 0, 30, 50, 70 and 100% (soil: sludge, w/w) per pot.The rhizomicrobial population sizes of the rhizosphere of the spring wheat and horse bean were increased with the increases of the sewage sludge concentration. These increases were significantly positive when the soil treated by 30% applied dose of sewage sludge, aerobic heterotrophic bacteria, aerobic spore-forming, Actinomycetes and microscopic fungi, while, it was not significant for aerobic phosphate solubilizers and cellulose decomposers in the rhizosphere of spring wheat. But, in the rhizosphere of horse bean at the same concentration, also, it was found that population size of fungi was significantly different with control. At 50% sludge treated soil, in the rhizosphere of horse bean, it was found that all counted rhizomicrobial groups were significant with control. However, in case of spring wheat, all population sizes of counted groups (except aerobic phosphate solubilizers) had significant differences comparing to the population sizes at 0% sludge concentration. In conclusion, the addition of sewage sludge had a stimulatory effect on general microbial activity and some special microbial groups in soils.

Key words: *Sludge, microbial population, wheat, rhizosphere.*

INTRODUCTION

Recycling of organic wastes within agriculture may help maintain soil fertility via effects on physical, chemical and biological properties. Efficient use, however, requires an individual assessment of waste products, and effects should be compared with natural variations due to climate and soil type. Application of different types of organic wastes may have a marked effect on soil microbial biomass and its activity. Sewage sludge is increasingly used as an organic amendment to soil, especially to soil containing low organic matter. However, little is known about the utility of this organic amendment in the reclamation of soil polluted with heavy metals. The widespread collection, treatment and disposal of wastewater effluent evolved in the mid-to late 19th century, before this time, wastes were often discharged into surface waters and polluted streams and rivers. As the technology of waste system has improved, the threat to our environment has been reduced because wastewater effluent has become cleaner and cleaner. However, in the process of producing clean effluent, the process itself accumulates residues or solids. The older, commonly used term for this solid is sewage sludge.

MATERIALS AND METHODS

Site and characterization of soil sample

Soil sample of acidic sandy brown forest soil of low humus content was taken from non-cultivated area of Gödöllő (Hungary), which is situated 30 km north-east of the capital Budapest. The soil sample was used to investigate the effect of sewage sludge application on the dry matter accumulation, nutrient status and heavy metal uptake, the changes in the microbiological characterization and the potential activities of some soil enzymes in the soil bulk and rhizosphere of growing plants.

The soil sample was collected from the upper 250 mm layer after removing the top 20 mm from a sample site. Soil sample was ground and sieved (2 mm) and stored in plastic bags at cold room temperature (less than 10 ± 2°C) for one week

Sewage sludge material

The sewage sludge material was received from Nyíregyháza and Regional domestic wastewater treatment plant Ltd., Nyíregyháza. The sample (code 1/2/2003/2) was aerobically digested and sand bed-dried.

The preparation of experimental soil-sewage sludge mixture

In two-kg pot capacity, the agro-ecosystem for plant growth was formed according to the following mixture:

Ratio of soil added to the mixture	Ratio of sewage sludge added to the mixture
100%	0%
70%	30%
50%	50%
30%	70%
0%	100%

The moisture content of the agro-ecosystem was kept constantly (approximately 60 ± 2%) throughout the 50 days as the time of cultivation.

Test plants

The experiments were carried out by cultivating the following two economical important test plants: Spring wheat and horse bean which was grown in greenhouse in pots containing various rates of the soil-sludge mixture

Methods

All in vitro investigations were carried out in the laboratories of Agricultural-, Environmental Microbiology and Soil Biotechnology, Budapest, and in the greenhouse of Soil Science and Agro-chemistry as well as the Central Laboratory of Szent István University, Gödöllő, Hungary.

RESULTS

Effect of sewage sludge application on the population size of some microbial groups in the treated soil rhizosphere

Numerous microbes, especially those associated with roots, have the ability to increase plant growth and productivity. In a few cases, this effect has been suggested to involve solubilisation of otherwise unavailable mineral nutrients. In soil, both macro- and micronutrients undergo a complex dynamic equilibrium of solubilisation and insolubilisation that is greatly influenced by the soil pH and microbes and that ultimately affects their accessibility to plant roots for absorption.

The rhizomicrobial population sizes of the rhizosphere of the spring wheat (Table 1) and horse bean (Table 2) were increased with the increases of the sewage sludge concentration. These increases were significantly positive when the soil treated by 30% applied dose of sewage sludge in the following cases: total aerobic heterotrophic bacteria, aerobic spore-forming, *Actinomycetes* and microscopic fungi, while, it was not significant for aerobic phosphate solubilizers and cellulose decomposers in the rhizosphere of spring wheat. But, in the rhizosphere of horse bean at the same concentration, also, it was found that population size of fungi was significantly different with control. At 50% sludge treated soil, in the rhizosphere of horse bean, it was found that all counted rhizomicrobial groups were significant with control. However, in case of spring wheat, all population sizes of counted groups (except aerobic phosphate solubilizers) had significant differences comparing to the population sizes at 0% sludge concentration.

Table 1: Effect of different applicable doses of sewage sludge on the different microbial groups in the spring wheat rhizosphere

Sewage sludge doses	**Mean of three replicates of different microbial counts / g soil**					
	Aerobic bacteria (x10^6)	**Aerobic spore-forming (x10^3)**	**Actinomycetes (x10^3)**	**Fungi (x10^4)**	**Aerobic phosphate solubilizers (x10^2)**	**Aerobic cellulose decomposers (x10^3)**
0%	85	6,5	1,4	6,4	4,4	4,1
30%	221*	15,1*	4,42*	9,6*	7,7	8,1
50%	332*	20,8*	6,2*	10,6*	9,6	11,2*
70%	399*	24,7*	9,7*	12,7*	15,2*	15,3*
100%	514*	28,6*	13,5*	17,7*	18,7*	22,4*
SD ($P < 0,05$)	**97,17**	**6,51**	**3,02**	**3,02**	**4,27**	**6,17**

The numbers labelled with (*) within the column is significantly different from the control at $P \leq 0.05$

Table 2: Effect of different applicable doses of sewage sludge on the different microbial groups in the horse bean rhizosphere

Sewage sludge doses	**Mean of three replicates of different microbial counts / g soil**					
	Aerobic bacteria (x10^6)	**Aerobic spore-forming (x10^3)**	**Actinomycetes (x10^3)**	**Fungi (x10^4)**	**Aerobic phosphate solubilizers (x10^2)**	**Aerobic cellulose decomposers (x10^3)**
0%	74	5,1	1,3	5,6	4,5	4,9
30%	136	11,1	3,5*	8,9*	7,3	9,1
50%	193*	18,4*	4,3*	10,7*	9,6*	12,2*
70%	253*	24,1*	5,2*	12,7*	13,2*	15,1*
100%	381*	29,3*	6,3*	14,7*	19,7*	21,4*
SD ($P < 0,05$)	**114,37**	**9,03**	**1,22**	**2,14**	**5,16**	**5,67**

The numbers labelled with (*) within the column is significantly different from the control at $P \leq 0.05$

Percentage of Gram negative and Gram positive rhizobacteria was determined and it was found that the ratios between the counted Gram negative to Gram positive rhizobacteria in the rhizosphere of spring wheat and horse bean were 7/3 and 8/5, respectively. While the ratios of rod shape bacteria to cocci forms were 4/1 and 5/2 in the rhizospheres of spring wheat and horse bean, respectively.

The symbiotic nitrogen fixing bacteria was determined by counting the root-nodule existing on the roots of horse bean. Also, the results showed that the maximum root-nodule number was found on the roots grown in the agroecosystem of 30% sewage sludge. The reason is that because of high nitrogen applied to the soil, the root-nodules were inhibited. But the highest number of isolated *Bacillus* species was found in the rhizosphere of spring wheat grown in a medium of 70% sewage sludge, while the highest number of isolated *Bacillus* species was found in the rhizosphere of horse bean grown in a medium of 50% sewage sludge, and the aerobic spore-forming bacteria were determined at maximum count in the rhizospheres of both plants at 100% of sludge.

DISCUSSION

This study shows that soils with sharply contrasting physical and chemical composition and properties of the soil amended with different rates of sewage sludge are metabolically active and contain substantial numbers of microorganisms. This has important implications for our understanding and modelling of the transformation of downward moving natural and synthetic organics. Bacterial resistance to toxic heavy metal ions is generally controlled by the genes on extra chromosomal resistance (R) factors that also house the genes conferring resistance to antibiotics. These R factors can be mobilised from cell to cell by direct conjugation and thus afford rapid mechanism for changing a population of microorganisms that is predominantly sensitive to antibiotics and toxic ions to a population that is predominantly resistant.

Katai (1999) summarised the results of changes in the microbiological population size in long-term fertilisation experiment with mono-, and triculture of maize. It was found that the total bacterial and cellulose decomposing bacteria in Hajdúböszörmény soil was increased by increasing the fertilisation doses in mono-, and triculture, while maximum microscopic fungi was obtained at medium dose applied to the monoculture. But in Látókép, the total bacterial count was increased by increases the fertilisation dose in triculture, and it was maximal at low to medium rate of fertiliser. The maximum population of microscopic fungi was at medium to high rate of applied fertilisation both mono-, and triculture. Also, it was found that the population size of cellulose decomposing bacteria was increased by increases the dose in monoculture and it was at maximum when the triculture treated with medium to high dose rate. Our results showed that in the rhizospheres of spring wheat and field growing common bean, the population sizes of the total aerobic bacteria, aerobic spore-forming, Actinomycetes, fungi, aerobic phosphate solubilisers and aerobic cellulose decomposers were increased by increasing the applied dose of sewage sludge.

Several researchers have demonstrated the existence of bacterial groups in the rhizosphere of various crops, which have the ability to solubilize the insoluble forms of phosphate compounds through the production of organic acids which are assimilated better by the plant (Alexander, 1980). Therefore, production of bio-preparations could improve the availability of soluble phosphorus, which in turn would cause a decrease in the use of phosphate fertilisers and thus, a decrease in the crop’s production costs, while simultaneously having a positive effect on the environment. Phosphate-solubilizing bacteria are commonly associated with the roots of a range of species (Halvorson et al., 1990). Also, we found that by increasing the rate of sludge, the counts of phosphate solubilizing rhizomicrobes increased (Tables 1 and 2).

Most of the recent literature containing microbial solubilisation of minerals in soil and their potential use for enhancement of soil fertility deals with phosphate solubilizing bacteria and vesicular arbuscular mycorrhizal fungi. However, the ability of a few filamentous non-mycorrhizal fungi, especially *Aspergillus* spp. and *Penicillium* spp., to solubilize phosphate has also been shown (Illmer & Schinner, 1992; Molla et al., 1984). A commercial formulation of *Penicillium bilaii* Chalabuda has been registered in Canada as a biological enhancer of plant nutrition (Cunningham & Kuiak, 1992). It was mentioned that using agar media with calcium phosphate and the pH indicator alizarin red S, the influence of the medium composition on phosphate solubility and medium acidification was recorded. The major acidic metabolites produced by the fungus in a sucrose nitrate liquid medium were found to be oxalic and citric acids. The release of organic acids that both sequester cations and acidify the microenvironment near roots is thought to be a major mechanism of solubilisation of phosphorus by plants and non-vesicular arbuscular mycorrhizal fungi.

The efficacy of various *Pseudomonas* spp. in dissolving rock phosphate from suspension, agar, and soil has received considerable attention during the last two decades (Azcon et al., 1976; Ralston & McBride, 1976; Gaur et al., 1980; Illmer & Schinnner, 1992). The dissolution of rock phosphate involves two steps: first production of the monocarboxylic acids (gluconic and 2-ketogluconic acids) by the bacteria and second dissociation of these acids (Moghimi & Tate, 1978) and subsequent dissolution of the rock phosphate by the resulting protons.

Maximum crop yields require sufficient P fertilisation. Current fertiliser technology supplies the soil solution with soluble P via the application of large amounts of phosphate salts. Problems with this technology include energy-intensive production processes with associated environmental consequences (Goldstein, 2000). The most promising approach is the phosphate solubilisation by heterotrophic microorganisms producing organic acids. Microbial mediated solubilisation of rock phosphate can be performed in condition of solid-state fermentations utilizing solid-industrial wastes (Vassilev & Vassileva, 2003). The resulting fermented materials, containing mineralised organic matter, soluble (plant-available) P, and microbial biomass, were further introduced into typical soil-plant systems. Analyzing the plant responses, plant growth increases of at least 300% were registered as compared to non-amended controls (Vassilev et al., 1996).

The large surface area increases the secretion of P solubilizing compounds into localised regions of the rhizosphere (Gardner et al., 1982). This is important in the natural environment where phosphorus acquisition is most likely to be limited by the low solubility and diffusion of phosphorus across the soil to the root absorbing surfaces.

Phosphorus is the least available element to sugar cane and to plants in general. This is due to two phenomena occurring when contacting the soil: the first phenomenon is called immobilisation, and is carried out by those microorganisms that populate the mineral’s deficient regions and which the nutriments amounts needed to perform their vital processes (Jungk et al., 1993). The second phenomenon is called precipitation or fixation to insoluble complex minerals, and is due to the union of phosphorus with elements such as iron and aluminium in acid soils, and calcium in alkaline soils, denying the plant up to 75% of all soluble phosphorus (Goldstein, 1986; Kucey et al., 1989), and thus, generating a 0.002-0.5% concentration of mineral in the soil (Chabot et al. 1993). This has forced many crop raisers to apply up to four times the required amount of phosphorus to plants. Higher plants have access to phosphate only a few millimetres around the root.

There are several potential mechanisms for phosphate solubilisation. These include the modification of pH by the secretion of organic acids or protons. Secretion of H^+ from roots into the medium in response to uptake of NH_4^+ and of OH^- for NO_3^- uptake are well documented, and the decrease in pH of the medium in the presence of NH_4^+ has been correlated with solubilisation of inorganic phosphates (Marschner, 1991). Kwabiah et al. (2003) established that soil microbial biomass is a major sink and sources of plant available phosphorus and transformer of soil organic phosphorus.

Datta et al. (1982) extracted an auxin named acid 3-indol acetic from a phosphate-solubilizing genus of *Bacillus firmus*. It is possible that microorganisms may have the ability to produce certain substances that act in a similar way; in fact, *Enterobacter* is used in soil recovery processes, due to its ability to transform nutrients and to produce vegetable growth stimulating substances. While using *Enterobacter* genus in corn seeds inoculation, Chabot (1993) observed root elongation due to production of auxins. Wenzel et al. (1994) isolated bacteria from cluster and non-cluster roots of waratah (*Telopea speciosisima*) seedlings are able to acidify the medium and solubilize calcium phosphates when grown in culture in the presence of ammonium salts and an appropriate carbon source. It was mentioned that this activity was not detected when nitrate ion was substituted for ammonium ion, and it is proposed that protons were secreted in exchange for ammonium ions. Cation exchange between these protons and calcium in the medium is a possible cause of the calcium phosphate solubilizing activity.

Altomare et al. (1999) investigated the capability of the plant growth promoting and biocontrol fungus *Trichoderma harzianum* to solubilize *in vitro* some insoluble or sparingly soluble minerals via three possible mechanisms: acidification of the medium, production of chelating metabolites, and redox activity. The fungus was able to solubilize calcium phosphate in a liquid sucrose-yeast extract medium. Phosphates were also solubilised by cell-free culture filtrates. According to Weaber (1980) cytokinins induce leaf elongation. And, according to a survey by Barea et al. (1976) cytokinins were extracted from the RNA of a phosphate- solubilising genus of *E. coli*. Solubilisation of $CaHPO_4$ was positively correlated with bacterial acidification of the medium below about pH 5. There are many reports of secretion of organic acids such as oxalic, malic or citric acids from bacteria or roots that solubilize phosphate (Marschner, 1986, Marschner et al., 1987).

From the above mentioned reports, we have found that when the spring wheat and horse bean were grown in media containing different mixing rates of sewage sludge for 50 days, the enumeration of the calcium phosphate solubilising rhizomicrobes were increased by increasing the sludge rate in the models.

Several different approaches for the selective enumeration of cellulose-utilising bacteria in soil have been described (e.g., Mahasneb & Stewart, 1980, Smith, 1977). The common basis of most methods is the hydrolysis of cellulose substrate. Hankin & Anagnostakis (1977) looked for zones of clearing surrounding colonies growing on agar containing cellulose. Furthermore, the colonies of cellulose-utilising bacteria are often difficult to differentiate from other organisms on solid media (Stotzky et al., 1993), even with polysaccharide precipitants, e.g., hexadecyltrimethylammonium bromide (Cruden Markovetz, 1979).

De Melo et al. (2002) mentioned that cellulase activity increased until 90 days after sewage sludge application and then decreased. Sewage sludge used in the experiment should already contain some amylase activity or a substance that was a soil enzyme activator and also a substance that was an inhibitor of soil cellulase inhibitor. Some of the plant nutrients contained in sewage sludge, mainly P, did not migrate down the soil column, an indication that sewage sludge should be incorporated into the soil to improve nutrient bioavailability.

Our speed and precision in enumerating cellulose-decomposing bacteria in a system were improved with the cellulose Congo red agar. We found the cellulose-utilising bacteria were more distinguishable on the used medium by definitive zones of clearing around the colonies that were generally red and, therefore extremely easy to count. The results were confirmed by the Hendricks et al. (1995).

CONCLUSION

In conclusion, the addition of sewage sludge had a stimulatory effect on general microbial activity and some special microbial groups in soils. The most frequent isolates were belonging to, *Acinetobacter*, *Azotobacter*, *Rhizobium*, *Brevundimonas*, *Cellulomonas*, *Chromobacterium*, *Corynebacterium*, *Enterobacter*, *Escherichia*, *Flavobacterium*, *Klebsiella*, *Micrococcus*, *Proteus*, *Streptococcus*, *Serratia* and *Zooglea*. *Streptomyces* was the genus of most dominant isolates of actinomycetes. The most fungal isolates were belonging to the genera of *Alternaria*, *Aspergillus*, *Cephalospoium*, *Cladosporium*, *Fusarium*, *Geotricum*, *Mucor*, *Penicillium*, *Rhizopus* and *Trichoderma*. Also, many isolates of the genus *Saccharomyces* were isolated from soil samples of the rhizospheres of the tested plants amended with communal sludge comparing with the control soil.

REFERENCES

Alexander M. (1980): Transformaciones microbianas. En Introducción a la Microbiología del Suelo. AGT editores. Segunda Edición. México: 356-375.

Altomare C., Norvll W.A., Björkman T., Harman G.E. (1999): Solubilisation of phosphates and micronutrients by the plant growth promoting and biocontrol fungus Trichoderma harzianum Rifai 1295-22. *Appl. Environ. Microbiol.*, 65, 2926-2933.

Azcon R., Barea J.M., Hayman D.S. (1976): Utilization of rock phosphate in alkaline soils by plants inoculated with mycorhizal fungi and phosphorus solubilizing.

Barea J.M., Navarro E., Montoya E. (1976): Production of plant growth regulators by rhizosphere phosphate solubilizing bacteria. *J. Appl. Bacteriol*., 40:129-134.

Chabot R., Hani A., Cescas M.M. (1993): Stimulation do la croissance du´mais et de la latitue romaine par des microorganismes disolvant le phosphore inorganique. *Canadian J .Microbio*l., 39, 941-947.

Cruden D.L., Markovetz A.J. (1979): Carboxymethyl cellulose decomposition by intestial bacteria of cockroaches. *Appl. Environ. Microbiol*., 38: 369-372.

Cunnningham J.E., Kuiack C. (1992): Production of citric and oxalic acids and solubilisation of calcium phosphate by *Penicillium bilaii*. *Appl. Enviro Microbiol*. 58: 1451-1458.

Datta M., Banik S., Gupta R.P. (1982): Studies of the efficacy of a phyotohormon producing by phosphate solubilizing B. Firmus in augmenting paddy field in acid soils of Nagaland. *Plant and Soil*, 69: 365-373.

De Melo Wanderley J., Marques M.O., Ferreira M.E., Gabriel M., de Melo Valeria Peruca (2002): Chemical properties and enzyme activity in a sewage sludge-treated soil Comm. *Soil Sci. Plant. Anal*., 33: 1643-1659.

Gardner W.R., Parbery D.G., Barber D.A. (1982): The acquisition of phosphorus by Lupinus albus L. II. The effect of varying phosphorus supply and soil type on some characteristics of the soil/root interface. *Plant and Soil*, 68: 33-41.

Gaur A.C., Mathur R.S., Sadasivm K.V. (1980): Effect of organic material and phosphate-dissolving culture on the yield of wheat and greengram. *Indian. J. Agron*., 25: 501-503.

Goldstein A.H. (2000): Bioprocessing of rock phosphate ore: Essential technical considerations for the development of a successful commercial technology. IFA.

Goldstein A.H. (1986): Bacterial solubilisation of mineral phosphates: historical perspective and future prospects. *Am. J. Alter. Agric*., 20: 51-57.

Halvorson H.O., Keynan A., Kornberg H.L. (1990): Utilization of calcium phosphates for microbial growth at alkaline pH. *Soil Biol. Biochem*., 22: 887-890.

Hankin L., Anagnostakis S.L. (1977): Solid media containing carboxymethylcellulose to detect Cx cellulase activity of microorganisms. *J. Gen. Microbiol*., 98: 109-115.

Hendricks C.W., Doyle J.D., Hugley B. (1995): A new solid medium for enumerating cellulose-utilizing bacteria in soil. *Appl. Environ. Microbiol*., 61: 2016-2019.

Illmer P., Schinner F. (1992): Solubilisation of inorganic phosphates by microorganisms isolated from forest soils. *Soil Biol. Biochem*., 24: 389-395.

Jungk A., Seeling B., Gerk J. (1993): Mobilization of different phosphate fractions in the rhizosphere. *Plant and Soil*, 156: 91-94.

Katai J. (1999): Talajmikrobiologiai jellemzők változása trágyázási tartamkísérletben. *Agrokémia és Talajtan*, 48: 348-360.

Kucey R.M. (1989): Phosphate solubilizing bacteria and fungi in various cultivated and virgin Alberta soils, *Canadian J. Soil Sci*., 63: 671-678.

Kwabiah A.B., Palm C.A., Stoskopf N.C., Voroney R.P. (2003): Response of soil microbial biomass dynamics to quality of plant materials with emphasis on P availability. *Soil Biol. Biochem*., 35: 207-216.

Mahasneb A.M., Stewart D.J. (1980): A medium for detecting β-(1-3) glucanase activity in bacteria. *J. Appl. Bacteriol.*, 48: 457-458.

Marschner H. (1991): Mechanisms of adaptation of plants to acid soils. *Plant and Soil*, 134: 1-20.

Marschner H., Romheld V., Horst, W.J., Martin P. (1987): Root-induced changes of nutrient availability in rhizosphere. *J. Plant. Nutr*., 10: 1175-1184.

Marschner H. (1986): Mineral nutrition of higher plants. London, Academic Press.

Moghimi A., Tate E. (1978): Does 2-ketogluconic chelate calcium in the pH range 2.4 to 6.4?. *Soil Biol. Biochem*., 10: 289-292.

Molla M.A.Z., chowdhury A.A., Islam A., Hoque S. (1984): Microbial mineralisation of organic phosphate in soil. *Plant and Soil*, 78: 393-399.

Ralston D.B., McBride R.P. (1976): Interaction of mineral phosphate-dissolving microbes with red pine seedlings. *Plant and Soil*, 45: 493-507.

Smith R.E. (1977): Rapid tube test for detecting fungal cellulase production. *Appl. Environm. Microbiol*., 33: 980-981.

Stotzky G.M., Broder M.W., Doyle J.D., Jones R.A. (1993): Selected methods for the detection and assessment of ecological effects resulting from the release of genetically engineered microorganisms to the terrestrial environment. *Adv. App. Microbiol*., 38: 1-99.

Vassilev N., Vassileva M. (2003): Biotechnological solubilisation of rock phosphate on media containing agro-industrial wastes. *Appl. Microbiol. Biotechnol*., 61: 435-440.

Vassilev N., Franco I., Vassileva M., Azcon R. (1996): Improved plant growth with rock phosphate solubilized by Aspergillus niger grown on sugar-beet waste. *Biores. Technol*., 55: 237-241.

Weaber R.J. (1980): Efectos biológicos y mecanismos de acción. Reguladores del crecimiento de las plantas en la agricultura. Editorial Trillas. Segunda Edición. México. 113-140.

Wenzel C.L., Ashford A.E., Summerell B.A. (1994): Phosphate-solubilizing bacteria associated with proteoid roots of seedlings of waratah [Telopea speciosisima (Sm.) R.Br.]. *New Phytol*., 128: 487-496.

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ECOLOGICAL STATE OF SOIL COVER OF THE URBAN AREA (UFA, RUSSIA)

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ABSTRACT

Complex research that combines assessment of biotoxicity soil samples from different places of the city territory with chemical-analytical control of the total content of toxic tm (zn, cu, pb, cd) in the soil, indicate the relationships between them. it is established that the soil becomes toxic properties at hm concentration of more than 200 mg/kg.

Keywords: *Heavy metals: Cu, Zn, Pb, Cd.*

INTRODUCTION

The city of Ufa is a major industrial center, a major site of roads and railways. Most of his residential area is in the zone of influence of large industrial enterprises located in its northern and southern parts. So technogenic load on the urban landscapes of these places is extremely high (State report, 2010).

So technogenic load on the urban landscapes of these places is extremely high. Pollution by heavy metals (HM) is one of the characteristics of urban natural environment of Ufa. A significant number HM enters the environment with exhaust gases of motor transport, atmospheric emissions of the enterprises of oil refining and petrochemistry, energy, engineering and radio engineering industries (Alekseenko et al., 2013).

The main part of HM accumulates in the soil and dust masses. For an adequate assessment of their negative effects on the environment, information about the emissions produced according to the statistical reporting of enterprises, are not enough. In our opinion, is extremely important and relevant comprehensive studies that combine chemical and analytical control their pollution HM c assessment of biotoxicity soil samples from different places of the city (Fomin et al., 1992, Kuramshina et al., 2013). Most of the city enterprises specialized in oil refining, machine building and put into the environment of highly toxic compounds of heavy metals - zinc, lead, cadmium (I hazard class); moderately dangerous metal - copper (II hazard class) (Mosina, 2000).

In the present work we studied biotoxicity samples of soils and pollution with heavy metals for formation of ecological information portrait of the territory, Ufa.

MATERIAL AND METHODS

Ground sampling of soils (n = 8) were selected from the main sources of emissions of large industrial enterprises, roads with intensive traffic of vehicles, from recreational areas. The content of HM in soil samples were carried out in accordance with RD 52.18.685-2006 and GOST 30178-96 using AAS instruments «Spectrum-3-P1»and «Quantum 2A».

Toxicological evaluation of samples of water extract of soils was performed by the method of biotesting with the use of daily culture of infusoria of Stylonychia – Stylonichia mytilus (Kuramshina et al., 2000). For biotesting used colonial-mixed culture of the laboratories of LLP "Biotest" (Moscow, VNIRO). Assessment of the degree of toxicity were performed in automatic mode. Biotoxicity test water in the % criterion toxicity was reduced survival of the ciliates 50 % (or more) in the analyzed water extract of the soil in comparison with the control.

For the environmental assessment of the degree of contamination of soil cover of the territory, Ufa used the pollution index $I_f = C_i^{HM}/ C_f^{HM}$, representing the ratio of the concentrations of heavy metals in the soil of the city territory (C_i^{HM}) to their background values (C_f^{HM}).

RESULTS AND DISCUSSION

Comparison of data on concentrations of Cu, Zn, Pb, Cd with the appropriate background values allowed to determine the levels of individual and total indexes of soil pollution, Ufa (table 1).

Table 1: Assessment of the degree of soil pollution of the urban area by heavy metals

Districts of the city of Ufa	HM	HM content in soil,mg/kg		The background concentration*, mg/kg	Index of soil contamination with HM (I_f)	
		interval	median		individual	total
Octobersky	Cu	17–53	35,0	10	1,7–-5,3	6,0–14,9
	Zn	46–89	67,5	70	0,7–1,3	
	Pb	4,2–11,9	8,0	2,6	1,6–4,6	
	Cd	0,41–0,74	0,58	0,2	2,0–3,7	
Demsky	Cu	28–40	34,0	10	2,8–4,0	5,2–10,8
	Zn	84–88	86,0	70	1,2–1,3	
	Pb	3,2–4,8	4,0	2,6	1,2–1,8	
	Cd	0,74	0,74	0,2	3,7	
Kirovsky	Cu	22–53	37,3	10	2,2–5,3	7,0–16,3
	Zn	72–140	109,0	70	1,0–2,0	
	Pb	5,8–11,5	8,7	2,6	2,2–4,4	
	Cd	0,3–0,92	0,62	0,2	1,6–4,6	
Kalininsky	Cu	28–50	39,0	10	2,8–5,0	7,0–24,7
	Zn	90–170	130,0	70	1,3–2,4	
	Pb	3,7–32,0	17,8	2,6	1,4–12,3	
	Cd	0,30–1,03	0,66	0,2	1,5–5,0	
Sovietsky	Cu	35–39	37	10	3,5–3,9	6,3–15,2
	Zn	157–160	158	70	2,2–2,3	
	Pb	1,6–13,5	7,6	2,6	0,6–5,2	
	Cd	0,76	0,76	0,2	3,8	
Leninsky	Cu	19–55	37	10	1,9–5,5	5,0–27,5
	Zn	67–240	153	70	1,0–3,4	
	Pb	3,0–30,2	16	2,6	1,1–11,6	
	Cd	0,19–1,40	0,80	0,2	1,0–7,0	
Ordzhonikidzevsky	Cu	1–70	43	10	1,5–7,0	5,1–34,3
	Zn	85–395	240	70	1,2–5,6	
	Pb	2,4–35,5	19	2,6	0,9–13,7	
	Cd	0,30–1,10	2,0	0,2	1,5–8,0	

* background concentrations of heavy metals in accordance with Kuramshina, 2013

As shown in table 1, the copper content in soils of different regions, Ufa ranges from half the size of the regional background to 7-fold exceeded. Contamination of land areas of the city with zinc has a uniform character, the excess of background values in conventionally clean areas is 1.3 times, and in the places of maximum pollution is 1.2-5.6 times. In the soils of the city, the content of lead varies from a fraction of background values to 13-fold its excess. The maximum value of the index of soil pollution with lead characteristic of Leninsky, Kalininsky and Ordzhonikidzevsky districts. The content of cadmium in the soil areas of Ufa is in the range from 0.6 - 2.0 to 3.7-8,0 fold excess of background values. In general, soil contamination of the territory of Ufa with by cadmium is a serious problem.

A summary indicator of soil contamination Cu, Zn, Pb, Cd to Demsky, Oktyabrsky, Sovetsky districts varies from 5.2-7.0 to 10,8-16,3 fold excess of background values for these HM. For contaminated areas of Ufa (Leninsky, Kalininsky, Ordzhonikidzevsky districts) the maximum value of the total indexes of soil contamination reaches 24,7-34,3. A summary assessment of the status of the territory, obtained by the summation of individual indexes shows that the contamination of soil Cu, Zn, Pb and Cd is a serious problem for Ufa.

Biotesting substantially complements the system of analytical methods of pollution control of the city territory with a new measure in the integral form to evaluate the quality of the soil as a habitat.

Toxicological assessment of water extract of the studied soil samples was performed by the method of biotesting with the use of infusoria – Stylonychia allowed us to assess the toxicity index of the soil cover various areas in the territory of Ufa (table 2).

Table 2: Assessment of the level of biotoxicity soils in the territory of Ufa

Place of sampling	HM content in soil, mg/kg				Survival of the ciliates, %	Index of toxicity, IT (0-1)
	Cu	Zn	Pb	Cd		
Octobersky district:						
– Bikbay-Gagarin st.	17	46	4,2	0,74	70	0,30
– factory "Promsvyaz"	53	89	11,9	0,41	63	0,37
– South of bus station	36	100	2,4	0,37	75	0,25
Kirovsky district:						
– Vorovskogo st.	53	140	11,5	0,92	50	0,50
– Validi st.	41	130	10,2	0,32	65	0,35
Kalininsky district:						
–Pervomayskiy-Kremlin st.	39	100	16,6	0,97	65	0,35
– m.r. Shaksha	35	1,7	3,7	1,03	55	0,45
– factory UMPO	44	94	14,1	0,80	60	0,40
Sovietsky district:						
– Galle District st.	39	157	13,50	1,57	40	0,60
– Parkhomenko st.	35	160	1,56	0,76	35	0,65
Leninsky district:						
– Krasin-Aksakov st.	43	110	3,0	0,77	55	0,45
– Akhmetov st.	45	103	12,8	0,72	65	0,35
Ordzhonikidzevsky distric :						
– Pervomaiskaya-Ulyanova	28	120	8,6	0,79	70	0,30
– TPP-4	36	194	7,7	0,53	40	0,60
– JSC"Ufaneftekhim"	46	220	6,8	0,74	35	0,65
– JSC"Ufaorgsintez"	33	140	7,2	0,34	60	0,40

As follows from table 2, soil Octobersky, Kirovsky, Kalininsky, Leninsky districts in the zones of influence of highways with heavy traffic and enterprises of machine-building and electronic industries are characterized by the toxicity index in the range 0,31-0,48. In the zone of influence of the plant of elastomer materials (Sovietsky district) and JSC "Ufaneftekhim", TPP-4 (Ordzhonikidzevsky district) toxicity index up to 0.60-0,65.

CONCLUSION

The comparison of the indicator of toxicity of different samples of soils with total content of toxic HM (Zn, Cu, Pb, Cd) in the soil indicates the relationships between them. It is established that the soil becomes toxic properties at a concentration of HM more than 200 mg/kg.

LITERATURE

State report "On the state of natural resources and environmental protection of the Republic of Bashkortostan in 2010," the Ministry of natural resources and environmental protection of the Republic of Bashkortostan. – Ufa, 2011.–352 p.

Alekseenko V.A. Alekseenko A.V. Chemical elements in geochemical systems. The abundances in urban soils. Rostov-on-Don. Pablishing of Southern Federal University, 2013. –388 p.

Kuramshina N.G., Imashev U.B. Geochemical, ecological and social condition of the main technological areas of Bashkortostan. – Ufa: Gilem, 2013. – 236 p.

Mosina L.V. Agricultural ecology (agricultural ecotoxicology). – M.: DSTI PSC RAS, 2000. – 184 p.

Fomin PS, Checkin A.B. Water. Control of chemical, bacterial and radiation safety according to international standards: a Handbook. - M, 1992. – 600 p.

Kuramshina N.G., Kuramshin E.M., Verzakov M.S., Erkeev M.I., Lapikov V.V., Chukturidi V.I. Indication dust pollution snow cover of the territory of Ufa and assessment of biotoxicity samples of snow. Bashkir ecological bulletin, 2000. No. 2. C. 32-35.

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RECLAIMING IDLE AGRICULTURAL AREAS ON PERIPHERY OF CITIES: CASE STUDY OF MANISA

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ABSTRACT

There are idle or unused areas on periphery of cities even they are suitable for agriculture. These idle areas are under the threat of urbanization especially in cities, urbanizing rapidly and growing their boundaries steadily. Aim of the study is to present a method to determine such areas and to develop land uses which will impact city life and ecology positively. The study was conducted in central district of Manisa, one of the western cities of Turkey. In this study, idle areas of Manisa were determined by overlapping peri-urban areas which are suitable for agriculture and the other areas farmed currently or covered by vegetation. For this, the main and sub factors required for determination of suitability for agriculture were entered into the GIS environment and the maps were produced for each of them. Weights of main factors were set by Simos Procedure and suitability points of sub factors were set by expert opinions. By overlapping factor maps, a result map showing the proper peri-urban areas for agriculture was obtained. The result map was compared with the existing land use plan and idle peri-urban areas were determined. These areas have different suitability level for agriculture. Considering their levels, land uses are proposed such as urban agriculture areas, nurseries, urban parks, natural recreation areas etc., and the impact of proposed land uses on city life and ecology were examined.

Keywords: *land evaluation, lands suitability, Simos Procedure, peri-urban agriculture, idle agricultural area.*

INTRODUCTION

Today, the rationalist use of natural resources is a significant component of economic growth and sustainable development. The land is not only a resource itself but it also contains many other resources. In the periphery of the cities, where the population growth and urbanisation have been increasing, certain areas are located or formed which are not put in use although they are ideal for agriculture. Among these lands, the ones which are close to the city are in danger of housing; and others that are far from the city are under the threat of abandonment. These lands, not having any specific potential of production, need to be determined and utilised through decisions of land use. This study aims to put forward a method for the determination of the idle peri-urban agricultural areas and develop certain land uses that will positively influence urban life and ecology.

According to Thapa and Murayama (2008) peri-urban zones are considered as a transitional zone between urban and rural areas. The habitat of a diversity of populations, the variation of land uses, the morphological conditions and densities of the built areas, the complex functional relations and the changing social structure are the characteristics of the peri-urban area (Adell, 1999; Tacoli, 2001; Allen, 2003). These characteristics of peri-urban area will be converted into the urban system. The transformation process decreases the cultivated area because of significant trend of city sprawl to urban and peri-urban agricultural areas (Zeng et al., 2005). As cities expand physically, the boundaries between urban, peri-urban and rural activity deface and merge, thereby, presenting opportunities for useful linkages (Rondinelli, 1985; Kaur, 1995).

For Branduini (2008) many zones are still agricultural spaces, traditionally cultivated or with new crops in vogue with the local population, or they are community gardens or areas illegally occupied by evermore permanent nomadic groups or by non-EU groups waiting for a visa (Russo et al., 2014). Whatever the configuration, they are “voids at the margins of the city” which will be inexorably absorbed or transformed by urbanisation (Russo et al., 2014). In developing countries, there is an important and continuously growing population in and near the cities including peri-urban areas. That population is depend on land which is one of natural resources, due to some needs such as food, water, fuel and harbouring (Allen, 2003). In urban and rural areas, sustainability is affected by some factors such as dynamic and changing commercial activities, natural resources, community and pollution in peri-urban areas which are intersection zones (Brook & Davila, 2000; Allen, 2003; Thapa & Murayama, 2008). Peri-urban agriculture shall enable a bypass for an ecologically negative development of large urban agglomerations, whereas urbanisation is driven by the desire for short run economic growth and wealth in ever growing cities (Neuppenau, 2002). According to Branduini (2008) other areas without significant agricultural value could provide support to urban activity for recreation, farm services (holidayfarms, riding schools, educational farms) and local produce (pickup fresh goods or products sale). Furthermore, maintenance costs for these ‘green’ areas are very low or negligible for society as long as they remain within the production system and are looked after by the same farmers. If they become urban parks, their management costs can be assimilated with those of the communal green belt which, if the agricultural land is amply extended, is the responsibility of society (Russo et al., 2014).

Among the idle areas near the cities, there might be certain lands which are suitable for agricultural activities and have nationwide commercial value, and besides them, there might also be areas that are appropriate for local agricultural activities and recreation. For the determination of the right uses, an important criterion is the suitability for agriculture. In previous studies, various features were analysed for the identification of suitability. Some of these features were topography, soil, hydrography, climate, geology, morphology and accessibility. For Akıncı et al. (2013) it is understood that there is no certain standard concerning the criteria to be taken into consideration when assessing land suitability potential for agriculture and that the criteria used in similar studies are usually those that are accessible. In these types of studies, the topographical and soil properties of land are widely used.

Collective usage of GIS (Geographic Information System) and multicriteria decision making methods have had many successful results. For instance, Thapa and Murayama (2008) used the criteria of soil, land use pattern, road accessibility, water resources accessibility and market accessibility in their studies. GIS and AHP (Analytic Hierarchy Process) were used for the analysis of the criteria. Mokarram and Aminzadeh (2010) considered chemical features of the soil, wetness, texture, slope, depth and topography and presented a GIS-based multicriteria land suitability evaluation using OWA (Ordered Weight Averaging). In another survey, Mendas and Delali (2012) developed a spatial decision support system using GIS and ELECTRE Tri (Élimination Et Choix Traduisant la Réalité) multicriteria analysis method. Their criteria were water reserve, drainage, chemical and structural features of soil, slope, labour availability and proximity. The parameters that Akıncı et al. (2013) used in their surveys were great soil group, land use capability class, land use capability sub-class, soil depth, erosion, other soil properties, slope, aspect and elevation. GIS and AHP were used for the analysis of the criteria. Jozi and Ebadzadeh (2014) considered various criteria under socio-economic and natural environment topics. Once again; GIS, Delphi method and AHP were used for the analysis of suitability.

This survey aims to determine the idle agricultural areas in the periphery of Manisa, a city in the west of Turkey; and put forward the agricultural and recreational activities that can be planned for this region. The main factors in this area, that are soil, hydrography, topography and accessibility, and the sub factors under this topic were mapped in GIS setting; and analysed through Simos Procedure, which is one of the multicriteria decision making methods. Manisa is the city that has the biggest increase in population proportionally in recent years and has a rapid urbanisation. Like the other cities that has the similar features, the periphery of the city is under the pressure of housing and settlement. Idle areas are becoming even larger as people living in country has the tendency to leave their lands and settle down the city. It is thought that if people attracted to the outside of the city at least for urban agriculture and recreational activities, it might have a positive effect on city life and ecology. For this reason, in the end of the survey various uses of idle areas in the periphery of the cities depending on their levels of appropriateness are suggested.

MATERIALS AND METHODS

Study Area

The study was carried out in the central district of Manisa, a western city of Turkey. The study area is located between the northern latitudes 38°27'17" and 38°55'55" and the eastern longitudes 27°6'58" and 27°39'41" (Figure 1). The square measure of the area is approximately 1250 km^2. According to the 2013 data of TUIK (Turkish Statistical Institute) (2014), the population of the centre, which consists of two districts - Şehzadeler and Yunusemre, is 364.332. It is the city that has the biggest increase in population proportionally in the region in recent 20 years, mainly due to immigrants from rural areas. (Manisa Municipality, 2014).

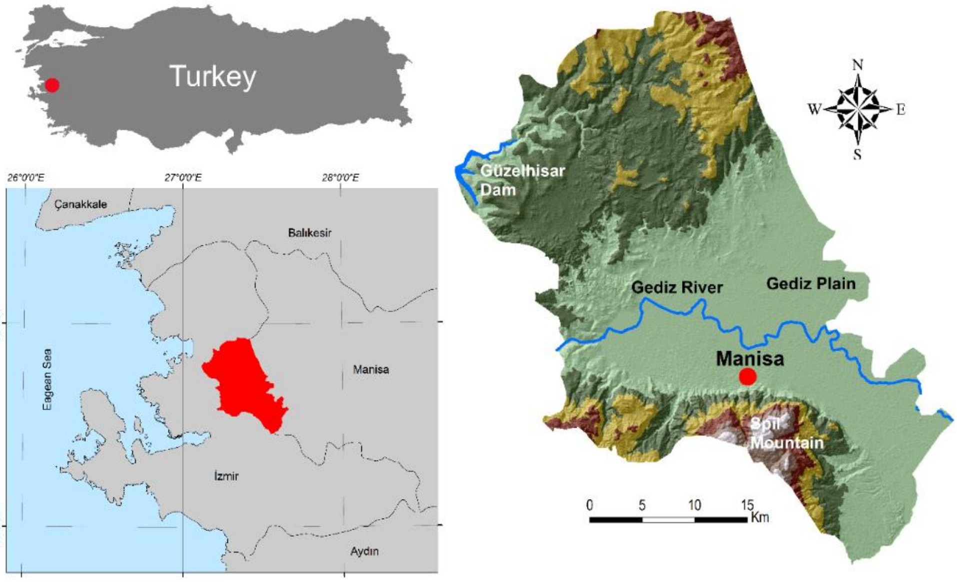

Figure 1. Location of study area

The city is settled at the foothill of Spil Mountain, the peak of which is 1517 m, and at the side of Gediz Plain, near River Gediz. Gediz Plain is significantly fertile, as it is full of alluvial deposits carried by streams and floods. A certain part of Gediz Plain, which has 30 km of length and 15 km of width, has become a residential and industrial area, owing to the growth in urbanisation in recent years. The development of the city is restricted by Spil Mountain and River Gediz in south and north. So, the growth of the city continues in west and southwest directions in a narrow lane. An anomalous housing move is seen in the east (Manisa Municipality, 2014). The city received 685.8 mm of rain between the years 1971-2013. According to the Erinc climate classification, the city has a sub humid climate, with a 31.73 Precipitation Effectiveness Index (MGM, 2014). Spil Mountain is a National Park and Tulipa orphanidea, which is known as ‘tulip of Manisa’ around the country, is the endemic species of it. The park area is a large field where various geological formations, a rich flora and historical and mythological characteristics coexist, and the highest examples of natural and cultural landscape are exhibited (DKMP, 2014).

The Mesir Paste Festival, held annually in the city, was added to UNESCO list of cultural heritage in 2012. Özbalcı and Var (2013) reported that Mesir is a big festival which has been celebrating for 500 years in Manisa. This festival is famous with a traditional paste. This special paste is very well known especially in Anatolian area. This paste is healthy, delicious and prepared with 41 different spices. Because of that Mesir Festival is related with both health and religion tourism.

When the soil characteristics of the field are analysed (Figure 2), it is seen that there are 9 GSG (Great Soil Groups) in the area. The proportion of alluvial soil is 22% and it covers Gediz Plain. Non-calcareous brown soil, mainly existing in north, has a rate of 22% and non-calcareous brown forest soil is 18%. When LUCC (Land Use Capability Classes) is examined, the proportion of class I, II, III and IV soil, that is the soil suitable for cultivation, is 46%. Agricultural lands, which are included in class I and II, are located in Gediz Plain, as it has a low altitude. On the other hand, Class VI and VII fields which are suitable for agriculture are also very common and they have a rate of 50%. According to LUCSC (Land Use Capability Sub-Classes), the area has a shortage of soil due to 50% loss of soil, resulting from slopes and erosion. This is a large area in the north, including Spil Mountain in the south. Northern and southern parts cover 40% of the area, where the level of erosion is severe. In low altitude areas, especially in the plain, the erosion level is no appreciable and these areas have a rate of 25%. However, it is at a moderate level at the hillside, which is the area that connects the plain to the mountains and forms 20% of the area. In the field, the soil with a depth over 90 cm has a proportion of 35%; soil with a depth between 0-20 cm has 34% and 20-50 cm deep soil has 27%. The deep soils are placed in the plain while shallow and too shallow lands lie across south-west-north direction. In the same lane, there is also a stony area with a rate of 43%. In 46% of the field, the OSP (Other Soil Properties) could not be determined owing to insufficient data.

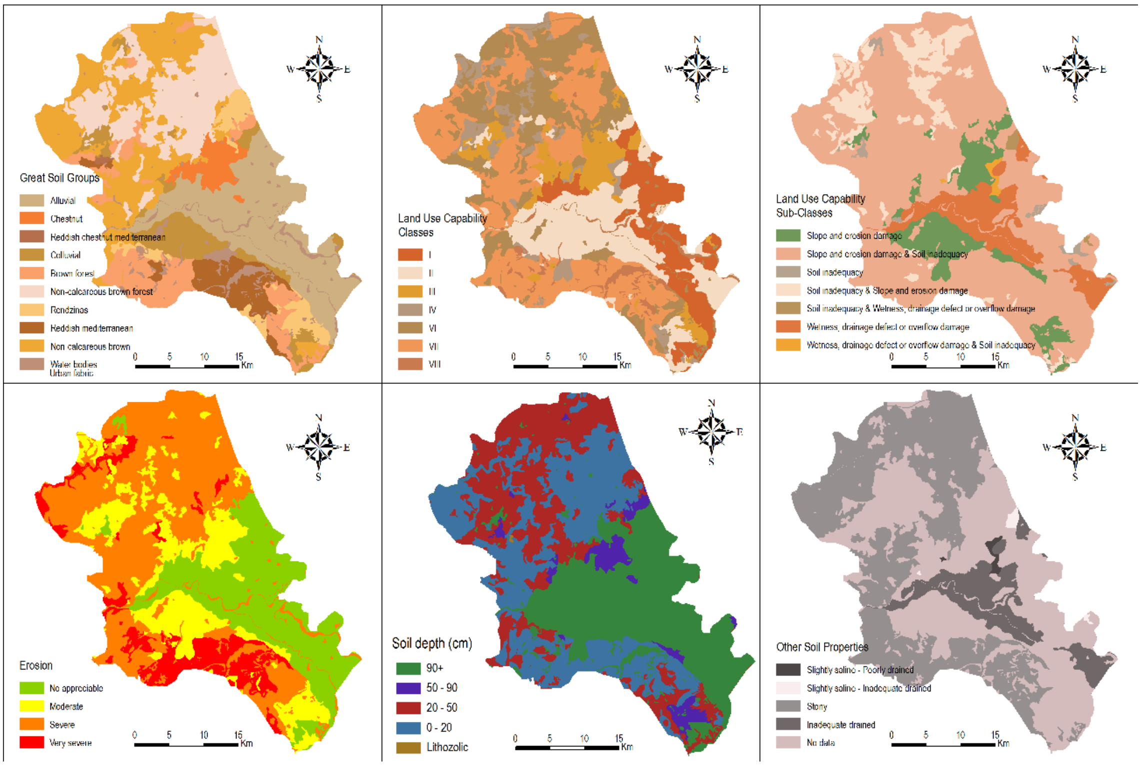

Figure 2. The soil feature maps: GSG, LUCC, LUCSC, Erosion, Soil depth, OSP

The peak of the field, as stated before, is Spil Mountain with a height of 1517 m. The lowest altitude is 18 metres and it is located in Gediz Plain. 82% of the area consists of fields with an altitude of 18-500 m. 12% land has 500-750 m height and the rest is above 750 m. The slope index map shows that 71% of the field has 0-2% of slope and 27% of it has 2-6% of slope. In the exposure map, only 6% of the area is flat and other aspects have an equal distribution. The topography maps were given on Figure 3.

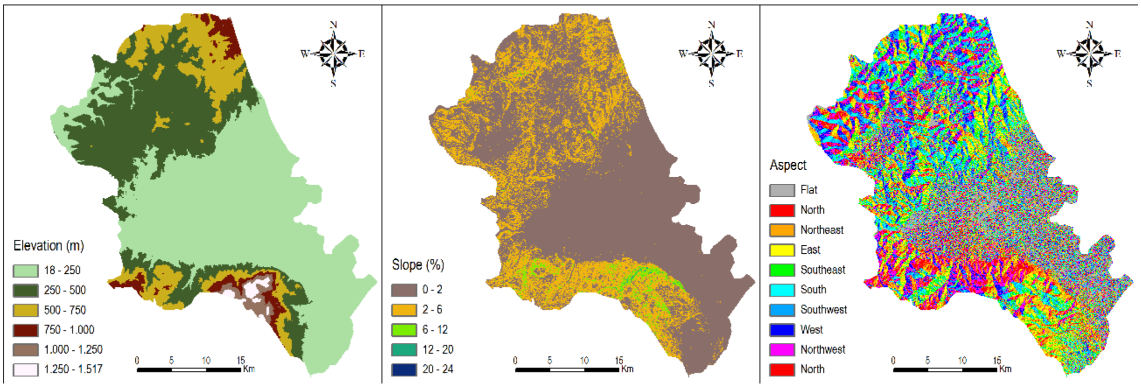

Figure 3. The topography maps: Elevation, Slope, Aspect

River Gediz, the largest stream in the area, divides the field into two, as north and south. Brooks Kara, Kemalpaşa, Irlamaz and many other brooks nearby feed River Gediz. In the north, brook and dam Guzelhisar are among the significant assets of water. Besides these, there are three lakes in the field; Akgöl, Lake Dambol and Lake Sülüklü, although they are not very large (Figure 4a).

The centre of Manisa city is set in the area between Spil Mountain and River Gediz. Other residential areas are mostly in the east. The highway between İzmir and Aydın runs across the city centre and divides the town into two. Similarly, the railway coming from the east in two lines passes through the city. There is also a transportation network in the area, consisting of 1st, 2nd and 3rd degree roads (Figure 4b).

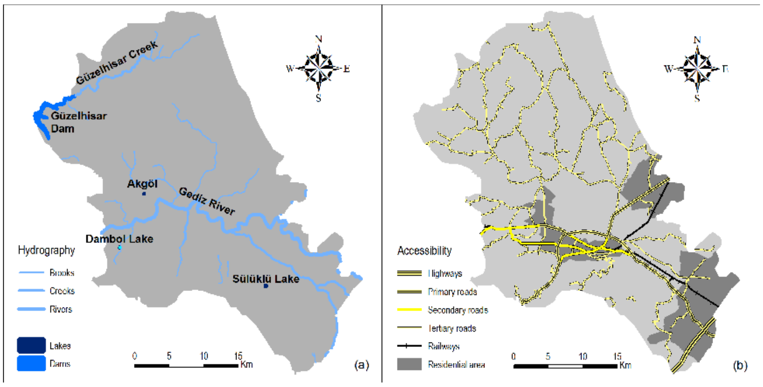

Figure 4. The hydrography map (a), The accessibility map (b)

Main and Subfactors Used in the Land Suitability Analysis

As stated above, this study aims to reclaim idle agricultural areas on periphery of Manisa. With this objective; firstly, certain areas, which are near the city and are left idle although they are appropriate for agriculture, are determined. A group of experts consisting of five individuals with different fields of specialty decided which factors will be considered on which level. These fields of specialty are Soil Science - Plant Nourishment, Horticulture, Landscape Architecture (2 persons) and Agricultural Structures - Irrigation. The specialists identified main and subfactors on Table 1, regarding the targeted urban agriculture and recreation based land uses.

Table 1: The main and subfactors

Main factors	Subfactors
Soil	GSG LUCC LUCSC Erosion Soil depth OSP
Hydrography	Distance to brooks Distance to creeks Distance to rivers Distance to lakes Distance to dams
Topography	Elevation Slope Aspect
Accessibility	Distance to highway Distance to other roads Distance to railway Distance to residential areas

Determining the Weights and Suitability Scores

The main and subfactors related to the area do not have the same rate of influence on land use suitability. So, the experts analysed firstly the main factors, and then the subfactors in themselves; and identified their weight. Simos Procedure, which is one of multicriteria decision making methods, was used for the assignment of the weights

In the decision process, the identification of the weights of the criteria is highly challenging, and Simos puts forward a simple method for this. Simos Procedure was developed and applied for wide-ranging problems. It is a process in which decision makers classify various criteria in various levels and this process is based on ‘card playing’ principal. It is a simple and practical technique continuing with the ranking and weighting of levels (Akpınar, 2003; Shanian et al., 2008).

For the application of the procedure, the decision maker is given a set of cards with main or subfactors written on them, besides some empty cards. Then, he / she is asked to array these cards in a specific order; starting with the most insignificant one and continuing with a regard to the importance level. Cards with the same level of importance are attached to each other to form a group. One or more empty cards are placed between the cards in order to increase the level of significance. A position number is assigned to each card; either an empty card or with a factor written on it. The position value of each factor is divided by the number of factors in that group; and the quotient is the starting weight of that factor. This arithmetic operation is not made for the empty cards. However, the normalised weight of each factor is calculated; the starting weight of the factor is divided by the sum of position values (except for the empty cards) and multiplied by 100. The normalised weights are written without a decimal (Akpınar, 2003). On Table 2, Simos Procedure, which was used by one of the decision makers, is given as an example. In this paper, the Simos Procedure is separately applied both to main and to subfactors. As there are multiple decision makers, the calculations are based on average weights.

Table 2: A sampe result of Simos Procedure

No	Main factor	Number of the cards n	Position of the card p	Beginning weight $W_b=p/n$	Normalized weight $W_n=(W_b/p_t)x100$	Integer weight	Main factor weight $W \sim W_n$
1	Topography	1	1	1	7.69	8	8
2	Discard	1	2	-	-	-	-
3	Accessibility	1	3	3	23.08	23	23
4	Soil Hydrography	2	4+5	4.5	34.62	35	70
			$p_t = 13$				101

Total weight of each subfactor (W_t) between 0-100 (±2) and among all subfactors is calculated by the following equation (1).

$$W_t = (W \times W_s)/100 \quad (1)$$

Where; W_t, total weight of the subfactor; W, weight of the main factor and W_s, weight of the subfactor. Subsequent to the identification of the weights, the specialists are asked to give suitability scores (between 1 and 5) to the targeted land uses regarding the suitability and eligibility. The weight of subfactor is multiplied by the suitability score; the product is the total suitability score of that sub factor qualification (2)

$$S_t = W_t \times S_{sq} \quad (2)$$

Where; S_t, total suitability score; W_t, total weight of the subfactor and S_{sq}, suitability score of the subfactor qualification.

Then, certain maps are created for each subfactor through GIS, and the scores are shown on these maps. The pixel size is determined to be 25 m x 25 m When the acquired analysis maps are overlapped, each pixel reaches the total suitability score. Through this process, a map of analysis is acquired; on this map, the range between the highest and the lowest scores is adjusted to PMUI (Physical Mapping Unit Index) (Table 3) and the suitability classes are determined for the targeted uses (FAO, 1977).

Table 3:Suitability classes according to PMUI

PMUI	Suitability class
0.90-1	S1: Highly suitable
0.75-0.89	S2: Moderately suitable
0.50-0.74	S3: Marginally suitable
0-0.49	N : Not suitable

On the final stage of the survey, the agricultural area suitability map is overlapped with the present land use map and the idle peri-urban areas are identified. Then, land uses are proposed regarding the characteristics of these areas.

FINDINGS

The Idle Areas Suitable for Agriculture

The suitability scores calculated through the applied method are shown on Table 4, 5, 6 and 7.

Table 4: The total suitability scores of the soil subfactor qualifications

Main factors and weights W	Subfactors and weights W_s		Total weight of the subfactor $W_t = (W \times W_s)/100$	Subfactor qualification	Suitability score S_{sq}	Total suitability score $S_t = W_t \times S_{sq}$
Soil 36.40	GSG	17.20	6	Alluvial	5.0	30
				Chestnut	3.6	22
				Reddish brown mediterranean	2.2	13
				Colluvial	3.6	22
				Brown forest	3.2	19
				Non-calcareous brown forest	2.6	16
				Rendzinas	3.4	20
				Reddish mediterranean	2.0	12
				Non-calcareous brown	3.4	20
	LUCC	28.00	10	I	5.0	50
				II	5.0	50
				III	4.4	44
				IV	3.6	36
				V	2.2	22
				VI	1.8	18
				VII	1.4	14
				VIII	1.2	12
	LUCSC	15.60	6	Slope and erosion damage	2.0	12
				Slope and erosion damage & Soil inadequacy	1.6	10
				Soil inadequacy	2.4	14
				Soil inadequacy & Slope and erosion damage	1.6	10
				Soil inadequacy & Wetness, drainage defect or overflow damage	1.0	6
				Wetness, drainage defect or overflow damage	2.0	12
				Wetness, drainage defect or overflow damage & Soil inadequacy	1.6	10
	Erosion	14.60	5	No appreciable	5.0	25
				Moderate	4.0	20
				Severe	1.8	9
				Very severe	1.0	5
	Soil depth (cm)	16.80	5	90+	5.0	30
				90 – 50	4.0	24
				50 – 20	2.6	16
				20 – 0	1.4	8
				Lithozolic	1.0	6
	OSP	8.80	3	Slightly saline – Poorly drained	1.8	5
				Slightly saline – Inadequate drained	2.6	8
				Stony	2.6	8
				Inadequate drained	3.0	8

Table 5: The total suitability scores of the topography subfactor qualifications

Main factors and weights W	Subfactors and weights W_s		Total weight of the subfactor $W_t = (W \times W_s)/100$	Subfactor qualification	Suitability score S_{sq}	Total suitability score $S_t = W_t \times S_{sq}$
Topography 16.20	Elevation (m)	33.20	5	18 – 250	5.0	25
				250 – 500	4.8	24
				500 – 750	4.4	22
				750 – 1000	3.8	19
				1000 – 1250	3.2	16
				1250 – 1517	2.4	12
	Slope (%)	30.00	5	0 – 2	4.2	21
				2 – 6	4.8	24
				6 – 12	4.4	22
				12 – 20	3.2	16
				20 – 24	2.6	13
	Aspect	37.20	6	Flat	3.6	22
				North	3.0	18
				Northeast	2.8	17
				East	3.2	19
				Southeast	4.2	25
				South	4.8	29
				Southwest	4.6	28
				West	3.6	22
				Northwest	2.6	16

Table 6: The total suitability scores of the hydrography subfactor qualifications

Main factors and weights W	Subfactors and weights W_s		Total weight of the subfactor $W_t = (W \times W_s)/100$	Subfactor qualification	Suitability score S_{sq}	Total suitability score $S_t = W_t \times S_{sq}$
Hydrography 34.60	Distance to brooks (m)	9.00	3	0 – 500	4.8	14
				500 – 1000	4.4	13
				1000 – 3000	3.2	10
				3000<	2.2	7
	Distance to creeks (m)	22.80	8	0 – 500	5.0	40
				500 – 1000	4.6	37
				1000 – 3000	3.4	27
				3000<	2.4	19
	Distance to rivers (m)	26.40	9	0 – 500	5.0	45
				500 – 1000	4.6	41
				1000 – 3000	3.4	31
				3000<	2.2	20
	Distance to lakes (m)	19.40	7	0 – 500	5.0	35
				500 – 1000	4.2	29
				1000 – 3000	2.8	20
				3000<	1.8	13
	Distance to dams (m)	22.40	8	0 – 500	3.8	30
				500 – 1000	3.8	30
				1000 – 3000	3.0	24
				3000<	2.6	21

Table 7: The total suitability scores of the accessibility subfactor qualifications

Main factors and weights W	Subfactors and weights W_s		Total weight of the subfactor $W_t = (W \times W_s)/100$	Subfactor qualification	Suitability score S_{sq}	Total suitability score $S_t = W_t \times S_{sq}$
Accessibility 13.00	Distance to highway	23.60	3	0 – 1000	4.0	12
				1000 – 2000	3.8	11
				2000 – 3000	3.6	11
				3000<	3.2	10
	Distance to other roads	25.40	3	0 – 1000	4.2	13
				1000 – 2000	4.2	13
				2000 – 3000	3.6	11
				3000<	3.0	9
	Distance to railway	11.60	2	0 – 1000	2.8	6
				1000 – 2000	2.8	6
				2000 – 3000	2.6	5
				3000<	2.4	5
	Distance to residential areas	39.60	5	0 – 1000	4.4	22
				1000 – 2000	4.4	22
				2000 – 3000	4.2	21
				3000<	3.2	16

The suitability scores are conveyed to the subfactor maps and each main factor is analysed in itself. So, the suitability maps are created (Figure 5).

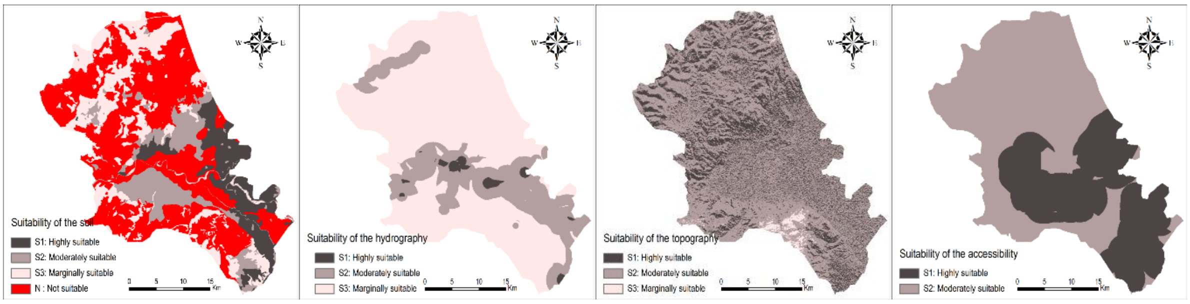

Figure 5. Suitability maps: Suitability of the soil, Suitability of the hydrography, Suitability of the topography, Suitability of the accessibility

The total suitability score map (Figure 6a) is formed through the overlapping of all suitability score maps. The suitability classes map (Figure 6b) is created by the classification made according to PMUI. The examination of the suitability classes map shows that the areas that are highly suitable for agriculture (S1) are the flat and almost flat lands of alluvial soil lying through Gediz Plain at the side of River Gediz. Right after them, the lands that have a moderate level of suitability (S2) are located on flat areas and hills with a slight slope. On the other hand, the lands that have a marginal level of suitability (S3) lie across the plateaus with a high altitude and wavy topography; they are also far from the plain and cover a very large surface. No not suitable (N) type areas are retained through the analysis.

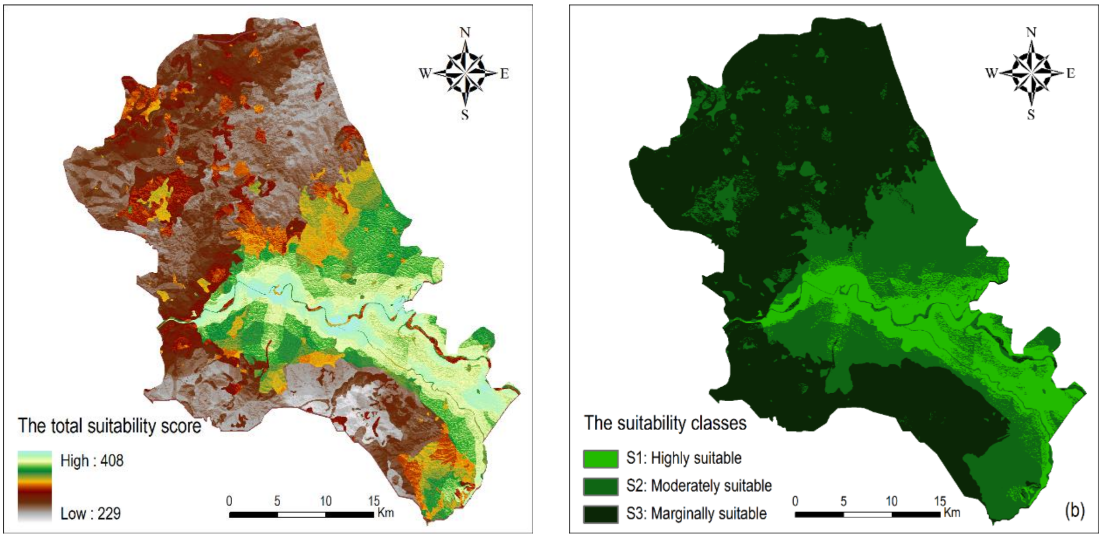

Figure 6. The total suitability score map (a), The suitability classes map (b)

The suitability classes map is compared to the data related to the use of available lands which is provided by the Ministry of Environment and Urban Planning (2011) (Figure 7a) and the idle agricultural peri-urban areas are determined, excluding the protected areas, residential areas, forests and agricultural areas (Figure 7b).

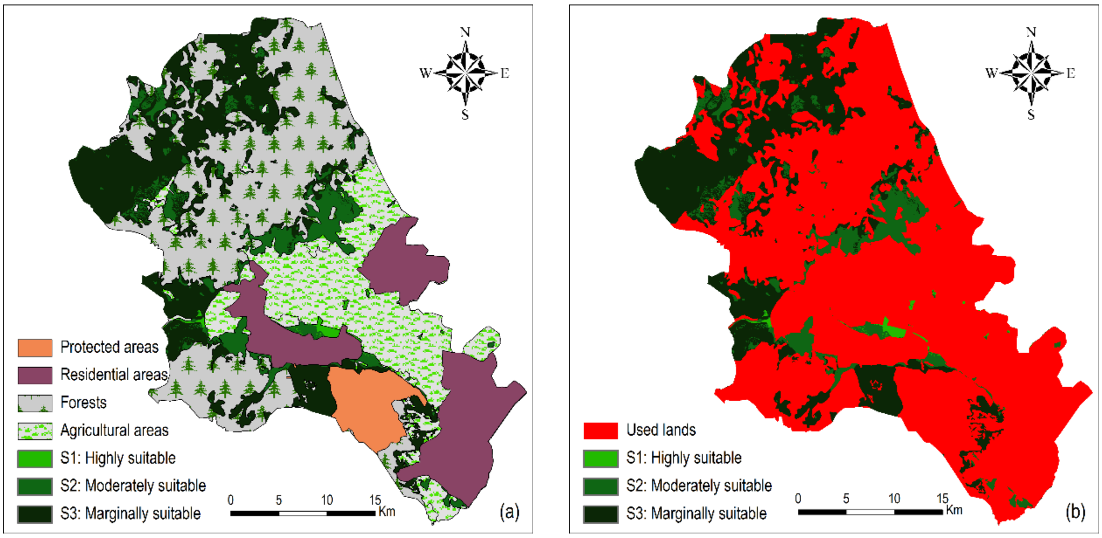

Figure 7. The comparison of the suitability classes and the present land use (a), Idle peri-urban agricultural areas (b)

The Land Use Proposals

To be able to make them recognisable, the areas that are left idle although they are suitable for agriculture are enumerated according to their features (Figure 8). The parts number 1 and 3 include the areas with the suitability class of S1 and S2. They are also close to the city centre and transportation network. It would be beneficial for the city if these areas are converted into urban green space areas without structural elements. According to Adinalfi et al. (2014), the green spaces in and near the cities are regarded as an important indicator of the ecology of the city and the quality of life in that location. They have direct influence on the climate of the city by decreasing the heat island effect, providing shadows and reducing the surface temperature. Moreover, they contribute to the decrease in emission rate and increase in air quality. They also absorb the dust and noise in industrial and residential areas. They are the habitat for the vegetation fauna. It is known that urban green spaces help the treatment of patients and reduce stress.

The area number 2, which includes the S2 lands is right along the Spil Mountain National Park and the city centre. It can be made use of similar to the area number 1, or utilised as urban agriculture, urban park, natural recreation and afforestation area. The distance between the part number 4 and the border of city centre is approximately 4 km. It mainly consists of class S3 lands. Due to its greatness and the nearness to the transportation network, it will satisfy the need of the city if it is planned to be city park including festival areas. The parts number 5 and 6 consist of class S3 lands which are included in the forestland. Specifically, it would be right for the part number 6 to be afforested and be a buffer zone between the residential area and the National Park. As the part number 7 contains class S2 lands, it should be used for agricultural activities. For instance; certain uses like organic farming, plant nurseries and peri-urban agriculture are regarded as the suitable preferences for this area. Part number 8 is the area that includes the class S3 lands near Güzelhisar Dam. It is 18 km to the nearest residential area. It would be proper that this area is planned to be natural recreation area, having the advantage of the view of the dam, and also as an afforestation area. The part number 9, which is in the north east of this area, seems to be suitable for agricultural activities. However, this part should be converted into an afforestation area as it is multipartite and far from the city. The part number 10 has class S3 lands and it is the furthest part of the study area from the city centre. It is ineligible for various uses as it is difficult to access and its class of suitability is low. It should be planted like the natural vegetation nearby. The part number 11 consists of the fragmentary class S3 lands, which are included in the forest. It is suggested that they are afforested according to the selection of appropriate tree species.

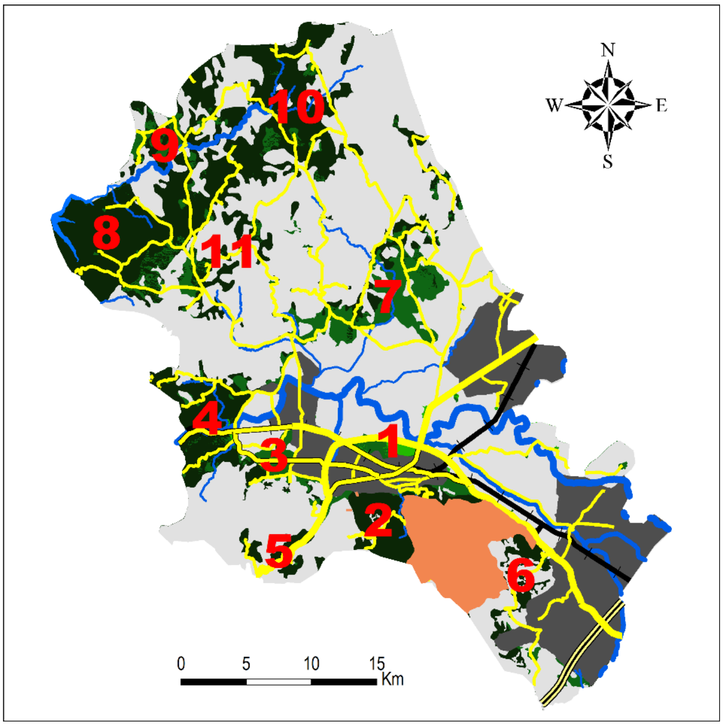

Figure 8. The result map (The numbered idle agricultural peri-urban areas)

CONCLUSIONS

It is possible to regain the idle agricultural areas near the city. The first step to do this is to determine these areas and identify their suitability for agriculture. This is a quite long and challenging process. In developing cities, the periphery of the city is specifically under threat and the right planning decisions related to these areas should be taken urgently. In this survey, GIS and Simos Procedure, one of the multicriteria decision making methods, are collectively applied; and a fast, practical and reliable technique is put forward. In GIS; certain and clear numerical analyses are made, which are also recognisable on maps. Also, as the experts applying the Simos Procedure are from various disciplines, the reliability of the method is increased. The areas that are not utilised for many reasons and not expected agricultural production despite being suitable can be converted into green spaces that will influence urban life and ecology positively. Some of these land uses are urban or peri-urban agriculture, urban parks, natural recreation areas, plant nurseries and reforestation. The acquired results will help the decision makers, who have a voice in planning, to evaluate the peri-urban resources properly and effectively.

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REFERENCES

Adell, G. (1999). Theories and models of the peri-urban interface: a changing conceptual landscape. *Strategic Environmental Planning and Management for the Peri-urban Interface Research Project,* Development Planning Unit, University College London, UK.

Adinolfi, C., Suárez-Cáceres, G. P., & Cariñanos, P. (2014). Relation between visitors' behaviour and characteristics of green spaces inthecity of Granada, south-easternSpain. *Urban Forestry & Urban Greening*, 13 (2014) 534–542.

Akıncı, H., Özalp A. Y., & Turgut, B. (2013). Agricultural land use suitability analysis using GIS and AHP technique. *Computers and Electronics in Agriculture,* 97 (2013) 71-82.

Akpınar, N. (2003). Sürdürülebilir Alan Kullanım Planlamasında Alan Kullanım Tiplerine Ait Önceliklerin Simos Prosedürü ve ELECTRE I Yöntemi ile Belirlenmesi. *Ankara University, Journal of Agricultural Sciences*, 9 (2), 234-242.

Allen, A. (2003). Environmental planning and management of the peri-urban interface: perspectives on an emerging field, *Environment & Urbanization,* 15 (1), 135-147.

Branduini, P., 2008. La gestione delle trasformazioni nel paesaggio agricolo periurbano. Permanenze storiche e paesaggi futuri. In: Colantonio Venturelli, R. (Ed.), I paesaggi d'Europa tra storia, arte e natura (European Landscapes: History, Artand Nature). *Conferenza Trilaterale di Ricerca 2005–2007*. Deutsch-Italienisches Zentrum Centro Italo-Tedesco, pp. 272–290.

Brook, R.M., & Davila, J.D. (2000). The Peri-Urban Interface: A Tale of Two Cities. School of Agricultural and Forest Sciences, University of Wales and Development Planning Unit, University College London, UK.

DKMP, (2014). Turkish Directorate of Nature Conservation and National Parks. http://www.milliparklar.gov.tr/mp/spildagi/index.htm, (Accessed online 15.08.2014).

FAO, (1977). A Framework for Land Evaluation. Wageningen: International Institute for Land Reclamation and Improvement/ILRI. Publication 22.

Jozi, S. A., & Ebadzadeh, F. (2014). Application of Multi-Criteria Decision-Making in Land Evaluation of Agricultural Land Use. *Journal of the Indian Society of Remote Sensing*, 42 (2), 363–371.

Kaur, R., (1995). Urban-Rural Relation: A Geographical Analysis. Anmol Publication Pvt. Ltd., India.

Manisa Municipality, (2014). Strategic Plan (2010-2014). http://www.manisa.bel.tr/files/Kurumsal/StratejikPlan/Stratejik_Plan_2010-1.pdf, (Accessed online 15.08.2014).

Mendas, A., & Delali, A., (2012). Integration of MultiCriteria Decision Analysis in GIS to develop land suitability or agriculture: application to durum wheat cultivation in the region of Mleta in Algeria. *Computers and Electronics in Agriculture*, 83, 117−126.

MGM, (2014). Turkish State Meteorological Service. http://www.mgm.gov.tr/iklim/iklim-siniflandirmalari.aspx?m=MANISA, (Accessed online 15.08.2014).

Mokarram, M., & Aminzadeh, F., (2010). GIS-based multicriteria land suitability evaluation using ordered weight averaging with fuzzy quantifier: a case study in Shavur Plain, Iran. *The International Archives of the Photogrammetry, Remote Sensing and Spatial Information Sciences,* 38 (II), 508−512.

Neuppenau, E. A. (2002). Agro-Ecologically Oriented Land Use and the Creation of Viable Rural Urban Interfaces. *2nd Newsletter March 2002,* Peri-Urban Development in South East Asia.

Özbalcı, S., & Var, T. (2013). Mesir Festival with an economic perspective. *Celal Bayar University, Journal of Social Sciences,* 11 (3), 488-497.

Rondinelli, D.A., (1985). Applied Methods of Regional Analysis: The Spatial Dimension of Development Policy. Westview Press, Boulder / London.

Russo, P., Tomaselli, G., & Pappalardo, G. (2014). Marginal periurban agricultural areas: A support method forlandscape planning. *Land Use Policy,* 41 (2014) 97–109.

Shanian, A., Milani, A. S., Carson, C., & Abeyaratne, R. C. (2008). A new application of ELECTRE III and revised Simos’ procedure for group material selection under weighting uncertainty. *Knowledge-Based Systems,* 21 (2008), 709–720.

Tacoli, C. (2001). Livelihoods impacts and strategies of the periurban poor. *In: Proceedings of the Conference on Rural-Urban Encounters:* Managing the Environment of the Periurban Interface, London, UK.

Thapa, R., & Murayama, B. (2008). Land evaluation for peri-urban agriculture using analytical hierarchical process and geographic information system techniques: A case study of Hanoi. *Land Use Policy,* Land Use Policy 25 (2008) 225–239

Zeng, H., Sui, D.Z., & Li, S., (2005). Linking urban field theory with GIS and remote sensing to detect signatures of rapid urbanization on the landscape: toward a new approach for characterizing urban sprawl. *Urban Geography*, 26, 416–434.

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PHYTOREMEDIATION OF CRUDE OIL POLLUTED SOILS

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ABSTRACT

Phytoremediation technology variants of crude oil with different species of plans is an important field of research and application in situ, in oil exploitation and processing regions. Value number of legume and grasses species tolerate and grown on soil with high pollution level of crude oil compounds. In a period of particular vegetative cycle plants cleaning efficiency of 18.5-28.6g$\cdot$*kg*$^{-1}$ *level crude oil polluted soil fertilized with sewage sludge increased for leguminous species with 12.5-16.5% for Vicia sativa and Glycine max., with 33.0% for Onobrychis viciifolia and for herbaceous species Lolium perenne with 64.4% vs. similar polluted unfertilized experimental variant. Addition of volcanic indigenous tuff amendment mixed with sewage sludge, increases reduction efficiencies of crude oil compounds in polluted soil for leguminous crops up to 73% and also for herbaceous crop of Lolium perenne which was cleaning polluted soil with 68% vs. similar polluted unfertilized and unamended experimental variant. The ability specific metabolic mechanism of plant species to removal crude oil compounds from high polluted soils can restore destroyed areas for further agricultural use. Choice of adequate plant species for phytoremediation technologies will be ultimately based on the quality and quantity of harvest.*

Key words: *phytoremediation, oil polluted soil, sewage sludge, volcanic tuff.*

INTRODUCTION

Phytoremediation technology of crude oil polluted soil with different species of plants is an important field of research and application in situ, in oil contaminated regions (Collins, 2009). Many plants, through their own metabolism, have the capacity to biodegrade soil crude oil compounds. Studies done in the area of phytoremediation of soils polluted with oil products report the biodegrading of certain hydrocarbons by plant species selected for this purpose. The selection of plants in the process of phytoremediation is the required condition which can determine an increased capacity of adaptation of cultures to specific conditions of the polluted soil. If appropriate plants are selected, they can cover a maximum area of vegetation on the polluted land and develop significantly their root system underground. The vegetative cover will be the framework of a restored landscape, the biomass will enter the matter circuit, and roots will be the ones determining to a high degree the biodegradation of crude oil compounds/ total petroleum hydrocarbon, (TPH).

THEORY

From an economic point of view, for phytoremediation are selected plants that necessitate the least support, based on common agricultural works. From this point of view, phytoremediation studies considered the Graminaceae family, composed of numerous herbaceous species that can develop under these conditions. The plants from this family develop a strong fibrous root network. These roots go gradually deep into the soil, both vertically and horizontally (Zhou et al., 2011). Leguminous plants can be used in phytoremediation of soils polluted with oil products (Bento et al., 2005) because their implementation is done with low cost and exhibit great capacity of adaptation to polluted soils. Many legumes (Fabaceae) establish symbiotic associations with nitrogen fixing bacteria and all the leguminous species are associated with mycorrhizal fungi. The relationship with the nitrogen fixing bacteria is favorable to leguminous species when developing on soils polluted with oil products with very high C:N ratio that (Bento et al., 2005). Legumes are dominant plants on 15 areas from Europe polluted with oil products (Gudin and Siratt, 1975).

There are many leguminous species studied, grown on different soils, having a C:N ratio within a large domain, in which carbon is given by pollutant substances, oil hydrocarbons (Farias et al., 2009; Kaimi et al., 2007). The results of the studies show that plant species from the Fabaceae family cannot survive under conditions in which the hydrocarbon content is very high (Kaimi et al., 2007).

It is recommended that more studies be done to elucidate how plant species from the Fabaceae family can be judiciously applied in the processes of biodegradation of oil products or detoxification of polluted soils (Bento et al., 2005; Gudin and Syratt, 1975), report that leguminous plats are more tolerant to the presence of hydrocarbons in soils, because these plants have the ability to fix nitrogen, which is deficient in the soils polluted with hydrocarbons. Nitrogen is up-taken by these plants from the atmosphere and is metabolically fixed in soil in the rhizosphere area. Another factor that can affect the germination of seeds in polluted soils is seed size.

Many studies show that big seeds tolerate better the conditions offered by a soil poor in nutrients, than small seeds due to the presence of different quantities of nutrients from the seed that represent the support for it during the first stages of development as plant (Kolawole and Kang, 1997).

Kirk et al., (2005), report that plants determine the increase of microorganisms’ number from rhizosphere, phenomenon known as rhizosphere effect. From our study it is suggested that 2 different plant species: a monocotyledon *(Lolium perenne* – a perennial grass with fibrous root) and a dicotyledonous species (*Medicago sativa* – a plant with tap roots), grown on a soil polluted with TPH (31 $g^{\cdot}kg^{-1}$of D.M.), use a specific mechanism to facilitate phytoremediation. The monocotyledonous species provides a support for the increase of the general activity of microorganisms, which leads to the increase of microbial number in the rhizosphere. Microorganisms’ metabolism is specifically catabolic. The leguminous plant determined the increase of the specific microbial number capable to degrade more complex hydrocarbons. Thus, plants, depending on the vegetative metabolism, determine important changes in the structure of biocenosis of polluted soils, both qualitatively and quantitatively.

Nyoku et al. (2009), report that selected plants to phytoremediate must be appropriate to the pedo-climatic conditions of the polluted areas. Nyoku et al. (2008), also report that plants must have the capacity to tolerate stress conditions and demonstrate that soy beans germinate and grow on soils polluted with crude oil. The leguminous culture of soy alters the physical-chemical characteristics of soils polluted with oil products. The results of this study indicate that soy cultivated on oil polluted soils modifies the physical-chemical properties of the soil and increase the intensity and degree of biodegradation of soil oil products. Important effects are produced on the pH of soil and degree of water retention. Plants determine a slight increase of soil pH. Water retention increases in time and is most obvious in crops cultivated on highly pollutes soils.

Soy plants (*Glycine max*) degrade anthracene (Edwards et al., 1982). Other authors have studied the potential of numerous plant species to biodegrade oil hydrocarbons. Reilley et al., (1996), have reported the behavior of plants from *Medicago sativa, Festuca arundinaceea* and *Sorghum vulgare* species.

There is no method accepted as standard. Some researchers suggest that the process of selection of plants for phytoremediation must be done monitoring the plant development stages. Other studies consider the abundance index of plants compared to the degree of pollution with oil products in the studied soil.

The aim of this study was to analyze, comparatively, the phytoremediation process of some soils polluted with 18.5-28.6g $TPH^{\cdot}kg^{-1}$ D.M. with leguminous species (*Vicia sativa, Glycine max* and *Onobrychis viciifolia)* and grass species *(Lolium perenne*): 1– the efficiency of TPH reduction at rhizosphere level, 2– the influence of a fertilizer – sewage sludge – on the TPH biodegradation level, 3– the influence of an amendment – ground indigenous volcanic tuff – used as fertilizer, 4– the biomass harvested from the experimental variants.

METHODS

The experimental study was done on non-polluted, control soils and soils sampled from a point of collection of crude oil. Soil pollution started with the activity of soil extraction of crude oil in the area, 10 years ago. The areas of polluted soil around the mining probes and pipes cover tens and hundreds of square meters and are caused by accidental leaks, failures etc. the experimental study was done in vegetation pots filled with 6.5 kg of soil polluted with 18.5-28.6 g $TPH_{\cdot}kg^{-1}$ D.M., well homogenized. Soil was sown with leguminous species (*Vicia sativa, Glycine max* and *Onobrychis viciifolia*) and grass species (*Lolium perenne*).

The experimental variants of studied soil were: 1. Non-poluted soil, M; 2. Soil polluted with oil products, P; 3. Soil polluted with oil products fertilized with sewage sludge anaerobically stabilized 15 t/ha D.M., PN; 4. Soil polluted with oil products, fertilized with sludge and treated with indigenous volcanic tuff in a quantity of 2.5% vs. soil quantity, PTN.

To determine the TPH from the soils an analysis is performed periodically of the concentration [8], in the upper level:1) 3-5g of dry soil are weighed (**M**), then add 5g Na_2SO_4 anhydrous and 25ml petroleum ether p.a.; 2) 30 minutes stirring at 50 rotations/min and then filtered; 3) the glass and filter paper are washed with petroleum ether, which is added to the filtrate; 4) the filtrate is evaporated on water bath; 5) the residue is dissolved in petroleum ether, then passed through the chromatographic column filled with aluminium oxide. The elute collected in a tarred capsule; $\mathbf{m_1}$ [g]; 6) petroleum ether is evaporated at room temperature and weighed at constant mass $\mathbf{m_2}$ [g]; 7) the same is done for the control from 28 ml petroleum ether ($\mathbf{m_3}$ – mass of capsule without control residue [g], $\mathbf{m_4}$ – mass of capsule with control residue [g]); 8). Calculating TPH: TPH [$g \cdot kg^{-1}$] $=1000\cdot[(\mathbf{m_2}-\mathbf{m_1})-(\mathbf{m_4}-\mathbf{m_3})]\cdot\mathbf{M^{-1}}$

FINDINGS

Sewage sludge characteristics: Sewage sludge had a humidity of 85.8%, an organic content of 66.4%, total nitrogen content 0.63%, phosphorous 0.55%, pH=6.8.

Characteristics of the indigenous volcanic tuff: Volcanic tuff comes from Marsid quarry and contains approximately 70% clinoptilolite. The used volcanic rock has a granulation of 0.2-2mm and was spread on soil before spreading the sewage sludge.

Characteristics of the leguminous species studied for phytoremediation:Onobrychis viciifolia is a melliferous and fodder plant. Spontaneously growing on plains. Perennial plant. Stalked spike of bright pink flowers. Hollow stems of 60-80 cm. Studies were done on soils with content of 28.6±2.3 g $TPH_{\cdot}kg^{-1}$ D.M. *Vicia sativa* is a sprawling annual herb, with hollow, four-sided, hairless to sparsely hairy stems which can reach two meters in maximum length. Spontaneous plant found in crops, cereals, pastures, meadows, and along roads. Grown in mixture with oats, forming spring fodder. Studies were done on soils with content of 28.6±2.3 g $TPH_{\cdot}kg^{-1}$ D.M. *Glycine max* – soy is a leguminous plant from the Faboideae subfamily. Soybeans play an important role in food industry, containing 39% proteins, 17% oils. Vegetation period is 108-145 days depending on maturity group. Harvest in September – October. Studies were done on soils containing 18.5±2.3 g $TPH_{\cdot}kg^{-1}$ D.M. *Loilum perenne* – generally prefers meadows and lowlands. It is one of the most valuable pasture perennial grass with exceptional quality in animal feeding. The species is characterized by high yields. It is the basic species in simple and complex mixtures of grasslands due to durability and competitiveness with other species. Uses well mineral and organic fertilizers, giving high and constant yields. It is typical grass for grazing as it withstands threading and has a quick recovery. Studies were done on soils containing 28.6±2.3 g $TPH_{\cdot}kg^{-1}$D.M.

DISCUSSION

The addition of the used fertilizing agent is needed as nitrogen supplement, as well as for the formation and maintenance of the activity of biocenosis in the polluted soil. Study reports from literature show that soils polluted with oil products must be fertilized with fertilizing agents that facilitate oil carbon conversion in humic products (Kim and Owens, 2010).

The indigenous volcanic rock was introduced in soil to increase the water retention capacity of soil. This decreases dramatically when oil products are present in the soil. Water is not capable to infiltrate in soil when it contains crude oil. Low water retention capacity determines de reduction of organic compound degradation by microorganisms. To increase water retention, specialty literature indicates the necessity to use amendment that contributes to the improvement of this soil characteristic. (Wyszkowski and Ziolkowska, 2009). Indigenous volcanic tuff was added to retain water in its porous structure, releasing small quantities when needed by plants (Liang et al., 2009).

Table 1 shows selectively reference values (according to MAPPM Order 756/1997) for the total hydrocarbons from oil present in soils. The studied polluted soils have a TPH content 9.0-15.5 times higher than the admitted values for pollutants imposed by the current normative (category: intervention threshold/use types: soil less sensitive at value of 2.0 $g \cdot kg^{-1}$ D.M).

Table 1: Selective reference values (according to MAPPM Order 756/1997) for total petroleum hydrocarbons present in soils [$mg \cdot kg^{-1}$ D.M.]

Pollutant	Normal values	Alert thresholds /Use types		Intervention thresholds/Use types	
		Sensitive	Less sensitive	Sensitive	Less sensitive
Total petroleum hydrocarbons	100	200	1000	500	2000

Table 2 shows the graph of agricultural works/vegetation periods of plants, destination of harvested biomass and quality of vegetative cover.

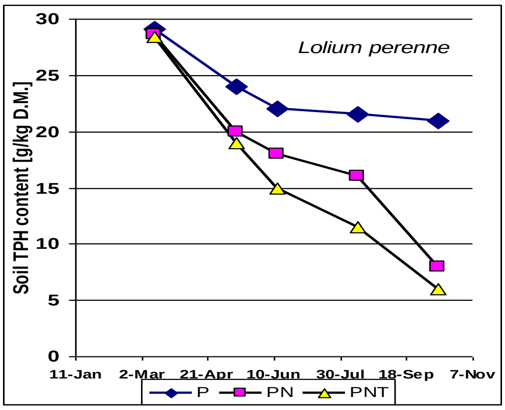
Table 2: Graph of agricultural works/vegetation periods of plants, destination of harvested biomass and quality of vegetative cover

No	Plant species/ culture destination	Seeding	Sprouting period	Vegetation period/ harvest	Observations
1	*Lolium perenne*/ Pollution reduction/Green mass for composting	29.03. 20xx	10-16.04. 20xx	200 days with three successive harvests	Installed vegetation: perennial vegetative cover
2	*Onobrychis viciifolia* Pollution reduction/Green mass for composting	29.03. 20xx	08-12.04. 20xx	65 days green biomass harvest	Vegetation dried after harvest
3	*Vicia sativa* Pollution reduction/Green mass for composting	29.03. 20xx	11-20.04. 20xx	45 days with one green biomass harvest	Vegetation dried after harvest
4	*Glycine max (L.)* Seed obtaining	04.03. 20xx	01-06.04. 20xx	145 days biomass harvest	Stems and beans were harvested

Table 2 shows that harvested green biomass is used for compost for *Lolium spp.*, *Onobrychis spp* and *Vicia spp* and to obtain seeds for subsequent seeding for *Glycine max*. Soy stems can be directed towards compost mixtures. *Onobrychis spp.* and *Vicia spp.*, after green mass harvesting, dry up, and the grass culture is maintained as a healthy perennial vegetative cover. The situation is similar with literature reports that demonstrated that leguminous plants do not survive on soils polluted with oil products a period as long as the grass species do (Kulakov et al., 2000).

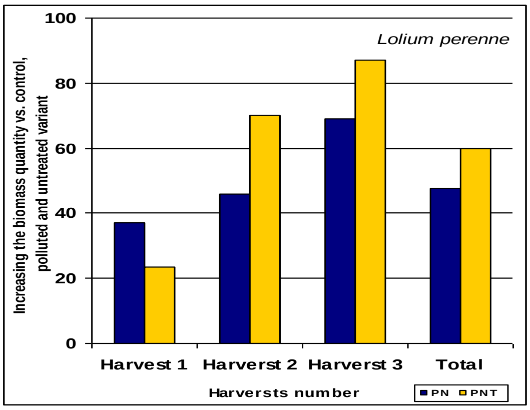
Phytoremediation of TPH polluted soil with *Lolium spp*.

Polluted soils having an initial pollution level at surface of 28.6±2.3 g TPH·kg^{-1} D.M., were used in the experimental study done with a culture of herbaceous plants from the grass species of *Lolium spp*, during 29.03.-26.10.20xx. TPH content variation in the studied soils during the analyzed period is shown in figure 1a. for the 200 day period monitored in the study, TPH quantity decreases in the polluted soils fertilized with sewage sludge by 64.4% vs. the remnant quantity at seven months in the non-fertilized polluted soil, cultivated with the grass species. Tuff addition to the polluted soil and fertilization with sewage sludge determined a decrease of TPH content up to 68.0% vs. the remnant quantity at 7 months in the non-fertilized polluted soil.



a)

Figure 1a. TPH variations from soil variants polluted with 28.6±2.3g TPH·kg^{-1} D.M., non-fertilized/fertilized in the absence/presence of volcanic tuff and 145 days cultivated with Lolium spp.



b)

Figure 1b. Increase of green biomass, Lolium spp., harvested from TPH soils polluted, fertilized in the absence/presence of volcanic tuff vs. harvested from the non-fertilized polluted soil

Figure 2 shows that the harvested biomass quantity from the polluted soil fertilized is up to 38% than the one from the non-fertilized polluted soil. Tuff addition determine a positive effect of increase of biomass quantity. At the second harvest the grass quantity increases up to 40% more than the one harvested from the non-fertilized polluted soil, and at the third harvest it goes up to 70%. Tuff addition determined at the second and third harvest an increase in grass mass compared to the first harvest. Indigenous volcanic tuff showed a stimulatory effect regarding plant metabolism and their development during warm summer months.

Phytoremediation of TPH polluted soil with *Onobrychis spp.* and *Vicia spp.*

Polluted soils having an initial pollution level at surface of 28.6 ±2.3 g TPH·kg^{-1} D.M. were used in the experimental study done with a culture of leguminous plants from species of *Onobrychis spp* and *Vicia spp.* TPH content variation from studied soils during the analyzed period is shown in figure 2. Figure 2a shows the variation of TPH in the case of soils cultivated with *Onobrychis spp* during a period of 65 days, and figure 2b shows the variation of TPH in the case of soils cultivated with *Vicia spp.* during a period of 45 days. TPH decreases in polluted soils fertilized with sewage sludge by 33.0% vs. the remnant quantity at 65 days in the non-fertilized polluted soil cultivated with *Onobrychis spp*. In the case of soil cultivated with *Vicia spp.* TPH quantity decreases in polluted soils fertilized with sewage sludge by 16.5% vs. the remnant quantity at 45 days in the non-fertilized polluted soil. Volcanic tuff addition to the variants fertilized with sewage sludge determined the activation of soil/plant metabolism, fact demonstrated by a high consumption of petroleum products and a decrease of soil TPH content up to 73% vs. the remnant quantity at 65 and 45 days in the non-fertilized polluted soil.

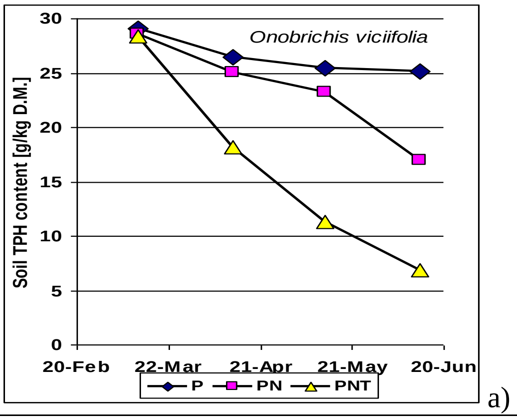


Figure 2a.Variation of TPH from variants polluted soil with 28.6±2.3 g·kg^{-1} D.M., non-fertilized/ fertilized in the absence/presence of volcanic tuff and 65 days cultivated with Onobrychis spp

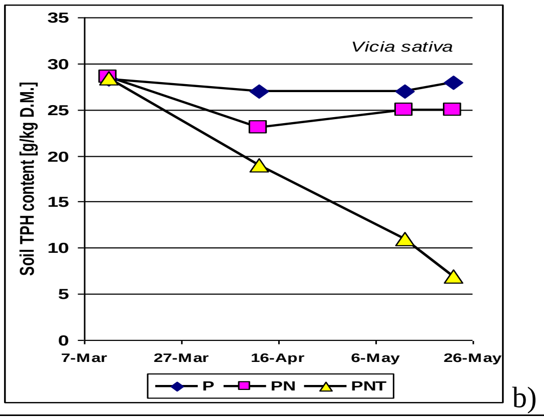


Figure 2b. Increase of green biomass, harvested from TPH soils polluted, fertilized in the absence/presence of volcanic tuff vs. harvested from the non-fertilized polluted soil. Phytoremediation for 45 days with Vicia spp.

Green biomass harvested from cultures of *Onobrychis spp.* and *Vicia spp.* From the soil variants fertilized in the absence/presence of indigenous volcanic tuff is shown in figure 3.

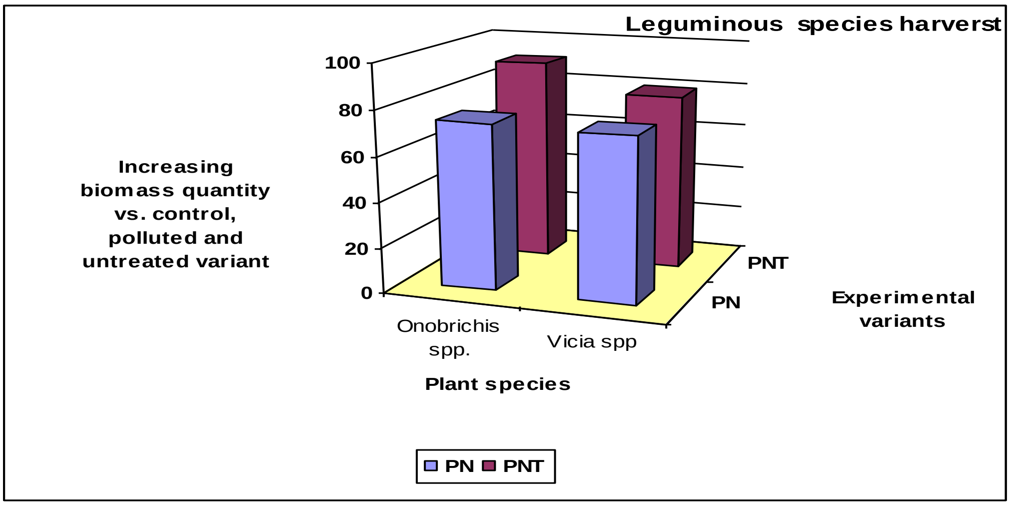
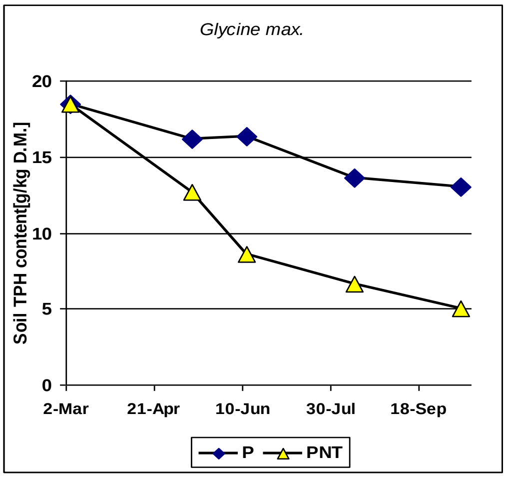


Figure 3. Green biomass quantity increase for leguminous plants from Onobrychis spp and Vicia spp., harvested from soil variants polluted with TPH, fertilized in the absence/presence of volcanic tuff vs. the quantity harvested from the non-fertilized polluted variant.

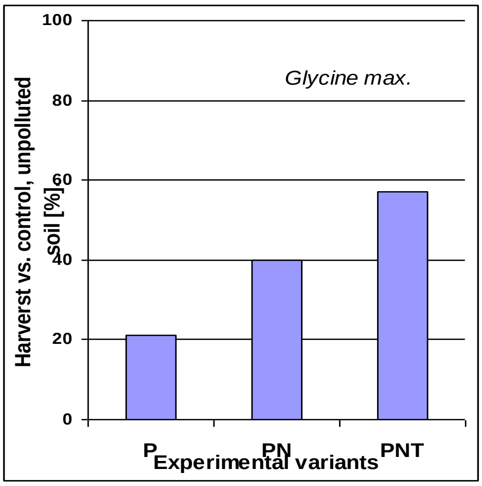
Phytoremediation of TPH polluted soil with species *Glycine max.*

Polluted soils having an initial pollution level at surface of 18.5±2.3 g TPH·kg^{-1} D.M. were used in the experimental study done with a culture of leguminous plants of *Glycine max.* TPH content variation from studied soils during the analyzed period is shown in figure 4a. During the 145 day period monitored in the study, TPH quantity decreases in the polluted soils fertilized with sewage sludge by 12.5% vs. the remnant quantity at 145 days in the non-fertilized polluted soil, cultivated with soy. Tuff addition to polluted soil fertilized with sewage sludge determined a decrease of TPH content up to 73.0% vs. the remnant quantity at 145 days in the non-fertilized polluted soil.



a)

Figure 4a. TPH variations from soil variants polluted with 18.5 ± 2.3 g TPH ·kg^{-1} D.M., non-fertilized/fertilized in the absence/presence of volcanic tuff. and 145 days cultivated with Glycine spp



b)

Figure 4b. Increase of quantity of beans in Glycine max., harvested from TPH polluted soil, fertilized in the absence/presence of volcanic tuff vs. the quantity harvested from the non-fertilized polluted variant

Figure 4b shows comparatively the quantities of soybeans. Soybean yield resulted on the non-fertilized polluted soil represented just 21% from the quantity harvested from the non-polluted variant. The use of sewage sludge determined the increase of soybean yield by 20% vs. the non-fertilized polluted variant (Hutchinson et al., 2001). When sewage sludge is enriched with volcanic tuff, soybean yield is 40% higher vs. harvests obtained on the non-fertilized polluted variant (Wyszkowski and Ziólkowska, 2009).

CONCLUSIONS AND IMPLICATIONS

Leguminous plants - *Vicia sativa* and *Onobrichis viciifolia* evidence as plants with potential of phytoremediation of soils polluted with 28.6±2.3 g TPH·kg^{-1}D.M. To obtain high efficiencies of reduction of TPH from soils, sewage sludge was used in association with an indigenous volcanic tuff based on clinoptilolite. Under these conditions, the biodegradation level of TPH from soil was of 73% in 45 days, respectively 65 days. The remaining quantity in the soil was of 7.2±0.8 g TPH·kg^{-1}D.M. Green biomass quantity produced under the conditions of combined fertilization with addition of tuff, was similar, 79-91% vs. the quantity obtained on the variant of soil polluted and not treated. Cultures of these plants dry after harvesting. Plants from species *Glycine max* demonstrated a high potential of phytoremediation for a soil polluted with 18.5±2.3 g TPH·kg^{-1}D.M. The period of reduction of TPH content from soil with 73% was 2.2-3.2 longer than the two species *Vicia sativa* and *Onobrichis viciifolia*. The quantity remaining in soil was of 4.86±0.54g TPH·kg^{-1} D.M. cultivation was done during a complete vegetative cycle. Herbaceous plant species *Lolium spp* cultivation was studied on variants of soils polluted with an initial level of pollution of at soil surface of 28.6±2.3 g TPH ·kg^{-1}D.M. and proved the formation of a vegetative cover adapted to stress conditions on the polluted land. Vegetative cover blends with the landscape. Biomass periodically harvested was composted. TPH content from studied soils during a period of 145 days decreases in polluted soils fertilized with sewage sludge in association with amendment – volcanic tuff, with 64.4-68.0% vs. the quantity remaining at 7 months in the polluted soil, non-fertilized, cultivated with the grass species. The ability specific metabolic mechanism of plant species to removal crude oil compounds from high polluted soils can restore destroyed areas for back agricultural use. Choice of adequate plant species for phytoremediation technologies will be ultimately based on the quality and quantity of harvest.

REFERENCES

Bento, F.M., Camargo, F.A.O. & Okeke BC, Frankenberger W.T., (2005), Comparative bioremediation of soils contaminated with diesel oil by natural attenuation, biostimulation and bioaugmentation. *Bioresource. Technology,* 96, 1049-1055.

Collins, C.D., (2009), Implementing Phytoremediation of Petroleum Hydrocarbons, Methods in Biotechnology In, Wiley N. (Eds.), *Phytoremediation: Methods and Reviews*, *vol. 23,* Humana Press Inc. Totowa, New Jersey, USA.

Edwards, N.T., Ross-Todd B.M. & Garver E.G., (1982), Uptake and metabolism of ^{14}C anthracene by soybean (Glycine max) Environmental and Experimental, *Botany*, 22, (3), 349–357.

Farias, V., Maranho, L. T., Vasconcelos, E. C., Carvalho Filho, M. A. S., Lacerda, L. G., Azevedo, J. A. M., Pandey, A. & Soccol, C. R., (2009), Phytodegradation potential of Erythrinacrista-galli L., Fabaceae, in petroleum-poluated soil, *Applied Biochemistry and Biotechnology*, 157(1), 10–22.

Gudin, C. & Syratt, W.J., (1975), Biological Aspects of Land Rehabilitation Following Hydrocarbon Contamination, *Environmental Pollution*, 8, 107-112.

Hutchinson, S.L., Schwab, A.P. & Banks, M.K., (2001), Phytoremediation of aged petroleum sludge: effect of irrigation techniques and scheduling, *Journal of Environmental Quality*, 30(5), 1516-1522.

Kaimi, E., Mukaidani, T. & Tamaki, M. (2007), Screening of twelve plant species for phytoremediation of petroleum hydrocarbon polluted soil, *Plant Product Science*, 10, 211–218.

Kim, K. R. & Owens, G., (2010), Potential for enhanced phytoremediation of landfills using biosolids – a review, *Journal of Environmental Management*, 91, 791-797.

Kirk, J.L., Klironomos, I. N., Lee, H. & Trevors, J. T., (2005), The effects of perennial reygrass and alfaalfa on microbial abundance in petroleum poluated soil, *Environmental Pollution*, 133, 455 – 465.

Kolawole, G.O., and B. T. Kang, (1997), Effect of seed sizeand phosphorus fertilization on growth of selected legumes, *Common Soil Science Plants Analysis. 28*, 1223–1235.

Kulakov, L.A., Allen, C.C.R., Lipscomb, D.A. & Larkin M.J., (2000), Cloning and characterization of a novel *cis*-naphthalene dihydrodiol dehydrogenase gene (*narB*) from *Rhodococcus* sp. NCIMB12038, *FEMS Microbiology Letters*, 182(2), 327-331.

Liang, Y. Zhang, X., Dai, D.& Li, G., (2009), Porous biocarrier-enhanced biodegradation of crude oil poluated soil, *International Biodeterioration and Biodegradation,* 63, 1, p. 80-87.

Reilley, K.A., Banks, M.K.& Schwab A.P., (1996), Dissipation of polycyclic aromatic hydrocarbons in the rhizophere, *Journal of Environmental Quality*, 25, 2012-1019.

Njoku, K.L., Akinola, M.O.& Oboh, B.O., (2008), Growth and performance of *Glycine max* L. (Merrill) in crude oil contaminated soil augmented with cow dung, *Nature Science* 6(1), 48-58.

Njoku, K.L., Akinola, M.O.& Oboh, B.O., (2009), Phytoremediation of crude oil poluated: soil: the effect of growth of *Glycene max* on the physico-chemistry and crude oil contents of soil, *Nature and Science*, 7(10), 79 – 87.

Zhou, Q., Cai, Z., Zhang, Z.& Liu, W., (2011), Ecological Remediation of Hydrocarbon Contaminated Soils with Weed Plant, *Journal of Resources and Ecology*, 2(2) 97-105.

Wyszkowski, M.& Ziolkowska, A, (2009), Role of compost, bentonite, calcium oxide in restricting the effect of soil contamination with petrol and diesel oil on plants, *Chemosphere*, 74, 860-865.

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DEVELOPMENT OF BASES OF ORGANIC FARMING FOR RICE CROP ROTATIONS IN AKDALA IRRIGATION AREA IN SOUTHEASTERN KAZAKHSTAN

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ABSTRACT

The article describes the results of a study on the impact of biomeliorants on biological activity, humus status of rice soil and rice yield. It was found that application of biomeliorants into soil – such as Green-Eco, Edagum and Sodium humate have effective influence on soil biological activity. Biomeliorant test results showed that the most optimal biomeliorant in formation of a positive humus balance and improvement of its quality indicators is Green-Eco in minimum dose of 50 kg / ha. But also Edagum in making 100 and 150 l/ ha increased the total content of humus, although slightly reduced its quality.

Keywords: *organic farming, humus, fertility of periodically flooded rice soils.*

The purpose of research. Comparative study of different sources of organic matter, microbiological agents and plant growth stimulants for creating elements of technology of organic farming in terms of periodically flooded rice soils.

Introduction. Technical progress brings to humans not only material wealth, but also causes ever-increasing technogenic impacts on biosphere - soil, water reservoirs, rivers, atmosphere, living organisms. Factors that cause it, include the use of chemicals in agriculture. High doses of mineral fertilizers, numerous processing plant protection chemicals, violation of application technologies, intensive soil tillage, deep plowing result in a whole range of negative environmental impacts. Chemization brakes self-regulation in live nature, weakens protection forces of plants, animals and humans. Old, experienced agricultural technologies are no longer able to cope with these problems. Mankind faces a problem of further development of land cultivation, search for alternative ways to maintain its high performance and environmental safety. Biotechnology should replace the old technology, and at present stage only it can help to solve environmental, energy and food problems of the humanity. One of such areas is the development of organic farming. Importance of organic farming in national aspect can be confirmed by the words of the President. According to the President of the Republic of Kazakhstan Nursultan Nazarbayev "we are already one of the largest exporters of grain. We have a huge eco-friendly areas and can produce environmentally friendly food products. We are able to make a qualitative leap in agricultural production. For this we will need a new type of public thinking" [1]. Importance at international level - is Kazakhstan's accession to the WTO, which means special attention to the quality of products. And the introduction of organic farming will give farmers the opportunity to receive high-quality environmentally friendly agricultural products.

Result and Discussion. Specificity of humification and mineralization of soil organic matter and the rate of mineralization of the litter and other organic matters entering the soil determines the biological activity of soil. As points Berestetskiy O.A. et al [2] the rate of transformation of various compounds, the decomposition of plant residues, the accumulation of plant nutrients and, ultimately, soil fertility depend on the activity and orientation of biological processes in soil. Therefore, we also studied the effect of application of biomeliorants into low-yielding rice soils on its biological activity. Protease activity and intensity of accumulation of amino acids have been investigated. Below are the details of the variation- statistical processing of data on the effect of different doses of drugs "Green Eco", "Edagum" and "Sodium humate" on protease activity of the soil. Reliability of the obtained secondary data was evaluated by Student t-criteria. Analysis of obtained actual values of Student t-criteria shows that statistical validity (tact.>ttab.) % of dilution of gelatin layer of photo paper exposed in soil on experiment options (table 1). Analysis of the degree of variability on experiment options also shows that the average mean values are statistically stable. The values of their variation coefficients serve as confirmation of this fact, which do not exceed 6.4% in the control, and 0.4 % in the option with "Green Eco", 3.6 % in the option with "Edagum" and 0.8 % in the option with "Sodium humate" and on the gradation scale insignificantly correspond to the limit.

Table 1: Effect of different doses of drugs "Green Eco", "Edagum", “Sodium humate” and soil protease activity, % of dilution of gelatin layer of photo paper (application method)

Options	M±m	Fluctuation range	t-criteria		± $t_{0,05}$ * m	V,%
			tact.	$t_{0,05}$		
Control	49,9±1,85	46,8÷53,2	26,9	3,2	7,9	6,4
Green-Eco 50 kg/ha	98,4±0,23	98,0÷98,8	42,0	3,2	1,0	0,4
Green-Eco 100 kg/ha	98,1±0,13	98,0÷98,4	73,0	3,2	0,6	0,2
Green-Eco 150 kg/ha	96,8±0,23	96,4÷97,2	41,0	3,2	1,0	0,4
Edagum 50 l/ha	97,2±0,23	96,8÷97,6	42,0	3,2	1,0	0,4
Edagum 100 l/ha	86,9±1,31	84,4÷88,8	66,0	3,2	5,7	2,6
Edagum 150 l/ha	77,6±1,60	74,4÷79,2	49,0	3,2	6,9	3,6
Gumat Na 50 kg/ha	95,6±0,46	94,8÷96,4	20,0	3,2	2,0	0,8
Gumat Na 100 kg/ha	98,9±0,27	98,4÷99,2	37,0	3,2	1,1	0,5
Gumat Na 150 kg/ha	97,2±0,46	96,4÷98,0	21,0	3,2	2,0	0,8

The fluctuation range of absolute values % of dilution of gelatin layer of photo paper, exposed in the soil on laboratory experiment option is also quite narrow, that also, although indirectly, points to statistical reliability of obtained average values of experiment options. So, we can say that the obtained average mean values % of dilution of gelatin layer of photo paper in soil on experiment options are statistically reliable and can be used to summarize the results obtained on the study of the effect of biomeliorants on protease activity of periodically flooded rice soils of laboratory experiment. The conducted analysis of average statistical data of proteolytic activity in soils on laboratory experiments options showed that among the tested biological meliorants most optimal variant was introduction of application of "Green-Eco" at a dose of 50 kg/ ha, in which there is maximum % of dilution of gelatin layer which is equal to 98,4% ± 0.23. Almost the same effect had application of Edaguma and Sodium humate, but in these options to achieve same effect was needed the application of twice higher dose than dose of Green-Eco. The analysis of average values of protease activity shows that all tested biomeliorants have significant effect compared with the control (figure 1). Increasing of the percentage of emulsion dilution in various options ranges from 27.7 to 49.0 percent. As the figure 1 shows the proteolytic activity is twice higher than in control in application of 1 dose of all used biomeliorants.

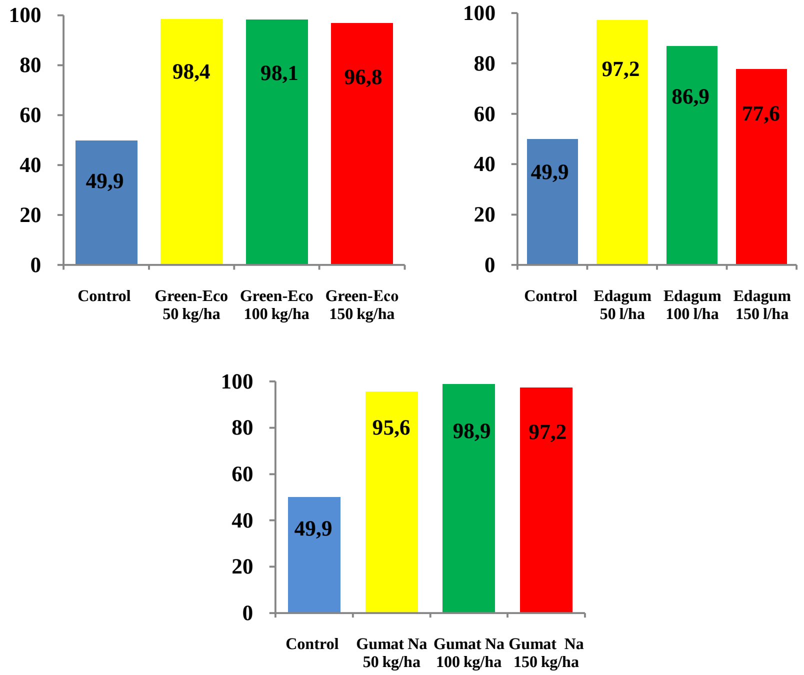

Figure 1. Impact tested for proteolytic activity biomeliorants

Cellulose activity of soil was determined by method of "applications" on decomposition of linen tissue in it. But since the degree of activity of cellulose microorganisms depends on the presence in soil of available nitrogen, phosphorus and other elements , the degree of decomposition , can be considered to reflect " the tension of microbiological processes in general" (3). Variation- statistical processing of obtained average data showed their statistical reliability, which was assessed by the Student t-criteria. At 0.95 % of probability of actual values of Student's t- criteria in all experiment options are higher than their table value that indicates their statistical reliability.

Table 2: Effect of different doses of "Green Eco" on the intensity of accumulation of amino acid in the experiment variants

Options	M±m	Fluctuation range	t-criteria		± $t_{0,05} * m$	V,%
			$t_{fact.}$	$t_{0,05}$		
Control	37,6±0,46	36,8÷38,4	81,4	3,2	2,0	2,1
Green-Eco 50 kg/ha	98,5±0,35	98,0÷99,2	27,0	3,2	1,5	0,6
Green-Eco 100 kg/ha	96,1±0,48	95,2÷96,8	20,0	3,2	2,1	0,9
Green-Eco 150 kg/ha	92,7±0,48	92,0÷93,6	19,0	3,2	2,1	0,9
Edagum 50 l/ha	99,2±0,23	98,8÷99,6	43,0	3,2	1,0	0,4
Edagum 100 l/ha	86,0±0,92	84,4÷87,6	9,3	3,2	4,0	1,9
Edagum 150 l/ha	78,3±0,93	76,4÷79,2	84,0	3,2	4,0	2,1
Gumat Na 50 kg/ha	98,7±0,35	98,0÷99,2	28,0	3,2	1,5	0,6
Gumat Na 100 kg/ha	96,4±0,46	95,6÷97,2	20,9	3,2	2,0	0,8
Gumat Na 150 kg/ha	96,5±0,35	96,0÷97,2	27,4	3,2	1,5	0,6

The analysis of the degree of variability of the experiment variants in which values of their variation coefficients range within 0,4-2,1 % according to grade scale slightly correspond to the limit value and indicates statistical stability. Limits of variation of particular average values and limits of confidence interval are quite narrow, which , although indirectly, indicates statistical stability of the obtained average values of the experiment variants. Thus, we can say that obtained average values % of intensity of destruction of linen fabrics in soils on laboratory experiment options are statistically reliable and can be used to summarize the results obtained on research of the effect of biomeliorants on the intensity of amino acids accumulation. The conducted analysis of average statistical data on intensity of amino acids accumulation in soils on experiment variants also showed that all tested biomeliorants have significant effect compared to the control. Increase of the percentage of decomposition of linen in various variants, as compared with the control range within 40,7-61,6 percent. The maximum effect is also obtained from the lowest doses of tested biological meliorants , in which the percentage of decomposition of linen reaches 98.5% -99.2 % (Figure 2).

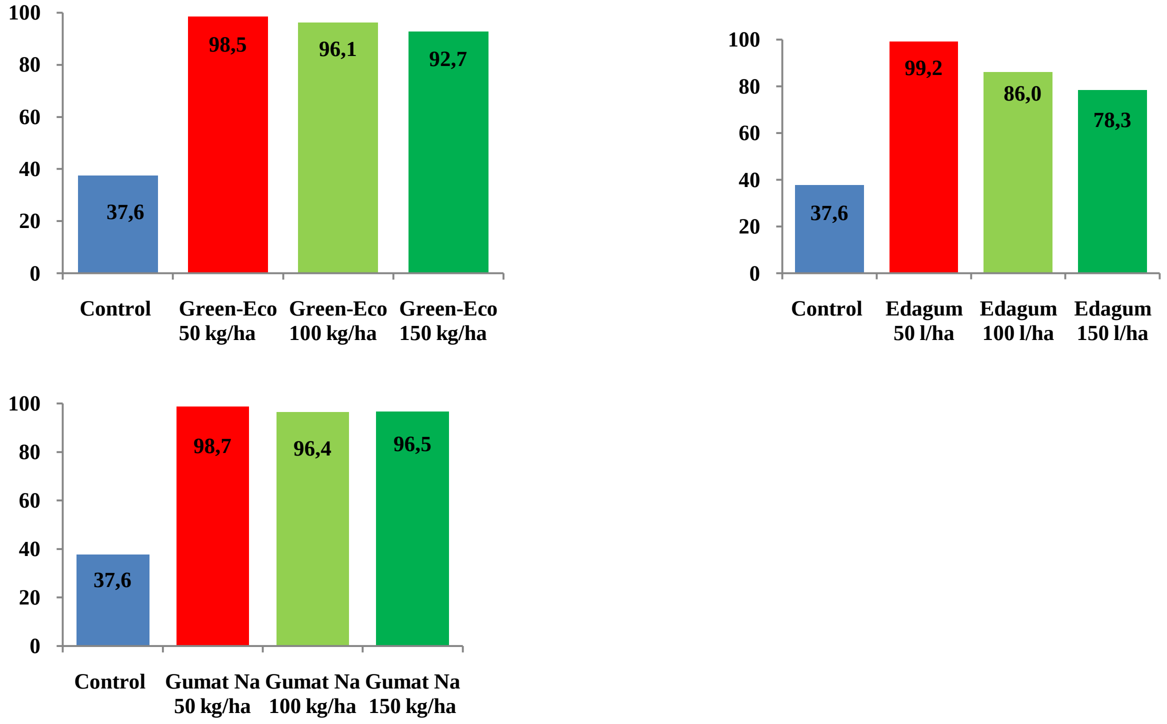

Figure 2: Influence on the intensity of the tested biomeliorantov accumulation of amino acids

It is well known that soil humus is a major source of nitrogen and other plant nutrients. In accumulation of humus occurs the biological accumulation of these elements in soil, and during its decomposition, they gradually release in form of mineral compounds absorbed by plants. Crop production, leaving many crop residues in soil (alfalfa, etc.), and application of bio-organic fertilizers contribute to the accumulation of humus in soil. We investigated the effect of different doses of application of “Green- Eco", "Edagum" and "Sodium humate" on indicators of humus condition of low productive rice- swamp soils. The results obtained show that the tested doses of biomeliorants have statistically reliable positive effect on total humus concentration (Table 3). Data on humus balance are proving this fact. In all variants of the experiment a positive balance is observed. The biggest increase in total humus concentration is observed in option with application of Green-Eco 50 kg/ha. Positive balance was +10.7%, whereas twice increase of its dose has reduced humus content to 10.7%, and increase three times to 7.1%. That is, the positive effect of biomeliorants Green-Eco is observed only in application of small doses, that is important for the farmers from the economic point of view. Opposite effect on the total humus content in soil was observed in application of different doses of Edagum. So, the application of 50 l/ha of this biomeliorant had no impact on the total humus content, and it was the same as in the control variant. Humus content increased by 7.1% in application of 100 l/ha and by 10.7% in application of 150 l/ha of Edagum. Application of sodium humate in the amount of 50, 100 and 150 kg /ha had a negative impact on total humus content. Their content decreased respectively by 10.7%, 3.6% and 10.7%. Evaluation of average values of all indicators of soil humus status of investigated soils using Student t-criteria shows their statistical reliability, actually in all studied options t_{fact}. is higher than t_{tabl}. Variation of total humus content and other indicators are low, and insignificant and average within grade limits.

Table 3: Effect of application of different doses of biomeliorants on soil humus status indicators of the laboratory experiment a month after flooding

Showing	M±m	Fluctuation range	t-criteria		± $t_{0,05}$ * m	V,%	Humus balans, ± %
			$t_{fact.}$	$t_{0,05}$			
1	2	3	4	5	6	7	8
Control							
Total humus, %	2,8±0,2	2,5÷3,3	11,5	3,18	1,06	8,7	
C:N	10,8±1,5	9,3÷13,8	7,4	3,18	6,32	13,6	
N in the humus content,%	5,5±0,7	4,2÷6,3	8,4	3,18	2,85	12,0	
Green-Эко, 50 kg/ha							
Total humus, %	3,1±0,2	2,7÷3,3	15,3	3,18	0,87	11,3	+ 10,7
C:N	11,6±1,5	8,6÷13,8	7,4	3,18	6,72	23,3	
N in the humus content,%	5,2±0,7	4,2÷6,7	6,7	3,18	3,34	26,0	
Green-Эко, 100 kg/ha							
Total humus, %	2,5±0,04	2,5÷2,6	63,7	3,18	0,17	2,7	- 10,7
C:N	8,7±0,54	7,9÷9,7	16,2	3,18	2,31	10,7	
N in the humus content,%	6,7±0,4	6,0÷7,3	16,8	3,18	1,73	10,3	
Green-Эко, 150 kg/ha							
Total humus, %	2,6±0,06	2,5÷2,7	46,7	3,18	0,24	3,7	- 7,1
C:N	8,8±0,5	7,7÷9,4	16,5	3,18	2,29	10,5	
N in the humus content,%	6,7±0,4	6,2÷7,5	15,5	3,18	1,84	11,1	8
Edagum 50 l/ha							
Total humus, %	2,8±0,04	2,7÷2,8	70,1	3,18	0,17	2,5	0
C:N	9,3±0,19	9,0÷9,6	49,9	3,18	0,80	3,5	
N in the humus content,%	6,3±0,13	6,0÷6,5	50,0	3,18	0,54	3,5	
Edagum 100 l/ha							
Total yumus, %	3,0±0,19	2,7÷3,3	15,5	3,18	0,82	11,2	+ 7,1
C:N	10,1±1,25	8,4÷12,5	8,1	3,18	5,36	21,4	
N in the humus content,%	5,9±0,67	4,6÷6,9	8,8	3,18	2,89	19,6	
Edagum 150 l/ha							
Total humus, %	3,1±0,05	3,1÷3,2	60,6	3,18	0,22	2,9	+ 10,7
C:N	9,5±0,21	9,1÷9,8	44,4	3,18	0,92	3,9	
N in the humus content,%	6,1±0,14	5,9÷6,4	43,8	3,18	0,60	4,0	
Gumat Na 50 kg/ha							
Total humus, %	2,5±0,03	2,5÷2,6	84,2	3,18	0,13	2,1	- 10,7
C:N	7,6±0,38	6,9÷8,1	19,8	3,18	1,65	8,8	
N in the humus content,%	7,7±0,40	7,1÷8,5	19,0	3,18	1,74	9,1	
Gumat Na 100 kg/ha							
Total humus, %	2,7±0,1	2,5÷2,8	27,3	3,18	0,42	6,3	- 3,6
C:N	7,9±0,61	6,9÷9,0	13,0	3,18	2,62	13,3	

N in the humus content,%	7,4±0,58	6,5÷8,5	12,7	3,18	2,50	13,6	
Gumat Na 150 kg/ha							
Total humus, %	2,5±0,01	2,48÷2,51	28,2,7	3,18	0,04	0,6	- 10,7
C:N	6,9±0,24	6,5÷7,3	28,4	3,18	1,04	6,1	
N in the humus content,%	8,4±0,29	7,9÷8,9	28,6	3,18	1,27	6,1	

The most important characteristic of easy degradable organic matter is its content of nitrogen, and the ratio of C:N, which affects the rate of decomposition of labile organic matter. As known, the main part of soil nitrogen comes precisely from the easy degradable organic matter. The ratio C:N in the soil is an indicator of humus which is relatively rich in nitrogen. Narrow correlation C:N in gray soil is probably the result of high population of soil microorganisms that facilitates enrichment of soil humus in microbial protein [4]. In our experience, as can be seen from the table, different doses of biomeliorants have different impact on these indicators. Thus, nitrogen content of humus in application of Green-Eco at 50 kg/ha has decreased compared with the control (5.5%) to 5.2%, i.e. humus became richer in carbon that is good for effective soil fertility. In increasing doses of biomeliorants to 100 and 150 kg/ha nitrogen concentration in humus has increased to 6.7% in both cases. C: N ratio in application of 50 kg/ha of Green-Eco was equal to 11.6 versus 10.8 in the control variant, i.e. humus has become more saturated with carbon, and in other two variants with high doses (100 and 150 kg/ha) this indicator was lower than in the control, 8.7 and 8.8 respectively. There is obvious negative impact on the quality of humus, although in general the total humus content has increased. Thus, application of a smaller dose of Green-Eco (50 kg/ha) had a positive effect on total content of humus and its quality. Application of different doses of Edagum into studied soils also had different impact on nitrogen content of humus and ratio C:N (Table 3), although exact opposite than Green-Eco. So, nitrogen content in humus in all experiment options increased compared to control (5.5%): in application of 50 l/ha to 6.3%, 100 L/ha to 5.9%, and 150 l/ha to 6,1%, i.e. humus became more saturated with nitrogen than carbon. Naturally, the ratio C: N also changed, it became narrower and was 9.3, 10.1 and 9.5, respectively, whereas in the control it was 10.8. Sodium humate also had different effect on the studied parameters of humus status. Nitrogen content in humus had significantly increased and was 7.7% at a dose of 50 kg/h, 7.4% at application of 100 kg/ha and 8.4% at 150 kg/ha, whereas in the control this indicator was equal to 5.5%. In soil humus of these variants the proportion of nitrogen has increased. Naturally the ratio of carbon to nitrogen has also decreased. C:N ratio decreased to values of 7.6, 7.9 and 6.9 respectively to experiment variants.

CONCLUSION

Thus, application of these biomeliorants into soil had effective impact on soil biological activity. Most optimal biomeliorant which has a positive effect on total humus content and its quality indicators is Green-Eco at dose 50 kg/ha. However Edagum in application 100 and 150 l / ha has also increased total humus content, although slightly reduced its quality. But sodium humate had negative impact on total humus content.

REFERENCES

N.A.nazarbayev Message of the President of the Republic of Kazakhstan - the leader of the nation to the people of Kazakhstan 2012. Strategy "Kazakhstan-2050"

O.A. Berestetskiy, Y.M.Voznyakovskaya, L.M. Dorosinsky: Biological basis of soil fertility. Publishing house "Kolos". M. 1984. S. 218 ž

E.N. Mishustin, I.S. Vostrov, A.N. Petrova: Definition of soil biological activity by different methods, Microbiology. 1961. V. 30. 4. - S. 665-672.

M.M. Kononov: Soil organic matter. M. Publ. Nauka. 1963. 314.

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SOIL DEGRADATION AND DESERTIFICATION PROCESSES WITHIN KAZAKHSTAN

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Abstract

Soil degradation and desertification is a common process in arid and semi-arid regions of Kazakhstan, especially in its southern parts, where areas are covered by a great variety of desert types. Deserts are the most arid regions of Kazakhstan. In deserts soil-forming processes take place in conditions of severe water shortage, and high level of soil degradation and desertification. The main natural factors for these processes are a flat terrain, a high degree of arid climate, salinity, carbonate content, a lack of structure and low natural soil fertility. However, the anthropogenic factors of desertification and soil degradation are became dominant last decades. The paper considers the actual problems of natural and anthropogenic factors of desertification or land degradation within Kazakhstan. The desertification of huge territories is accompanied by soil contamination, waterlogging by surface water and groundwater, soil salinization, erosion (water, wind), degradation of vegetation cover, dehumidification and a decrease in general regional biological capacity. Analysis of the current status of the soil cover has shown intensive land degradation and desertification processes and more than 75 % of the territory of Kazakhstan is subjected to degradation and desertification; over 14 % of pastures have reached an extreme degree of degradation or are completely degradated. The Aral Sea region, Northern Caspian Sea and Southern Balkhash deserts can be observed as areas of intensive soil desertification, salinization and deflation processes. As well as the desertification process are progressing in the irrigated soils of the deltas of Syrdarya, Shu, Ile and Karatal rivers.

Key words: *soil degradation, desertification, anthropogenic factor, arid region, Kazakhstan.*

INTRODUCTION

Deserts are the most arid regions of Kazakhstan. In deserts soil-forming processes take place in conditions of severe water shortage, and high level of soil degradation and desertification. The deserts span of the south undrained territories of the Caspian lowlands, Mangyshlak, Usturt and Betpakdala plateaus, areas of the Aral Sea region, Shu-Moyinkum and Balkhash-Alakol basins, as well as foothills sloping surface of the Tien Shan, Zhetysu (Zhongar), Altai and Saur-Tarbagatai mountains (Faizov et al., 2006). Unlike other natural zones, there are vast areas occupied by sandy massifs, plains on solonchaks (saline soils) and takyrs (Asanbayev and Faizov, 2007).

The main natural reasons for these processes are a flat terrain, a high degree of arid climate, scarcity and uneven distribution of water resources, causing of widespread sand (up to 30 mln ha) and saline lands (127 mln. ha), soil salinity, xero-halophytic vegetation, widespread brown calcareous saline and structureless soils, which are characterized by low natural soil fertility (Faizov et al., 2006).

Desertification process is the loss of ecosystems, loss of soil fertility and biomass productivity. The process contributes to environmental instability of natural landscapes and anthropogenic pressures. A large area in Kazakhstan are subject to desertification that is 120 million hectares of deserts and 180 million hectares of desertification by anthropogenic factors (Iskakov and Medeu, 2006; Almaganbetov and Grigoruk, 2008).

The intensive development of land resources occurred during last ten years. And as consequence, every year it is noted the degradation increasing of many areas, which have strong negative impact on the surrounding regions. Degraded soil areas bring a lot of problems for the land using. And for solving, this problem demands organization of terrestrial and satellite monitoring, study of soil cover and texture, physical and chemical prosperities of soil. In Kazakhstan land degradation began in the 1950-60 s due to development of Virgin Lands, increasing of livestock numbers and changing in grazing practices (Robinson et al., 2003; Almaganbetov and Grigoruk, 2008). The influence of anthropogenic factors is seen almost in all natural landscapes, especially in the Aral Sea region, where degradation and desertification processes are becoming more widespread. Additionally, the northern Caspian Sea and southern Balkhash deserts belong to significant and high degree of Land degradation under the influence of grazing (Medeu, 2010; Issanova et al., 2014). A well as pasture degradation touched mostly desert and semi-desert landscapes in Kazakhstan.

STUDY REGION AND METHODS

Kazakhstan is one of the rapidly developing and youngest independent countries in the world. It lies between the Siberian Taiga in the north and the Central Asia deserts in the south, the Caspian Sea in the west and the mountain range of the Tien-Shan and Altay in the east (UNDP 2002). About 60 % of Kazakhstan is flat lands. Deserts and semi-deserts occupy approximately 50 % of the territory, most of them situated in the Turan plain. Arid territories spread from Caspian Sea to foothill plains of Zhetysu (Zhongar) Alatau and Tien-Shan mountains. These vast territories have various geological structure and landscape features such as sandy deserts: Ryn, Kyzylkum, Pre-Aral Karakum, Moiynkum, Saryesikatyrau (Fig.1). The northern parts of Kazakhstan are steppes and forest-steppes (Danayev 2008; Vilesov et al. 2009).

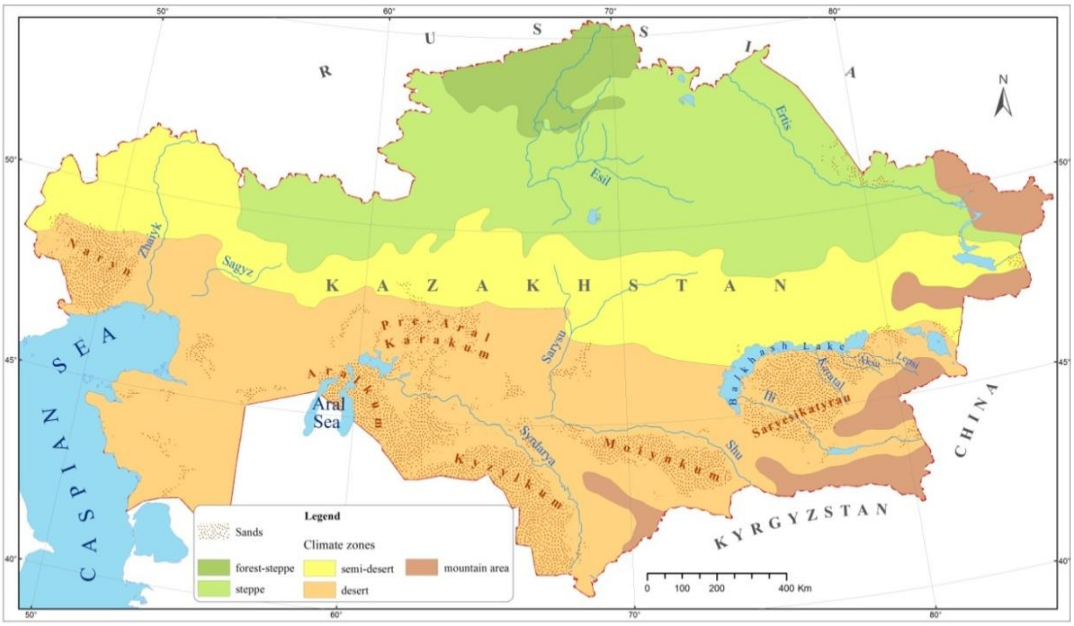

Figure 1. Distribution of sandy deserts and climate zones within Kazakhstan

Kazakhstan's climate is a sharp continental with uneven distribution of precipitations within the territory. Plain areas are generally dry and have precipitation from 100 mm in the southwest up to 400 mm annually in the north. In the plains the saline soils are distributed widely. In the mountainous regions, the precipitation ranges between 400 mm and 1600 mm (ADB 2003; Almaganbetov and Grigoruk 2008). Average temperature is -18 °C in January in the north and -3 °C in the south. Average temperature in July increases gradually from 19 °C in the north up to 28-30 °C in the south.

The study object is soil cover in Kazakhstan. We used such as methods: GIS, comparative geographical, landscape and dynamic, based on field studies to assess the current state of the soil cover in Kazakhstan.

RESULTS AND DISCUSSION

Review on land degradation and desertification processes within Kazakhstan

The main factors of the soil degradation is soil salinization, soil erosion (wind/water erosion), dehumification processes, soil deflation, and reduction in the productivity of arable lands. Analysis of the current status of the soil cover has shown intensive land degradation and desertification processes. According to the data of the Agency on Land Resources Management, more than 75 % of the territory of Kazakhstan is subjected to degradation and desertification; over 14 % of pastures have reached an extreme degree of degradation or are completely degradated (Almaganbetov and Grigoruk, 2008; Orlova and Saparov, 2009; Mueller et al., 2014). Conditions for the development of land degradation and are in violation of the seasonal features of soil formation under the influence of drought. Prerequisite of desertification is also weak formedness of land cover and its dynamics. These natural features of Kazakhstan cause poor resistance of the environment to human impact (Asanbayev and Faizov, 2007; Faizov et al., 2006).

In the regional environmental case, in northern Kazakhstan on chernozems and dark chestnut soils the dehumification processes are progressing and as a result, soil erosion, deflation and reduced productivity of arable land (Medeu, 2010; Iskakov and Medeu, 2006).

The regions of Central and East Kazakhstan, which are the major industrial centers, are involved to technogenic disturbances and the industrial pollution of soils with toxic chemical and radioactive elements. Every year, about 3-4 mln tones of polluting chemicals are emitted to the atmosphere or deposited on the soil surface (Mueller et al., 2014). The region are characterized by radioactive pollution and man-made destruction of the soil cover in the test sites of nuclear missiles, mining and processing mineral resources.

In the oil and gas regions of western Kazakhstan and Torgay plain created large pockets oil and radioactive contamination of soil, soil salinization by wastewaters, and industrial transformation of the soil cover (Faizov, 1980; Kovda, 1950; 2008).

On the vast territory of Kazakhstan, there are a number of regions where the combination of various forms of environmentally damaged soils has resulted in a crisis situation. Disastrous environmental conditions can be observed in the Aral Sea region. The ecological crisis in the Aral Sea region remains as the main problem in Southern Kazakhstan. The area is subjected to irreversible processes of desertification, intensive soil desertification, salinization and deflation (Faizov and Tapalova, 2003; Pankova et al., 1996; Issanova et al., 2014). In the most fertile delta-alluvial plain of the Syrdarya river, the area of desertified land is 1.1 mln ha, and in the dried –up bottom of Aral Sea it is 1.5 mln ha, of which saline march soils occupy 0.8 mln ha. In contrast to other natural zones, these vast areas are occupied by sand (17.5 mln ha), saline soils (2.6 mln ha) and takyr plains (0.3 mln ha). The total are of saline soils in the desert zone with brown and grey-brown soils exceeds 60 mln ha, and alkaline complexes are present in 22 mln ha (Mueller et al., 2014; Borovsky, 1978; 1982).

The most fertile delta-alluvial plain of Syrdarya river is the main rice granary of the country, as well as the Balkhash-Alakol region is widely noted processes of secondary soil salinization of irrigated lands and destruction; land erosion and digression is occurring in foothill and mountain areas (Issanova et al., 2013; Otarov, 2011).

The degradation is accompanied by the intensive soil salinization, which leads to the increasing of solonchaks desert areas in inland drainless basins and salinization of irrigated land (Orlova and Saparov 2009; Orlova and Seifullina,2006). The degradation processes as a soil erosion and deflation (more than 30 million hectares), soil salinization, chemical pollution and soil alkalinity (60 million hectares), dehumidification of arable land (more than 10 million hectares) have the constant are progress (Iskakov and Medeu 2006).

Soil salinization and soil erosion (wind/water erosion)

Soil salinization widely and commonly manifests in all areas of natural zones and it is associated with poor drainage of the territory, the initial salinity of the lake-marine and alluvial-deltaic parent rocks and mineralized groundwater. The problems of soil salinity are most widespread in the arid and semi-arid regions but salt affected soils also occur extensively in sub-humid and humid climates, particularly in the coastal regions where the ingress of sea water through estuaries and rivers and through groundwater causes large-scale salinization (Gamalero et al., 2009; Lopatovskaya and Sugachenko, 2010; Pachikina et al., 1975). The soil salinity is also a serious problem in areas where groundwater of high salt content is used for irrigation (Kovda, 2008).

A saline soil is an indispensable component of steppe and desert landscapes (Borovsky 1978; 1982). They are widespread in arid and semi-arid regions of the world. According to the data of International Institute for Environment and Development and World Resources Institute about 10 % of the surface of continents covered by saline soils. They are mostly distributed in arid lands, as well as zones of dry and desert steppes (Lopatovskaya and Sukachenko 2010; Kovda 2008). The saline soil is defined as having a high toxic concentration (0.25 %) of soluble salts in any soil profile to affect plant growth (Munns, 2009).

The saline soils mostly distributed in Central Asia and Kazakhstan, including West Siberia, West China. The most part of saline soils (70%) in the CIS countries occurred in Kazakhstan. Numerous reports were done about origin, development, conditions of saline soil formation in the territory of Kazakhstan (Glinka, 1931; Getroids, 1955; Borovsky, 1982). Saline soils are widely distributed in the southern and central parts of the Kazakhstan. In these arid regions, where rainfall is 100-150 mm y^{-1} and evaporation exceeds precipitation. Saline soils are soils that contain high concentrations of soluble salts: sodium, magnesium and calcium sulphates, and some sodium chloride, but have normal pH values (Borovsky, 1978; Faizov, 1980).

On the territory of Kazakhstan allocated four salt accumulation provinces: sulphate-chloride basin of the Caspian Sea, chloride-sulphate basin of the Aral Sea, soda-sulfate basin of the Balkhash Lake and chloride-sulfate basin of the Kara Sea (Borovsky, 1978; 1982). Each province has an own type of salinity and chemical features and differ in their genesis, composition and transport of salts. Depending on the chemical composition and the amount of soluble salts in the profile there are following degree of soil salinity: the amount of salt is 0.1-0.3 % in slightly saline soils, moderately saline is 0.3-0.5 %, strongly saline is 0.5-1.0 %, solonchanks more than 1.0 % (Saparov and Faizov, 2006).

The soil salinization is one of the most common land degradation and desertification processes. Anthropogenic stress to soil cover and ecosystem in Kazakhstan year by year increasing in the all geographical zones. Irrational use of the natural resources leads to ecological violation. The total area of Kazakhstan is 272 million hectares, at present day 180 million hectares is under the danger of degradation, or 60 % of the total territory (Saparov and Faizov, 2006; Issanova et al., 2014).

Soil erosion (wind/water erosion) appear in all natural zones, but is particularly strong in the long-term arable land, sand massifs, as well as in mountain and foothill areas (Almaganbetov and Grigoruk, 2008; Medeu, 2010). Development of wind erosion is due to soils with light-textured, carbonate, structureless of soils and intensity of anthropogenic pressure. The anthropogenic pressure increased in the sandy deserts of southern Pre-Balkhash region, Aral Sea and Northern Caspian Sea regions. As a result, sources of soil deflation appeared in these regions that lead to high concentration salts in the atmospheric flows. These salts provoke deterioration of pastures, reduction of biodiversity, salinization and desertification of soils (Issanova et al., 2014). Protection against to soil erosion and destruction requires erosion reclamation (agrotechnical, biological, chemical).

Dehumidification and soil contamination

Ecological state of the soil cover in many areas of Kazakhstan is characterized by near-critical and requires urgent measures of fertility reproduction and preservation of the environment.

Dehumidification takes place on chernozems and dark chestnut soils with long-term non-irrigated arable land in the northern regions of Kazakhstan and as well as the mountainous regions of irrigated arable land (Saparov and Faizov, 2006). Monoculture cultivation of grain and industrial crops on low agrotechnical conditions causes of dehumidification process and loss of soil fertility by 20-30 % and southern chernozems on virgin soil is 4.5-5.5%, long-term arable land by 3.0-3.5 %, dark chestnut soil is 3.5-4.4 and 3.0-3.3 % (Medeu, 2010). Micro aggregation of soil are deteriorate in cultivated soils, there is a real risk of suffering from water and wind erosion, which requires immediate action for the conservation and restoration of soil fertility (organic and mineral fertilizers, minimizing the processing, the introduction of grass crop rotation, planting trees, bushes and shrubs). According to the map of the soil dehumidification the loss of humus up to 5 % is weak degree of it, moderate is 5-10 %, a strong and very strong is 10-15 %, 15-20 % respectively (Saparov and Faizov, 2006).

Soil contamination (chemical, petrochemical, radioactive) is reflected in the areas of industrial, oil and gas, as well as of landfill testing of nuclear missiles. Chemical contamination of individual regions occurs among the arable chernozems and dark chestnut soils, irrigated soils in the south part of Kazakhstan under the immoderate use of organic and mineral fertilizers, pesticides, herbicides and other, which lead to the accumulation of toxicants in soils (Otarov, 11; Ustemirova and Suleimenov 2011). According to the toxicity, the arsenic, cadmium, mercury, selenium, lead, zinc, fluorine are high toxic elements; moderately dangerous is cobalt, boron, nickel, molybdenum, copper, chromium and barium, strontium, tungsten, manganese is belong to low risk (Ustemirova…). Decomposition and detoxification of chemical elements in the soil profile is due to the pH of the medium, mechanical, mineralogical composition, temperature, humidity, intensity of microbiological processes.

Petrochemical contamination of soil is allocated in all areas of oil and gas companies and routes of the oil/gas pipelines in Western Kazakhstan. The contamination occurs at all stages of field development.

Radioactive contamination of soil is occur in the places allocated former test radioactive sites (Semei, Kapustin Yar, Pribalkashe et al.), as well as in the areas of oil and gas complex such as Ozen-Zhetybai, Bozashy, Karachyganak.

CONCLUSION

The desertification and land degradation of large territories is accompanied by soil salinity, dehumidification, soil erosion, deflation, soil contamination, waterlogging by surface water and groundwater and a decrease in general regional biological capacity as well as reduced productivity of arable land.

The Aral Sea region, Northern Caspian Sea and Southern Balkhash deserts can be observed as areas of intensive soil desertification, salinization and deflation processes. As well as the desertification process are progressing in the irrigated soils of the deltas of Syrdarya, Shu, Ile and Karatal rivers. In Kazakhstan apart from natural environmental factors, the anthropogenic pressure increased their effect seriously during the last 50 years. All these actions destroy seriously the environmental processes and led to the serious forms of rapid soil/land degradation and desertification processes. The influence of anthropogenic factors is seen almost in all natural landscapes, especially in the Aral Sea region, where degradation and desertification processes are becoming more widespread.

REFERENCES

Almaganbetov N, Grigoruk V. 2008. Degradation of soil in Kazakhstan: Problems and Challenges. Soil Chemical Pollution, Risk Assessment, Remediation and Security, 309-320 pp.

Asanbayev I K, Faizov K Sh. 2007. Soil science with the basics of ecology and geography of soils. Almaty: Kazakh State University, 218 pp (in Russian).

Asian Development Bank, TA No 3898-KAZ “Participatory Rural Sector Planning and Development”, February, 2003.

Borovsky V M. 1978. Geochemistry of saline soils in Kazakhstan. Moscow, Nauka, 191 pp (in Russian).

Borovsky V M. 1982. The data concerning salt-affected soils and halo-geochemical provinces of Kazakhstan. Nauka, KazSSR. 253 pp (in Russian).

Danayev E. 2008. Feasibility of Wind Energy Development in Kazakhstan. Technical-Economical Analysis of Wind Farm Construction in the Almaty Region. MSc Thesis, Energy Systems and the Environment. Strathclyde University, United Kingdom, 1-134 pp.

Faizov K Sh. 1980. The soils of desert zone in Kazakhstan. Almaty. 134 pp (in Russian).

Faizov KSh, Tapalova AS. 2003. The ecological crisis in Aral Sea region and their solution problems. Almaty, 110 p.

Faizov KS, Kenenbaev SB, Mamutov ZU. 2006. Geography and ecology of the soil in Kazakhstan. Kazak Universiteti, Almaty, 348 pp (in Russian).

Gamalero E, Berta G, Bernard R G. 2009. The use of Microorganisms to Facilitate the Growth of Plants in Saline Soils. Microbial Strategies for Crop Improvement, 1-22 pp.

Glinka K D. 1931. Soil science. Moscow-Leningrad (in Russian).

Getroids K K. 1955. Selected works, Parts 1-3. Moscow (in Russian).

Iskakov NA, Medeu AR. 2006. Republic of Kazakhstan. Volume 3: Environment and ecology. Almaty, 289 pp (in Russian).

Issanova G, Jilili A, Semenov O. 2013. Deflation processes and their role in desertification of the southern Pre-Balkhash deserts. Arab J Geosci. DOI 10.1007/s12517-013-1106-z

Issanova G, Kaldybayev A, Jilili A, Semenov O, Dedova T. 2014. Dust storms in Kazakhstan: Frequency and Division. J of the Geolog Soc of India. Volume 84, Issue 4.

Kovda V A. 1950. Soils of Caspian plain. Moscow.

Kovda V A. 2008. Problems of desertification and soil salinization in arid territories of the world. Moscow, Nauka, 415 pp. (in Russian).

Lopatovskaya O G, Sugachenko A A. 2010. Soil melioration. Saline soils. Irkutsk.101 pp (in Russian).

Medeu A.R., (Eds). 2010. Republic of Kazakhstan. Volume 3. Environment and Ecology. Almaty, 520 pp (in Russian)

Mueller L, Saparov A, Gunnar L (Eds) (2014) Novel Measurement and Assessment Tools for Monitoring and Management of Land and Water Resources in Agricultural Landscapes of Central Asia. Springer.

Munns R. 2009. Strategies for Crop Improvement in Saline Soils. Salinity and Water Stress. Chapter 11. 99-110 pp.

Orlova M A, Seifullina S M. 2006. The main regularities of dust-salt transference in the desert zone of Kazakhstan. Volume II: West and Central Asia, Chapter 10, 121-128 p.

Orlova M A, Saparov A S. 2009. Global self-regulated circulation of salts in the nature. Poligraphia-servis K°, Almaty (in Russian).

Otarov A. 2011. The main factors and degree of soil degradation in the Shieli irrigated massif. Journal of Soil Science and Agrochemistry 1, 30-39 (in Russian).

Otarov A, Ustemirova, Mamyshev M. 2007. Patterns of distribution of lead in the soil-plant system at different levels of pollution. Journal of Research and results. Almaty, 141-145 pp (in Russian).

Pachikina L I, Osina A N, Kolesnikova N T. 1975. Water and salt regime of the saline soils in the lower reaches of the Ural river. Alma-Ata.

Pankova E I, Aidarov I P, Yamnova I A, Novikova A F, Blagovolin N S. 1996. Natural and human-induced salinization of soils in the Aral Sea basin: Geography, Genesis and Evolution. V.V. Dokuchaev Soil Science Institute, Moscow, 186 pp (in Russian).

Saparov AS, Faizov KSh. 2006. Degradation and soil conservation problems in Kazakhstan. Vestnik of Agricultural Sciences of Kazakhstan. Almaty, Bastau, 22-26 pp (in Russian).

UNDP, 2002. Human Development Report, Kazakhstan.

Ustemirova A, Suleimenov B. 2011. Contamination of arable land Pasture by heavy metals (Zn, Pb,Cd) in Maktaaral district of the South Kazakhstan region. Proceedings of the conference: «Actual problems of agriculture and crop production”, 211-213 pp (in Russian)

Vilesov E N, Naumenko A A, Veselova L K. 2009. Physical Geography of Kazakhstan. Almaty, Kazakh University. 362 pp (in Russian).

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CHANGES OF SOIL FERTILITY IN RELATION TO THEIR USE IN THE SOUTH AND SOUTH-EAST OF KAZAKHSTAN

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ABSTRACT

The data for the study of fertility change the main settings was obtained, depending on the use of arable land in the south and south-east of Kazakhstan. In the practice of irrigated agriculture soils undergo significant changes, giving the basis for allocating them to a group of irrigated soils. Irrigated soils have a number of features that distinguish them from virgin soils. Under the influence of irrigation they change color and the addition of genetic horizons, which becomes gray color. Irrigated soils are characterized by a deeper occurrence of carbonate and gypsum horizons. On these soils formed agroirrigation horizons, compared to virgin soils occurs weighting texture. Irrigation reduces the humus content in the soil and more evenly spread over the profile. Within the soil profile soil deplete water-soluble salts of potassium and sodium, and water-soluble enriched with calcium and magnesium salts. All irrigated soils have a high saturation of the soil absorbing complex alkaline bases. Among them, calcium predominate (70%) and magnesium (20%). In soils of ancient irrigation increases humus content, total and available phosphorus, exchangeable potassium, weighting texture. With increasing duration of the period of irrigation gray soils enriched with humus, nitrogen and phosphorus changes quantitative composition of humus in the form of readily towards increasing and improving soil nutrient regime, at permanent cropping and low agricultural soil degradation occurs even in long gray soils irrigated.

Key words: *light gray soil, irrigation, soil fertility, soil property.*

INTRODUCTION

In recent years there has been a strong degradation of the soil, which is caused by a decrease the humus content in the soil, intensive development of the wind and water erosion, salinization, technogenic pollution, which leads to a reduction the productivity of the agricultural sector (Dzhalankuzov et al., 2013; Otarov and Ybrayeva, 2010; Saparov et al., 2010). This situation is one of the main causes of exacerbation of the food problem as a whole and an acute shortage of environmentally safe products in particular. The solution to this problem should be regarded as a problem of importance to the State to maintain a healthy genotype nation and ensure the future of country. The study of patterns of change in soil fertility depending on the functional state of the soil is an important task.

The degradation of land resources and land use are inextricably connected mutually and also relevant to irrigated and rainfed drylands of Kazakhstan and Central Asia (Kovda, 2008). Any attempt to slow down the degradation process in the region requires consideration of land use and land use policies as the main initial measures for more sustainable use of land resources.

These days, it is necessary to make decisions that will have economic and political consequences. There is an urgent need for fundamental changes in strategies and systems in order to be able to make the transition from extensive agriculture to agriculture, efficient use of resources based on sustainable practices. Consequently, research and dissemination of more efficient from an economic point of view,

farming practices is essential to enhance the competitiveness of farmers and their income, while providing long term sustainability of the increase of the agricultural sector of the country.
Comprehensive analysis of the biogeocenotic soil functions due to its physical, chemical and physical-chemical properties is currently actual task in restoring of soil fertility.

Establishing patterns of change in soil formation processes: to study the transformation of mineral and organic part of the soil; to study the migration of nutrients in the soil and the possibility of changing these processes under external influence on soil, considered as a functioning system (Tanirbergenov and Suleymenov, 2013). Differentiated approach (systematic approach) to the soil system is one of the ways of solving this problem.

Science-based technology of reproduction of soil fertility allow rational use of soil resources.

Knowledge of the laws in modern soil formation which occurring under the influence of climatic factors, serve as a basis for predicting the actual status of soil fertility in different soil-climatic zones of the country and crop productivity.

The main aim is to study soil processes and to establish patterns of their changes in different soil-climatic zones of the Kazakhstan.

STUDY AREA AND METHODS

Study area is irrigated light gray soils of Maktaaral district in South Kazakhstan region (south part of Kazakhtan) and rice-swamp soils of Akdala irrigation massif in Almaty region (south-east part of Kazakhstan).

Southern light gray soils distributed in the territory of South Kazakhstan region. They are located below the ordinary gray soils within the southern altitudes from 200 to 350-400 m. The relief of this band (50-60 km) is sloping slightly undulating plain. Parent rocks are loess and loess differs by more lightweight mechanical composition and salinization in some cases. The vegetation of the region consists of ephemeroids-ephemeral groups. Light gray soils are used for irrigated and rain-fed agriculture.

The features characteristic of climate zone of gray soils in South Kazakhstan region are low rainfall, their uneven distribution on seasons, high temperatures in the summer and quite low in winter, very dry air during the warm season, strong evaporation from the soil surface. In summer, the region is under the influence of air masses of three types: of warm and moist continental polar air, cold and dry arctic masses and tropical air, which is formed over Central Asia.

Manifested sharply expressed periodicity of precipitation pattern and they are confined to the winter and spring months, when the fall of 75-85 % of the annual amount. Winter and spring rainfall partially provide a washing out salts harmful to plants of arable soil layers, creates reserves of productive moisture in soil.

Uneven humidification throughout the year and a rapid increase in air temperature from spring to summer determines the kind of water-thermal mode, substantial feature of which is a manifestation of hydrothermal two of periods: warm moist of spring and a hot dry summer.

Second field is to rice-swamp soils of Akdala irrigation massif in Almaty region (south-east part of Kazakhstan). The main background is represented in different degrees of takyr-like and saline soils. For takyr-like soils in lower reaches in Ili River is characterized by fissured surface, light gray, strongly porous or spongy, weakly compacted crust of flake structure. Light loamy (friable, structureless), and heavy loamy (lumpy) is divided by mechanical composition. Soil salinization is chloride-sulfate and sulfate-chloride.

According to climatic parameters the Akadala irrigation massif covers the desert zone with sharply continental climate, characterized by a large amplitude of air temperature, a minor amount of atmospheric precipitation (135-150 mm / year) and a large evaporation (991-1198 mm). Route-key approach is soil profiles.

On the basis of holding of route-key field researches will be examined interrelation of chemical and physical-chemical properties of soils which depending on duration of soil use and climatic factors.

In field conditions, on the soil profiles were studied parameters of soils was refined genetic affiliation of soils sampling was carried out on selection of soil samples. Analyses of soil samples was carried by Standard methods. On the basis of the approved of ecological criteria land evaluation was determined a degree of degradation of the soil cover (Republic of Kazakhstan. Ordinance, 2007).

RESULTS AND DISCUSSION

The influence of long use of gray soils in the production on morphological and chemical properties. Anthropogenic transformed soils, which disrupted humus horizon, low soil fertility and high bedding of carbonates arise under influenced agrotechnical methods. Violations of soil cover and of soils that related with the category of fallow lands, refers to a strong degree of anthropogenic disturbances, which are associated with destruction of the integrity of the structure and adding together parts of humus horizon when plowing, a decrease of humus content and nutrients in their alienation with the crop.

The influence of crop plants cultivation that using in irrigation system led the study and redistribution in the soil profile of basic physical-chemical properties of soils. As a result, the studied areas in irrigated soils with different salinity are currently in agricultural production for more than 50 years, the total content of humus is much lower (Dukhovny, 1996). Distribution of total humus on the soil profile of the arable layer is uneven. If the layer of 0-40 cm on the virgin lands the total humus content is 1.23%, while on irrigated gray soils is 0.61%, ie less on 40-50 % (table 1). Thus, on virgin soil plots site is enriched with total humus content because of the plant mass, whereas on irrigated gray soils is a sharp decrease in humus content at arable soil layer.

Table 1: Humus contents in light gray soils at layer of 0-40 cm

Soil profile	Field-Plot	Humus, %	Bulk forms,%		
			N	P	K
10	Virgin Lands	1,23	0,112	0,15	2,3
11	Nonsaline	0,61	0,063	0,19	2,3
12	Strongly saline	0,61	0,049	0,20	2,3

The content of nitrogen in virgin lands at the layer of 0-40 cm average is 0.112 %, and down along the soil profile is a gradual reduction of up to 0.056 %. Content of nitrogen in irrigated gray soils (non-saline and strongly saline plots) is somewhat smaller and makes from 0.063 up 0.049 %. If we compare the total nitrogen content in the arable layer, then on non-saline plots is less than 46 %, on plots strongly saline less on 56 % compared to the virgin lands.

Bulk forms of phosphorus is important indicator of soil fertility. The content of phosphorus (P_2O_5) in virgin lands plots is slightly lower compared with irrigated gray soils associated with entering of phosphate fertilizers at cultivation under cotton. In the plowing layer (0-40 cm) phosphorus in the virgin lands of 0.15 %, while during irrigation increases to 0,19-0,20 % (table 1).

In the virgin lands plot and in irrigated gray soils the total potassium content is 2.3 % at 0-40 cm layer.

If bulk forms of nitrogen, phosphorus and potassium make up the reserve those of elements soil, then mobile forms are used directly for power supply by plants.

Content of hydrolysable-nitrogen in the virgin lands is 82 mg / kg soil at arable layer of soil. In non-saline site the content of hydrolysable-nitrogen slightly less - 55.6 mg / kg. In strongly saline site the mobile nitrogen is less than 53.0 mg / kg, due to lower revenues and lower nitrification of organic mass (table 2).

Table 2: Content of mobile forms of nitrogen, phosphorus and potassium, and the absorbed bases in light gray soils at the layer of 0-40 cm

Soil profile	Field-Plot	Mobile forms mg / kg			Absorbed bases- mEq / 100 g				
		N	P	K	Ca	Mg	Na	K	Sum
10	Virgin Lands	82,0	11,9	487,5	10,6	7,4	0,56	0,64	19,2
11	Nonsaline	55,6	19,0	274,9	7,3	7,1	0,38	0,26	15,0
12	Strongly saline	53,0	28,5	289,7	10,3	9,5	0,25	0,48	20,5

In accordance with the bulk content of mobile phosphorus on the virgin lands and is significantly lower at the layer of 0-40 cm a total of 11.9 mg / kg soil (table 2). The content of mobile phosphorus in irrigated gray soils at the arable layer ranges from 19.0 to 28.5 mg / kg of soil, which is associated with the introduction of these areas of phosphate fertilizers, which have long aftereffect.

Plants is used exchangeable potassium (Saparov et al., 2011), it is amount in the virgin lands on average is 487.5 mg / kg soil at 0-40 cm layer. Mobile potassium content in irrigated gray soils decreases sharply to 274,9-289,7 mg / kg in the plow layer with more uneven distribution over the layers.

Cations located in the external layer of soil colloids and micelles are able to exchange reactions with cations of the soil solution, called absorbed or exchangeable cations.

Content of absorbed bases in the investigated soils ranges from 15 to 20.5 mg-Eq. 100 g of soil. Calcium and magnesium cations are up to 93-96 % of the capacity of absorption, and the sodium and potassium cations are only 4-7%. In the virgin lands the total absorbed bases is 19.2 mEq. 100 g of soil. In nonsaline site the absorption capacity decreases to 15.0 mEq. 100 g of soil, and with a substantial reduction of calcium cations and magnesium cations in part, of potassium and sodium as compared with a virgin lands site. In strongly saline field-plot is different situation observed. The total absorbed bases in the virgin lands and highly saline plot is on one level. This is due to the fact that the salinity those site is on the same level.

The studied soils are subject to secondary salinization is why with one important indicator is cation-anion composition. Analysis of aqueous extract carried out to determine the salinization of the soil. Considered soil salinization, in which the water-soluble of salts is more than 0.2 %.

The most harmful to an cotton plants are chlorides. In the period emergence on nonsaline plots the content of chlorides in meter layer within the limits 0.004 %, and in strongly saline plots 9 times greater (0.035%), which is reflected on the growth and development of cotton plant (table 3).

Table 3: Aqueous extract in % for the absolutely dry soil after washing during spring and autumn after harvest of raw cotton at layer of 0-100 cm

Site-field	Sum of salts, %	Alkalinity		Cl^-	SO_4^{--}	Ca^{++}	Mg^{++}	Na^+	K^+
		HCO_3^-	CO_3^{--}						
Before sowing, April									
Nonsaline	0,184	0,019	no	0,004	0,118	0,025	0,013	0,011	0,002
Strongly saline	0,513	0,015	no	0,021	0,334	0,071	0,033	0,033	0,004
After harvesting, October									

Nonsaline	0,216	0,020	no	0,009	0,128	0,027	0,014	0,016	0,002
Strongly saline	1,043	0,014	no	0,078	0,657	0,130	0,068	0,088	0,007

The degree of soil salinity in October compared to April after washing it increases double. Thus, in the nonsaline plots - up to 0.216 % and strongly is 1.043 %. During this period, there is a stabilization of soil salinity at the termination of the impact on the water-salt regime of soil washing and irrigation. We studied irrigated gray soils with sulfate type of salinity, the total amount of salts in the proportion of sulfate ions account for 56-65 %, the rest of them is calcium, magnesium, sodium, chloride and potassium.

In the period of completion of the harvest of raw cotton (October) the total stock of salts in the upper meter thickness of the studied areas was as follows: on the nonsaline 30.24 t / ha and strongly by 4.8 times more than nonsaline plots 146 t / ha. Increase in soil salinity at all sites is by increasing the amount of calcium and magnesium sulfates. The greatest influence on cotton yield had salinity in strongly saline site where harvest of raw cotton is less than 60 % compared with non-saline site.

The maximum accumulation of salts observed in the autumn, and the lowest in spring and summer, and depending on the cultural condition and irrigation and reclamation measures.

Mineralization of water used to wash the soil and irrigation is 1.1-1.3 g per 1 liter. Together with water in irrigated soils significant amount of calcium and sodium sulfates, and also is a source of chloride and nitrate.

Thus, the processes of secondary soil salinization affect the geomorphological and hydrogeological conditions of soils. The greatest number of secondary saline soils are concentrated in a drainless "Pahtaaral depression" (Umbetayev and Bigarayev, 2005). Factor of primary salinity influences the development of secondary salinity in the early stages of irrigation, when water table is at a considerable depth, and with the approach of the groundwater level to the surface of the primary differences in salinization of soil progressively smoothed out.

Experience on irrigated agriculture shows that naturally irrigated oases undrained conditions exist for salinity. Methods and irrigation rates play an important role in the development of secondary salinity. Excessive, without taking into account the needs of crops, the water supply leads to a rise in highly saline groundwater and promotes rapid growth of saline lands. For soil salinization and desalinization process is greatly influenced by the culture of agriculture.

The main land of Akdala irrigation massif presented by takyr like soils. They are divided into many types, differing in degree of salinity and solonetz. According to the results of route-key studies the following data were obtained:

Soil profile of virgin takyr like soils is poorly differentiated. The upper horizon of 2-3, up to 6 cm crust is light gray, porous. Next horizon is stratified-scaly, flabby, more gray, with capacity up to 5-12 cm. Below are a few compact, structureless horizon, 15-30 cm, which goes into the rock. In the upper, the horizon humus content is less than 1 %, with a gradual decrease of humus in the lower horizons. In the surface soils are calcareous.

Soil profile -1 laid down on alfalfa fields in 3rd year. The coordinates are N44°37.250, E076°49.731. The soil is slightly saline. Content of humus in arable layer low 0.54 %, respectively, and the total nitrogen content is low - 0.028 %, 0.31 % of total carbon. The nitrogen content (N) in the humus is 5,19 % (table 4). Existing amount of hydrolyzable nitrogen is very low - 28.0 mg / kg, mobile phosphorus is low of 16 mg / kg, exchangeable potassium is also low of 150 mg / kg.

Table 4: The content of humus, bulk and mobile forms of nitrogen, phosphorus and potassium in Akdala irrigation massif

Soil profile	Depth, cm	Humus %	Bulk forms, %			Mobile forms, mg/kg		
			N	P_2O_5	K_2O	N	P_2O_5	K_2O
P-1	0-32	0,54	0,028	0,132	2,19	28,0	16	150
	32-66	0,33	0,014	0,120	2,45	19,6	5	130
P-2	0-20	0,68	0,028	0,132	2,19	25,2	13	100
	20-48	0,14	0,014	0,212	2,3	22,4	8	100
P-3	0-5	1,05	0,056	0,128	2,5	28,0	40	1800
	5-28	0,42	0,014	0,120	2,45	25,2	16	700
	28-69	0,17	0,014	0,096	2,45	19,6	8	410

Soil profile-2 laid down under winter wheat. The soil is slightly saline. The humus content is 0.68 %, at the 0-20 cm layer, below a sharp decrease to 0.14 %. The soil is characterized by a very low content of readily hydrolyzable nitrogen - 28 mg / kg, available phosphorus is 13 mg / kg and exchangeable potassium is 100 mg / kg.

Soil profile - 3 laid down under hydromorphic soils with deposit of 15 years. Strongly saline soils characterized by a relatively high humus content of 1.05 %, mobile phosphorus is 40 mg / kg and exchangeable potassium is 800 mg / kg at 0-5 cm layer.

CONCLUSION

We obtained the data of results from the study of changes in the basic parameters of fertility depending on the use of arable land and climate change in southern and south-eastern of Kazakhstan.

In the practice of irrigated agriculture, soil undergo significant changes that give reason to isolate them in a group of irrigated soils. Irrigated soils have a number of characteristics that distinguish from virgin soils. Under the influence of irrigation they change color and the addition of genetic horizons, which becomes gray. Irrigated soils are characterized by a deep occurrence of carbonate and gypsum horizons. Agro irrigation horizons are formed in these soils; compared to virgin soils occurs weighting of mechanical structure.

With increasing duration in irrigation season of the serozems enriched with humus, nitrogen and phosphorus; changes at quantitative composition of humus upwards of readily forms and improving of soils nutrient regime; at permanent cropping and low agricultural soil degradation occurs even in long irrigated gray soils.

For land reclamation of Hungry Steppe in southern Kazakhstan to improve the culture of agriculture and soil fertility, to obtain high and stable yields of all crops need investment as a part of the State, as well as loans from the World Bank for the reconstruction of the collector-drainage and irrigation network.

System of irrigated agriculture in the soil-reclamation conditions of Akdala irrigation massif requires the following basic measures: drainage, rice-alfalfa and other crop rotation, capital and current land leveling, soil washing, the regulation of irrigation norms of water, taking into account the level of occurrence of saline groundwater and improve agronomic work.

Fallow plots of irrigated massifs, even if they were in the initial state is non-saline with the passage of time to salinization with extremely high degree. All reclamation activities should be carried out against the backdrop of better farming techniques, fertilization and water management.

REFERENCES

Dzhalankuzov T., Suleymenov B., Bauer P., Busscher W., Stone K. 2013. Irrigated Cotton Grown on Sierozem Soils in South Kazakhstan. *Communications in Soil Science and Plant Analysis, USA, Taylor & Francis*, 44:3391-3399.

Dukhovny VA. 1996. *Report on land reclamation of Dzhetysay zone.* Tashkent, 199 p.

The Republic of Kazakhstan. Resolution. 2007. On approval of the ecological criteria for valuation of land, Astana.

Kovda VA *Problems of desertification and salinization in arid regions of the world.* 2008. Inst Phys-Chem. and biol. Problems in Soil Science. Ed. EI Pankov, IP Aidarova, Moscow, Nauka, 415 pp.

Umbetayev I., Batkayev ZY. 2000. *The system of cultivation of cotton in the south of the Republic of Kazakhstan.* Almaty, pp. 143-149.

Umbetayev I., Bigarayev O. 2005. *Scientific basis of development of cotton.* 304 p

Saparov AS, Eleshev RE, Suleymenov BU. 2011. *Recommendations for the rational use of potash fertilizers in terms of irrigated areas of south and south-east of Kazakhstan.* Astana, 21 p.

Saparov AS, Suleymenov BU, Tanirbergenov SI. 2014. Agromeliorative techniques to improve productivity of cotton in the context of Kazakhstan. *International Congress on green infrastructure and sustainable societies of the city, 8-10 May, Izmir, Turkey,* 166 pp.

Otarov A, Ybrayeva MA. 2010. Salt regime of soils farms beneficiary in Akdala irrigation massif. *Soil Science and Agricultural Chemistry, №4,* pp. 50-57.

Tanirbergenov SI, Suleimenov BU. 2013. The study of the influence of the vertical drainage on soil-reclamation state of light serozem in South Kazakhstan region. *Research and results KazNAU, №1,* pp 129-132.

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RESERVOIR SEDIMENTATION AS A CONSEQUENCE OF LAND USE IN THE CATCHMENT

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ABSTRACT

Reservoir sedimentation is a very complex problem. Natural conditions and anthropogenic activities have strong influence on sedimentation intensity and hydrological processes, which is represented at the experimental watershed of the Dičina River, in Western Serbia. Reservoir of 340000 m^3 was formed after construction of a 17 m high dam, in 1966. Sedimentation of the „Velika Dičina“ reservoire was determined on the basis of a survey from October 1966 to October 2011, along longitudinal profile, 750 m upstream from the dam, with 15 cross section profiles (at a spacing of 50 m). Land use changes were analyzed on the basis of a comparison of watershed conditions in 1966 and 2012, using the CORINE methodology and the MapInfo software. Sediment yield of the area and intensity of erosion processes were estimated on the basis of the “Erosion Potential Method” (EPM). The hydrological conditions in 1966 and 2012 (after the performed Erosion and Torrent Control Works-ETCWs) were assessed on the basis of a historical overview of land use changes and their impact on computed maximal discharges. Total quantity of deposited sediment in the reservoir amounts to 18750 m^3. Intensity of sedimentation has continuously been decreasing since 2002 as the consequence of land use changes, performed ETCWs and depopulation. The realization of restoration works contributed to a decrease in the annual yield of erosive material from $Wa=16007\ m^3$ to $Wa=1930\ m^3$. Presented are the comparative results of sediment transport for rivers in Serbia, with catchment area smaller than 1000 km^2.

Key words: *catchment area, sedimentation, erosion processes, depopulation, land use, sediment yield.*

INTRODUCTION

Dams and accumulations have been successfully used for collecting, storage and managing of water resources throughout history. Today, there are a large number of constructed dams with multiple functions, including the production of electric power, flood protection, water supply, irrigation, recreation, fishery and many others. Reservoir siltation is a very complex problem in Serbia, both in big and small reservoirs. The huge Djerdap reservoir in the Danube River, on the border between Serbia and Romania, has a volume of $2\cdot10^9\ m^3$, and traps $15\cdot10^6\ m^3$ of sediment every year. However it has not been significantly endangered due to sedimentation yet (Petković et al., 1999). In contrast to that, the small Gvozdac reservoir at Goč mountain in Central Serbia, has a volume of $60\cdot10^3\ m^3$ that is completely filled with sediment and out of function for water storage (Ristić & Ljujić, 2004). Sediment yield due to soil erosion depends on the complex interaction among a number of factors, including the natural characteristics of the area, population growth and fall rates, educational and cultural issues, the institutional conditions, as well as environmental and agricultural policy(Ananda & Herath, 2003; Ceylan et al., 2011). The intensity of erosion processes varies depending on storm conditions, hillslope aspect, lithological properties and human impact (Ristić et al., 2012a).

In the 60s of the 20th century over one hundred small reservoirs were formed in the hilly-mountainous regions of Serbia. These reservoirs were faced with a serious risk of sedimentation due to intensive anthropogenic activity in the watershed areas (IWRMJČ, 2001). However, already in the 80s of the last century the process of depopulation of rural areas was initiated as a result of the migration of people to cities, which reduced the pressure on the forest and agricultural areas. In the same period, Water Resources Management of Serbia performed large scale erosion and torrent control works (ETCWs), including technical works (check dams, bank protective structures, torrent training) and biotechnical works (afforestation, forest protective belts, silt-filtering strips, grassing, terracing and contour farming). In addition, spontaneous restoration of forests in large areas of abandoned arable land was observed in the hilly-mountainous areas characterized by intensive depopulation (Ristić & Nikić, 2007). The large-scale land use changes have produced some favorable effects, including decrease of sediment yield, less intensive reservoir sedimentation and reduced watershed potential for the formation of fast surface runoff. These phenomena were measured and analyzed at the experimental watershed of the Dičina River in Western Serbia.

MATERIALS AND METHODS

Study Site Description

Reservoir sedimentation and the hydrological effects of land use changes should be assessed at watershed scale, on the basis of complex investigations, including a historical overview of the process of erosion and land use changes, intensity of sedimentation, computations of sediment yield and hydrographic characteristics of the watershed. This paper presents an investigation carried out at the experimental watershed of the Dičina River, profile P at the “Velika Dičina“ dam, (Fig. 1).

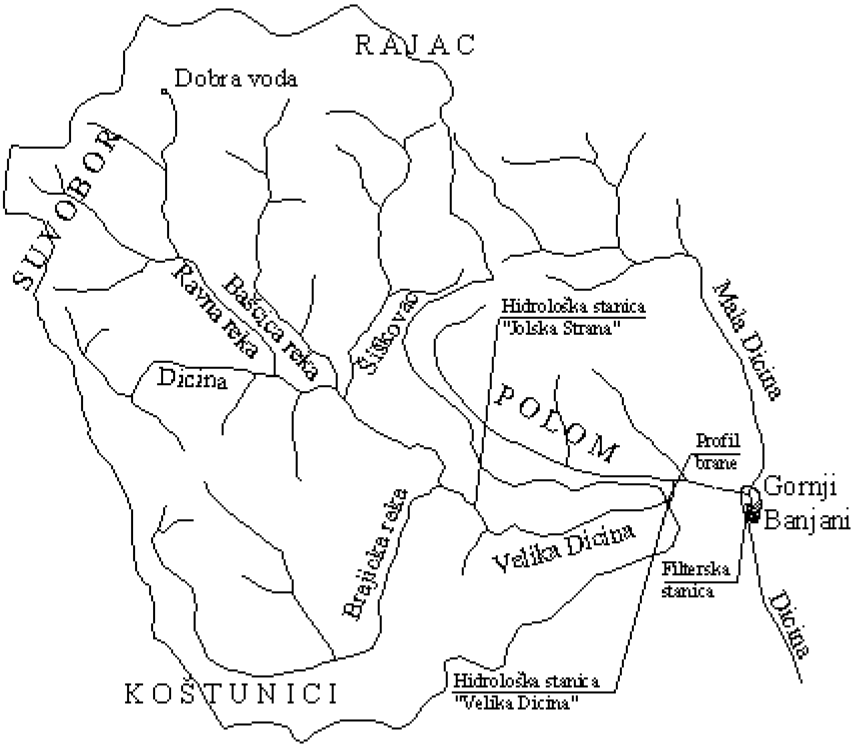

Figure 1. The experimental watershed of the Dičina River

The dam „Velika Dičina“ (made of stone with clay core) was built in the 1965-66 period, above the village of Gornji Banjani, as a water retention area for flood protection with a continuously open outlet. The main characteristics of the dam and reservoir are as follows: construction height of the dam, Hbr=17.0 m; dam crown width, B=3.50 m; dam crown length, Ld=65.20 m; and volume of the reservoir, V=340000 m3.

The main hydrographic characteristics of the experimental Dičina River watershed (up to the control profile P at the “Velika Dičina” dam), are presented in Tab. 1:

Table 1: Main hydrographic characteristics of the experimental watershed

Parameter	Mark	Unit	Dičina river
Magnitude	A	km2	21.98
Perimeter	P	km	23.64
Peak point	Pp	*m.a.s.l.	794
Confluence point	Cp	m.a.s.l.	492
Mean altitude	Am	m.a.s.l.	684.10
Length of the main stream	L	km	8.20
Absolute slope of river bed	Sa	%	3.68
Mean slope of river bed	Sm	%	2.05
Mean slope of terrain	Smt	%	23.99
Density of hydrographic network	D	km·km-2	2.57

**m.a.s.l.-meters above sea level*

Methodology

The intensity of sedimentation was surveyed from October 1966 to October 2011. Sediment yield was measured by survey along longitudinal profile, 750 m upstream from the dam, with 15 cross section profiles (at a spacing of 50 m). The measurements were taken in 1966, 1997, 2001 and 2011, using a theodolite (from 1966 to 2000) and a laser total station (Topcon GPT-3100N) from 2001 to 2011.

Land use changes were analyzed on the basis of the existing technical documentation and the data collected from 1966 to 2012, field investigations, usage of aerial and satellite photo images, as well as topographic, geological and soil maps. Land use classification was made on the basis of the CORINE methodology (EEA, 1994) using the MapInfo software. The area sediment yield and the intensity of erosion processes were estimated by the “Erosion Potential Method” (EPM). This method was created, developed and calibrated in Serbia (Gavrilović, 1972) and it is still in use in all the countries which originated from former Yugoslavia.

The aim of this investigation is to show how land use changes caused by ETCWs and lowered anthropogenic pressure can help improve the hydrological conditions in watersheds, mitigate erosion processes, decrease deposition of sediment and reduce the risk of torrential floods.

RESULTS OF INVESTIGATION

Land use changes

The land use changes were determined on the basis of comparison of land use maps from 1966 and 2012 in figures 2a and 2b.

There are no settlements in the watershed. However, the villages of Koštunići and G. Banjani are located in the vicinity (Fig. 1). The inhabitants of these villages are the owners and the users of the land. The anthropogenic pressure on the soil in the watershed was very strong during the 1960s of the last century, because the population of the neighboring villages amounted to more than 1473 people or 67 persons per 1 km2. In 2011, there were 747 inhabitants or 34 per 1 km2 (SORS, 1971-2011).

The erosion and torrent control works (ETCWs) in the watershed started in the mid-60’s of the 20th century. In the 1966–2012 period a wide scope of biological and biotechnical activities were performed. Dominant biological and biotechnical activities included: afforestation of bare land with

Pinus nigra and Pinus silvestris (219 ha; steep, deforested and eroded slopes; 700-1100 seedlings per ha, two to three years old); systems of wattlings (197 wattlings were built in 21 gullies; average height - 0.8 m; material - Salix alba). The autochthonous forest cover dominantly consists of beech and oak trees. The beech forests are located at northern exposures, whereas the oak forests can mostly be found in the south.

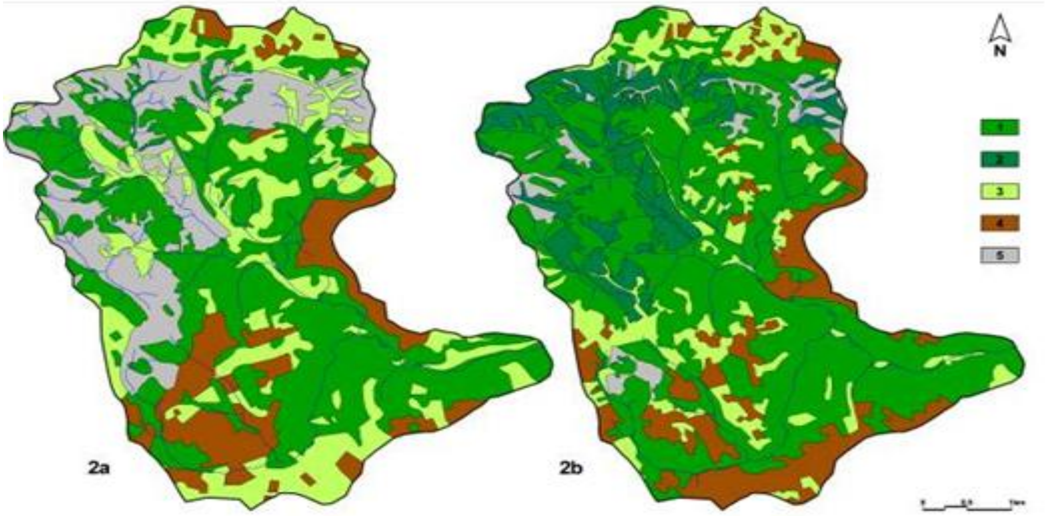

Figure 2. a) Land use in the watershed of the Dičina river (1966): 1– Broad-leaved forest (9.58 km2-43.58%); 3 – Pastures and grasslands (5.49 km2-24.97%); 4 - Land principally occupied by agriculture, with significant areas of natural vegetation (2.94 km2-13.42%, of which 2.34 km2 are arable land and 0.60 km2 are shrub land); 5 – Bare lands (3.97 km2-18.06%); b) Land use in the watershed of the Dičina river (2012): 1 – Broad-leaved forest (12.53 km2-57%); 2 – Coniferous forest (2.19 km2-9.96%); 3 – Pastures and grasslands (3.25 km2-14.79%); 4 – Land principally occupied by agriculture, with significant areas of natural vegetation (3.17 km2-14.43%, of which 2.53 km2 are arable land and 0.64 km2 are shrub land); 5 – Bare lands (0.84 km2-3.82%)

The process of erosion and sediment yield

Dispositions of different categories of destru-ctivity of erosion processes (classification by EPM) in 1966 and 2012 are presented in figures 3a and 3b. Some characteristic outputs of computations of sediment yield are presented in Tab. 2, as well as the representative values of the coefficient of erosion Z, before the ETCWs (1966) and at present (2012), including Wa-annual yield of erosive material and Wasp-specific annual yield of erosive material.

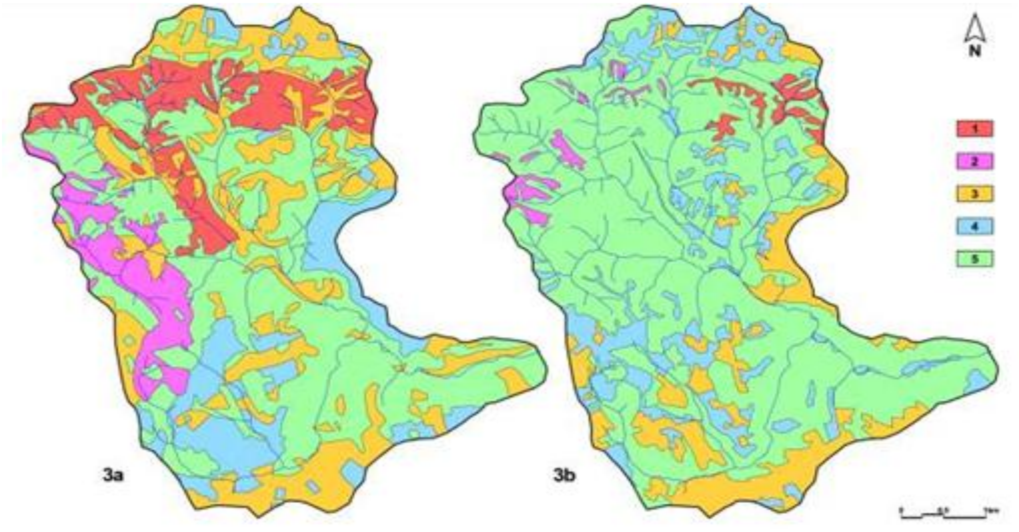

Figure 3. a) The intensity of erosion processes in the watershed of the Dičina river (1966): 1 – Excessive erosion (2.42 km2 - 11.02%); 2 – Strong erosion (1.55 km2 - 7.05%); 3 – Medium erosion

(5.49 km2 - 24.98%); 4 – Weak erosion (2.94 km2 - 13.37%); 5 – Very weak erosion (9.58 km2 - 43.58%); b) The intensity of erosion processes in the watershed of the Dičina river (2012): 1 – Excessive erosion (0.36 km2 - 1.64%); 2 – Strong erosion (0.35 km2 - 1.59%); 3 – Medium erosion (3.11 km2 - 14.15%); 4 – Weak erosion (3.24 km2 - 14.74%); 5 – Very weak erosion (14.92 km2 - 67.88%);

Table 2: Characteristic outputs of computations of sediment yield in the conditions before the ETCWs (1966) and actual conditions (2012)

Parameter	Before ETCW-1966	Actual conditions-2012
Wa [m3]	16007	1930
Wasp [m3·km-2·year-1]	728.3	87.8
Z	0.439	0.187

Reservoire sedimentation

The sedimentation of the „Velika Dičina“ reservoire was determined on the basis of a survey conducted from October 1966 to October 2011 along longitudinal profile, 750 m upstream from the dam,

with 15 cross section profiles, at a spacing of 50 m (Fig. 4). The total quantity of deposited sediment in the reservoir amounts to 18750 m3, i.e. 15800 m3 (509.6 m3/yearly on average), in the 1966-1997 period, 2280 m3 (570 m3/yearly on average), in the 1998-2001 period and 670 m3 (67 m3/yearly on average) in the 2002-2011 period. The maximal depth of deposited sediment close to the dam amounted to 3.1 m. The process of reservoire sedimentation starts at the distance of about 450 m upstream from the dam (profile 9, Fig. 4).

The levels of reservoir sedimentation were measured in 1966, 1997, 2001 and 2011. Cross section profile 2, at the distance of 100 m upstream from the dam (Fig. 4, 5) has a deposited surface of 44.32 m2 and a maximum thickness of deposited material of 2.1 m.

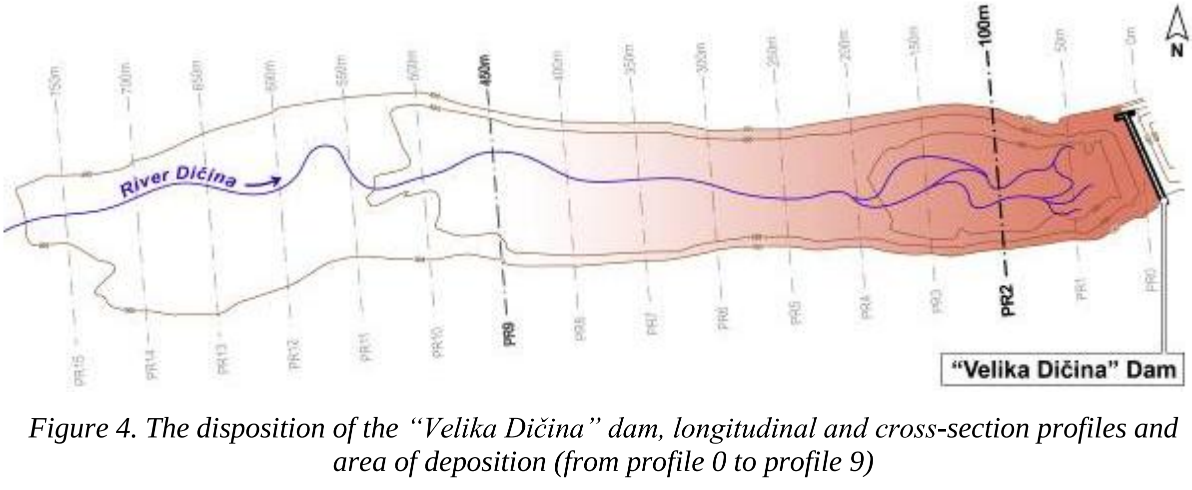

Figure 4. The disposition of the "Velika Dičina" dam, longitudinal and cross-section profiles and area of deposition (from profile 0 to profile 9)

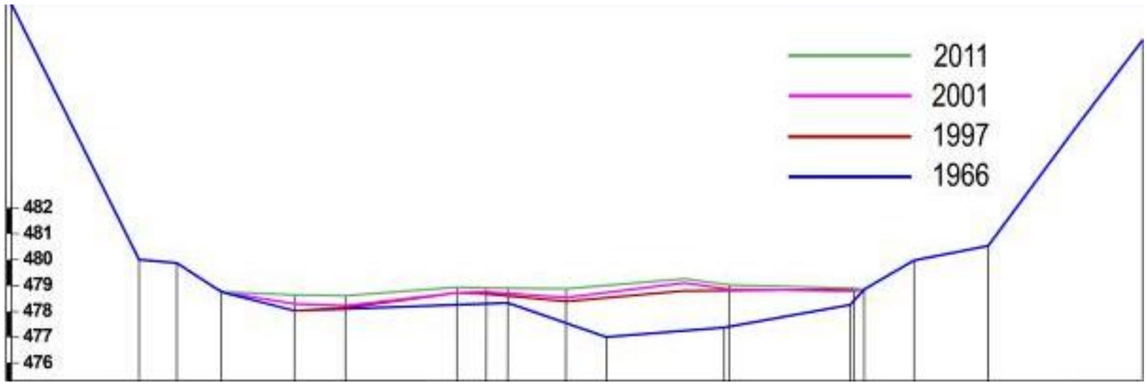

Figure 5. The cross-section of the profile 2 and levels of reservoir sedimentation in 1966, 1997, 2001 and 2011

COMPROMISION OF RESEARCH RESULTS WITH DATA FOR OTHER BASINS IN SERBIJA

Database on sedimentation in the territory of Serbia includes the results of measurements of suspended sediment in several larger and smaller rivers, as well as results of reservoir siltation monitoring. This database is analyzed by Petkovic (Ljujić & Petković, 2010).

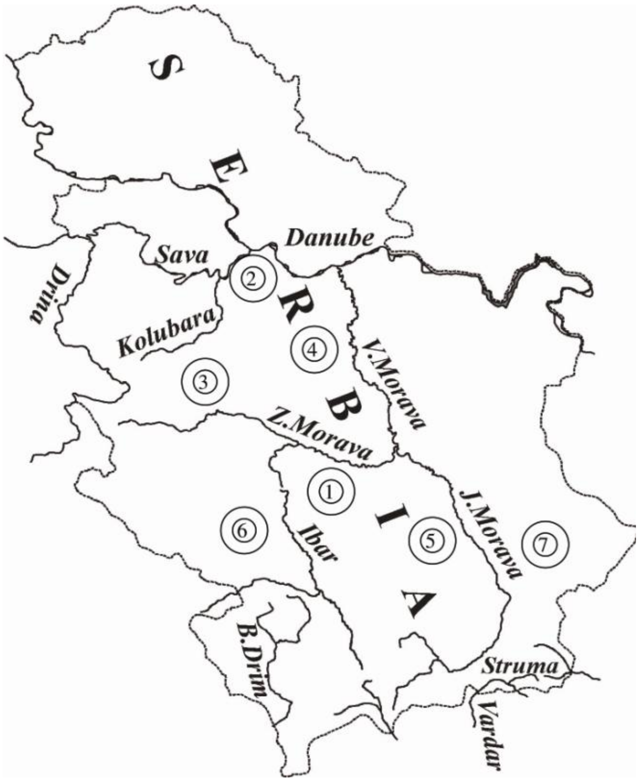

Figure 5. Disposition of investigated catchments

Table 3. presents the comparative results of measurement and calculation of sediment transport (formula by Petkovic) for some rivers in Serbia, with catchment area smaller than 1000 km2.

Table 3: Comparative results of measurements and calculation of sediment transport for Serbia

No.	River	F km2	I	Q m3/s/km2	H	E	gmeasur m3/km2/yr	gcalc m3/km2/yr
1.	Gvozdac river	14	0.17	0.014	0.0042	0.03	214	177
2.	Topcider river	16	0.08	0.005	0.0013	0.08	100	126
3.	**Velika Dicina**	22	0.11	0.011	0.0022	0.06	90	158
4.	Grosnica river	30	0.13	0.008	0.0022	0.40	900	688
5.	Toplica river	349	0.13	0.010	0.0022	0.24	380	415
6.	Veliki Rzav	437	0.09	0.014	0.0025	0.12	230	354
7.	Vlasina river	972	0.10	0.009	0.0027	0.41	500	466

Based on the results from Table 3, a diagram of a specific correlation between sediment transport (g) and water shed area (F) is obtained, shown in Figure 6. On the diagram are specified the range of values g (F), obtained on the basis of sediment measurement applied to a number of river flows in Serbia.

From Figure 6 it can be concluded that the sediment transport in the Velika Dicina basin, registered at the dam, is lower than the range for the territory of Serbia, which stems from the fact that part of the water and sediment is lost due to infiltration in the reservoir area.

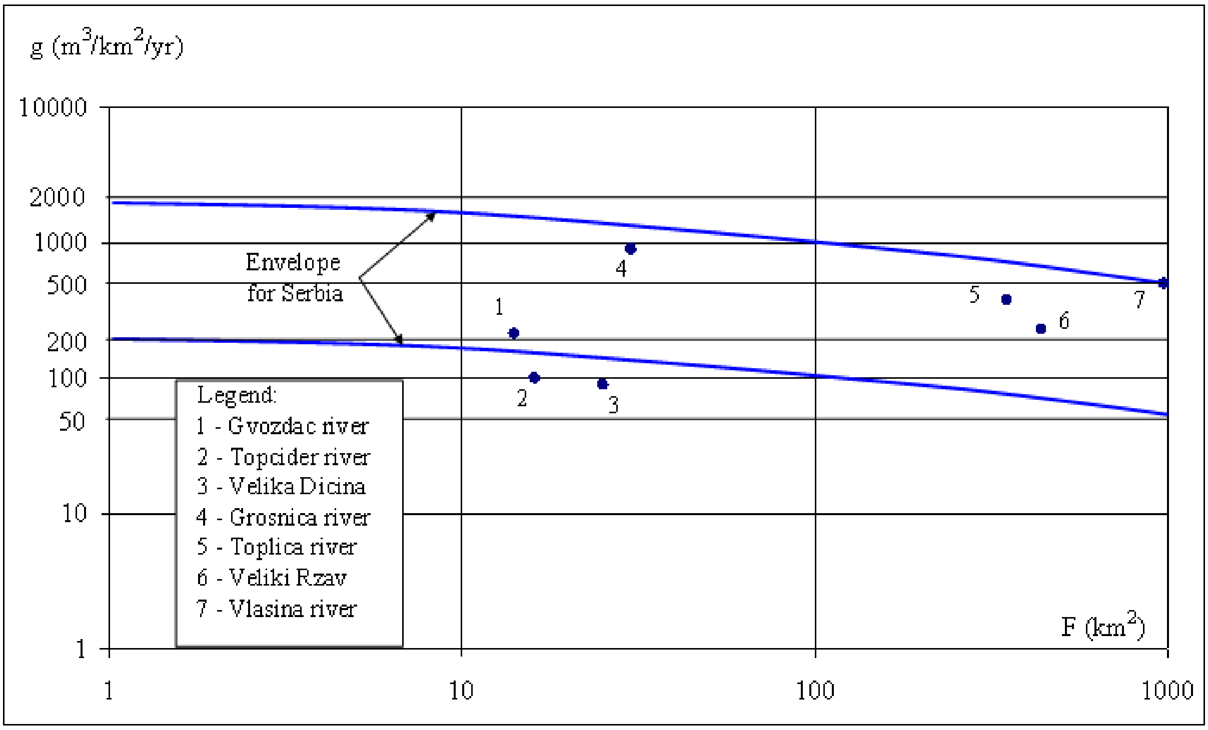

Figure 6. Correlation of specific sediment transport (g) and watershed area (F), for basins up to 1000 km2

DISCUSSION

The processes of erosion and sedimentation are related to the conditions in a watershed, including climate, topography, geology and soil characteristics, hydrology, population density and land use. The natural conditions in the watershed of the Dičina River are favorable for the development of the process of erosion, fast surface runoff formation and sediment transport. These natural conditions include frequent rainfall events of a short duration (2-3 hours) and strong intensity, I > 1 mm·min-1 (Ristić et al., 2012b), steep slopes of the terrain (Smt=23.99%) and river bed (Sa=3.68%). In addition, the dominant part of the experimental watershed consists of waterproof rocks (serpentine) or erodible rocks (marls and sandstones, dolomite, porphyritic breccias, tuffs with porphyritic flows, claystones and diabases). The existing soil types (Eutric Leptosol and Calcic Cambisol) are characterized by a moderate water storage capacity and resistance to erosion under sustainable land use (dense vegetation cover, contour and terrace farming, limited number of live stock, controlled urbanization and forest cuttings). However, a significant part of the soil (39%) was eroded, during the 1960s of the last century, due to inadequate land use (massive clear forest cuttings, overgrazing, and straight row farming down the slope). The consequences were reduced water infiltration capacity and intensive sheet, furrow and even gully erosion.

The average population density in the vicinity of the watershed amounted to 67 persons per 1 km2 during the 1960s of the last century and 34 per 1 km2 in 2011. The comparison of the land use maps from 1966 and 2012 shows great differences in the structure of surfaces (Fig. 2a and 2b). Until the end of 1960s, the watershed of the Dičina River was covered with bare lands on 18.06% of the total area (3.97 km2). The forests were used for timber and fuel. The meadows and pastures had a degraded grass cover and a compacted surface soil layer, because of the abundant cattle and sheep populations, while farming was carried out down the slope, in straight rows. Numerous activities initiated intensive sheet and rill erosion with embryos of gullies, and decreased water storage capacity of the soil. In this way, ideal conditions for fast surface runoff formation, development of the process of erosion and loss of soil were created. About 40 years later (spring of 2012), bare lands cover just 3.82% of the total area (0.84 km2). In the same period, the broad-leaved forest area increased from 43.58% of the total area (9.58 km2) to 57% of the total area (12.53 km2). In addition to that, new coniferous forests were established in almost 9.96% of the total area (2.19 km2), mostly on the former bare lands and abandoned arable land.

The depopulation caused a decrease in the anthropogenic pressure on the agricultural and forest surfaces in the watershed, so that the pastures and grasslands were reduced from 24.97% (5.49 km2) to 14.79% (3.25 km2) of the total area. In addition, 13.42% of the total area (2.95 km2) containing mostly bare land, abandoned arable land and pastures became spontaneously overgrown with trees and shrubs.

The establishment of stable forest stands on bare land is a key anti-erosion measure applied to protect reservoir storage capacity from sedimentation. The effects of this measure are the following: increase of transpiration and interception, reduction in the loss of water by evaporation, the development of the soil and its infiltration capacity, as well as lower, but longer specific runoff. Pinus nigra on serpentine rock produced the above effects, 7 years after planting in the experimental site at Goč mountain in Central Serbia (Ristić & Macan, 1997). The performed ETCWs in the watershed of the Dičina River (afforestation of 219 ha of deforested and eroded slopes, systems of wattlings for gully restoration) helped decrease the sediment yield and balance the runoff regime.

Total sedimentation in the „Velika Dičina” reservoir in the 1966-2011 period, amounts to 18750 m3 or on average 416.7 m3/yearly, i.e. 19 m3·km-2 expressed as specific annual intensity of sedimentation. Deposition of the reservoir was more intensive (570 m3/yearly on average, or 25.9 m3·km-2) in the 1998-2001 period, than in the 1966-1997 period (509.6 m3/yearly on average, or 23.2 m3·km-2), as the consequence of the highly intensive and uncontrolled forest exploitation on steep slopes. The intensive afforestation of bare lands and restoration of gullies with wattlings, as well as better control of cuttings and depopulation, contributed to a decrease in the intensity of deposition in the 2002-2011 period to 67 m3/yearly on average (3.05 m3·km-2). The total loss of reservoir volume in the 1966-2011 period amounts to 5.51%, or on average 0.122% yearly.

The initial state of the process of erosion (1966) was characterized by the coefficient of erosion Z=0.439 (medium erosion). ETCWs were carried out in order to decrease the yield of erosive material, increase water storage capacity of the soil and reduce flood runoff. The present state of the process of erosion is characterized by the coefficient of erosion Z=0.187 (very weak erosion). The realization of restoration works helped decrease the annual yield of erosive material from Wa=16007 m3 to

Wa=1930 m3 (Tab. 2). The comparison of erosion maps from 1966 and 2012 shows great differences in the intensity of the process of erosion (Fig. 3a and 3b). Until the end of the 1960s, the watershed of the Dičina River was endangered by excessive erosion (the hardest category of terrain destruction with deep gullies, landslides, and removed soil) on the 11 % of the total area (2.42 km2), while in the spring of 2012 it amounted to 1.64% of the total area (0.36 km2).

Comparing erosions parameters of the catchment area of the river Velika Dičina with other river basins in Serbia, it was found that only Gvozdac river is more beneficial to the erosion factor. This means that only the basin of this river has a smaller percentage of areas under severe erosion of the basin Velika Dičina. In terms of annual values of sediment transport in the basin (g) has the lowest specific transport of sediment from the basin, expressed in m3/km2/year. Compared with, the size and decline, similar river basin Grošnica river four times lower value of specific transport of sediment from the basin of Velika Dičina. Catchment area of the river Velika Dičina has the lowest specific sediment transport.

CONCLUSIONS

The experimental watershed of the Dičina River still has the natural potential, in terms of climate, topography, geology and soil characteristics and hydrology, for the development of intensive processes of erosion, sediment yield and reservoir sedimentation. Soil erosion in the watershed, during the 60s of the last century, was initiated by the removal of forest (clear cuttings, trunk transport down the slope) and inadequate agricultural activities (straight row farming down the slope, overgrazing). In addition to that, population density, educational and cultural conditions contributed to the process of degradation.

The anthropogenic impact was significantly reduced after the ETCWs and the change towards sustainable land use. The depopulation contributed to a significant decrease in the pressure on agricultural and forest surfaces in the watershed. The ETCWs in the watershed of the Dičina River (afforestation of 219 ha of deforested and eroded slopes, systems of wattlings for gully restoration) helped decrease the sediment yield and balance runoff regime. The establishment of forest stands on degraded surfaces and appropriate technical works in the hydrographic network are effective anti-erosion measures for the protection of reservoir storage capacity from sedimentation (Ljujić et al., 2013).

Once extremely disturbed watershed with intensive sediment yield is now restored after large-scale biological and biotechnical ETCWs, which were performed in the 1966-2010 period. Land use changes in the watershed helped balance the runoff regime by increasing the low discharges (their amount and duration) and decreasing the maximal discharges. The intensity of the process of erosion has been reduced from medium erosion (Z=0.439) before the ETCWs, to very weak erosion (Z=0.187). Most of the former bare land, abandoned and degraded arable land and pastures were transformed into forest surfaces or transitional woodland- shrub land. This transformation and the restoration of 21 gullies with systems of wattlings helped decrease the sediment yield about 8 times.

The natural conditions in the watershed of the Dičina River are favorable for the development of the process of erosion. Because of this, be applied erosion protection based on biotechnology works and increasing the forest coverage of the watershed. The afforestation should be done with appropriate types and form a stable stand, at least 7-10 years before the exploitation of the dam. Afforestation and increase the area under vegetation allows for the preservation of biological diversity. Protective function of the vegetation is reflected in the creation of favorable hydrological conditions in the basin, the development of land and the infiltration capacity, mitigation of erosion, reducing the maximum flow and volume of flood, reduce sediment accumulation in the reservoir and the risk of torrential floods.

Large forest fires a frequent occurrence in the region. The last fire was in 2012, destroyed more than of 100 ha forest and raised plantations. The basic network of fire protection on the ground should make the fire streaks associated with roads and watercourses. Water for fire fighting should be provided from capped sources, and in the upper reaches of streams and rivers form a mikroa-accumulations. In unpopulated places should raise watchtowers of the dominant points and arrange service monitoring and alert.

REFERENCES

Ananda, J. & Herath, G., 2003. Soil erosion in developing countries: a socio-economic appraisal. Journal of Environmental Management, 68, 343-353.

Ceylan, A., Karabork, H. & Ekizoglu, I., 2011. An analysis of bathymetric changes in Altinapa reservoir. Carpathian Journal of Earth and Environmental Sciences, 6 (2), 15 – 24.

EEA (European Environmental Agency), 1994. Coordination of information on the Environment. 152 pp.

Gavrilovic, S., 1972. Engineering of Torrents and Erosion. Construction, Special Issue, Belgrade.

Institute for Water Resources Management „Jaroslav Černi“ (IWRMJČ), 2001. Water Resources Management Basic Plan of Serbia. Ministry of Agriculture, Forestry and Water Resources Management, Belgrade, Serbia.

Ljujić, M. & Petković, S., 2010. Sedimentation of small reservoir on a torrent stream in central Serbia, Water and Sanitary Engineering, (ISSN 0350-5049), Vol. 40, No. 2, pg. 31-46. Belgrade, Serbia.

Ljujić, M., Ristić, R., Despotović, J., Aleksić, V., 2013. Reservoir sedimentation and hydrological effects of land use changes-case study of the experimental Dičina river watershed, Carpathian Journal of Earth and Environmental Sciences, (ISSN Online: 1844-489X), Vol. 8, No. 1/2013, pg. 91-98.

Petković, S., Dragović, N. & Marković, S., 1999. Erosion and sedimentation problems in Serbia. Hydrological Sciences Journal, 44(1), 63-77.

Ristić, R. & Macan, G., 1997. The Impact of erosion control measures on runoff Processes, Red Book- IAHS, 245, 191-194, England.

Ristić, R. & Nikić, Z., 2007. Sustainability of the System for Water Supply in Serbia from the aspect of Erosion Hazard. Journal for Water Resources Management, 225-227, 47-57.Ristić, R., 2003. Runoff lag time on torrential watersheds in Serbia. Journal of Faculty of Forestry, 87, 51-65, Belgrade.

Ristić, R., Kostadinov, S., Abolmasov, B., Dragićević, S., Trivan, G., Radić, B., Trifunović, M. & Radosavljević, Z., 2012b. Torrential floods and town and country planning in Serbia. Natural Hazards and Earth System Sciences, 1 (12), 23-35.

Ristić, R., Kostadinov, S., Radić, B., Trivan, G. & Nikić, Z., 2012a. Torrential Floods in Serbia – Man Made and Natural Hazards. 12th Congress INTERPRAEVENT 2012, Proceedings (ISBN 978-3-901164-19-4), pg. 771-779, Grenoble, France.

Ristić, R., Ljujić, M., Bukvić, Z. & Đeković, V., 2004. Sedimentation at small reservoires in Serbia. XXII Conference of the Danubian countries on the Hydrological Forecasting and Hydrological Bases of Water Management, Proceedings, Brno.

Statistical Office of the Republic of Serbia (SORS), 1971-2011. Statistical Year Book. Belgrade, Serbia.

CLIMATE CHANGES AND URBAN POLLUTION

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REVISITING URBAN PLANNING FRAMEWORK IN SERBIA: TOWARDS ADAPTIVE URBAN PLANNING AND DESIGN FOR CLIMATE CHANGE

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ABSTRACT

In following decades, according to the regional climate projections, Serbia will experience an increase in temperature of 4˚C, and decrease in summer precipitation up to 50%, and increase possibilities of heavy rain falls. We already witnessed serious challenges for urban population caused by recent flooding in Serbia. Adaptation to those changes, and other caused by changing weather patterns, calls for the re-definition of urban planning and design framework and the integration of climate change in planning processes. In order to set a ground for development of adaptive approach in urban planning process, which will reduce potential vulnerability of the urban population to climate change, we have firstly to understand strength and weaknesses of the current urban planning and design framework to integrate such an approach. The paper explores whether or not we have to rethink existing urban planning framework and tools in the context of climate change and natural hazards focusing on larger urban centers in Serbia, and looking at regulative planning tools. Recommendations to further strengthen adaptive urban planning and design are derived.

Key words: *Urban planning and design, Climate change, adaptation, Serbia.*

INTRODUCTION

The scientific consensus on the inevitability of climate change is constantly growing, pointing to anthropogenic factor as an important actor in this process (IPPC 2013; OECD 2009, 2010). One of the most documented anthropogenic processes that contribute to climate change is the rapid urbanization. Shift towards profit-oriented urban development has led to uncontrolled constructions often at the expense of environmental quality in urban areas. As urban growth and development patterns contribute to increasing emissions of greenhouse gases (OECD 2010) the urban population and infrastructure are also more at risk from the adverse effects of climate change.

Climatic treats will have severe impacts on European cities due to the large concentration of built-up impermeable areas, and a high population density in a relatively concentrated space (ICLEI and CEPS, 2013). According to a survey carried out in spring/summer 2012, among 196 European cities within the framework of the EU Cities Adapt project,[1] the main hazards European cities have faced or are expected to face are: 1) periods of very hot weather or heat waves (often made even more severe by the Urban Heat Island Effect); 2) Flooding from heavy rainfall; 3) Storms; and 4) Water scarcity and droughts (EU Cities Adapt Survey Report, 2012). For example, estimations shows the heat waves in Europe in 2003, took nearly 35,000 victims (Larsen, 2003), while 2013 floods caused 25 deaths and more than €9 billion in estimated physical and agricultural damages (J. Carter et al. 2012). Incidents of flooding in Europe resulted in an increased number of physical and mental patients in urban centers (Reacher et al. 2004, Baxter et al., 2002). On the other hand the life span of built environment and infrastructure is often over 75 years (Rodriguez 2009) and structures being built now will likely operate under different climatic conditions in the next decades. Long-term nature of the existing urban

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[1] http://eucities-adapt.eu/cms/

infrastructure, and long periods of planning and building a new one, make them complex challenges in addressing the impact of changing weather patterns, especially given the uncertainty of local and regional climate scenarios (OECD, 2010).

The scenario of climate change in Serbia is not very positive, similarly to region of South East Europe, which expects significant climate change in the near future. Regional climate models predict the average temperature rise on annual basis by the end of this century in range from 2.4 ° C to 3.8 ° C (IPCC, 2007; CEPS, 2008). As Sekulic et al. (2012) comment, all regions of Serbia will most likely experience rise in the average temperature, with some regional differences. On the other hand, according to one scenario, rainfall will decrease in the entire territory of Serbia, with somewhat less pronounced decreased in Vojvodina, and some parts of eastern Serbia, while according to another in Vojvodina, the amount of rainfall will increase, while in other parts of Serbia it will remain the same or will decrease. Also, there are projections that indicate frequent natural disasters in Serbia, in the first place floods, droughts and fires. Data from the International Database on Disasters (EMDAT)[2] for the period 2000-2011 indicates that Serbia was more pronounced to the risk of natural disasters, which accounted for 62% (of which 55% were flooding) than from technological accidents.

Recent catastrophic floods in Serbia have confirmed this trend. According to officially adopted Serbian Government flood damage assessment report[3], floods caused direct damage of €810.1 million, while estimated losses are €661.9 million. Estimated share of damage on residential buildings is €231 million, while infrastructure sector, including transport, communications and water supply, is estimated at €192.1 million. More than fifty municipalities are affected, and many cities and towns experienced extreme destruction. Current adaptive capacity to climate change in Serbia is modest (Sekulic et al. 2012). Official policies do not recognize vulnerability of the whole society in changing climatic situation as a planning priority.

Current Spatial Plan of the Republic of Serbia (MŽSPP 2010) recognizes the planning challenges related to climate change only as recommendations. Reflecting on basic challenges plan revels following problems: 1) the use of climate data and information in the planning and design still relies on methods and guidelines based on the stationary climate, 2) there is lack of awareness of the need for inclusion of climate change as factors of sustainable development into sectorial strategies, particularly for vulnerable sector to climate change (agriculture, water, forestry, energy, tourism, health, construction, transport, etc.), 3) state lack climate change adaptation strategy, and 4) limited resources for strengthening capacity (system, or institutional and individual), education, training and information. Based on that, plan points to the importance of including climate change as a factor of sustainable and environmental development into all sectorial strategies, and developing sustainable management of climate change risks procedures.

Adjusting current urban planning practices (building codes, infrastructure standards, land use, land regulations), and the regulatory framework are important steps in this direction. We can achieve that as Hallegatte (2009) suggests by selecting ‘‘no-regret’’ strategies that yield benefits even in absence of climate change, partly through flexible strategies and buying safety margins in new investments. This approach is particularly useful in light of uncertainty to identify climate change impacts at the urban level. While the cross-linkages between climate change and urbanization are increasingly recognized in the literature and the perspectives integrated accordingly (e.g. Solecki et al., 2011; Lankao and Qin, 2011; Birkmann et al., 2010) considerable gaps remain when moving the focus beyond the conceptual level to penetrate practical tools and applied institutional dimensions of urban planning and management. Climate change is a development challenge for urban areas and adaptation to its impacts needs to be considered a learning process and not a single product, and thus, this paper is attempt to generate knowledge about urban planning and design procedures in Serbia and its *state of the art* capacity for adaptive processes.

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[2] www.emdat.be

[3] available at http://www.parlament.gov.rs/upload/archive/files/cir/pdf/akta_procedura/2014/2220-14.pdf

METHODS AND RESEARCH QUESTIONS

Against this background the paper analyzes current General urban and Master plans of four largest Serbian cities addressing the core question:

> Do we have to rethink existing urban planning framework in the context of climate change?

In order to shape the research following sub-questions are formulated:

1) To what extent plans built upon collaboration across the sectors?

2) To what extent urban plans considers sectors that are most vulnerable to climatic change (such as Water resources management, Human health, Agriculture, Ecosystems etc.)?

3) Do current plans, and in which way, recognize risk related procedures?

The research is conducted as desk study including the literature review and analysis of the selected plans focusing primarily on regulation and planning procedures. It considers following Master Plans (MP) and General Urban Plans (GUP): MP of Novi Sad 2021[4], GUP Niš 2010-202[5], MP of Subotica-Palić 2020[6], and GUP Kragujevac 2015[7]. We analyzed plans on questionnaire based assessment. In line with research objectives, these questions are formulated to indicate whether/or to what extent current urban planning and design plans (planning framework) are suitable to integrate climate change adaptation strategies. Bearing in mind that important aspects for adaptation strategy are cross-sector collaboration, risk management and efficiently defined priorities according to the most vulnerable groups or sectors, questions are formulated in following groups:

Table 1:

General considerations	Methodological considerations	Coordination and cross-sector planning	Monitoring and risk management
- the role of the institutions - main stakeholders in the planning process - operational purpose of the plan	- consistency of the methodological framework - flexibility - overarching priorities	- collaboration with external experts - feedback from implementation to planning level - inclusion of relevant sectors in planning process	- monitoring mechanism - climate sensitive sectors - risk assessment procedures

These answers should indicate potentials and obstacles in current plans, which may help or hinder integration of climate adaptation strategies into planning procedures.

DISCUSSION

Development of spatial plans in Serbia recognizes three levels of planning, national, regional and local. Regional administrative level is still missing. All local government units (which have more than

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[4] Generalni plan Novog Sada *do 2021*. Godine, “Sl. list grada *Novog Sada”* br. 39/06.

[5] Generalni urbanisticki plan Nisa od 2010-2015, “Sl. list grada Nisa” br. 43/11.

[6] Generalni Plan Subotica-Palic 2020, “Sl. list opština Subotica, br. 16/2006, 17/2006 ispr. i 28/2006”

[7] Generalni Urbanisticki Plan Kragujevca do 2015, Sl. list Grada Kragujevca, br. 3/02.

30,000 inhabitants) develop GUP / MP (Law on Planning and Construction 2009 –from hereon called Law, Articles 23 and 24). Even though, GUP / MP have strategic considerations, they are developed with focus on the elements of spatial development, relying largely on General Regulation Plans (GRP) as an instrument for its operationalization. As a plan of lower order, GRP is mandatory for all towns/cities that are the seats of local government units, and can be adopted for other settlements in the municipality or city, when considered by the spatial plan of the local government. GRP are drawn up for the entire construction area of settlement (Law, Article 25). The same law oblige local governments to conduct the urban planning process and adopt plans within specific period. Considering that, local governments initiate planning process regarding GUP/GRP as the only legislatively relevant stakeholder in planning process.

Although, in accordance with the law, planning documents can be funded from other sources then public, cities and municipalities usually finance GUPs and GRPs from the municipal budgets. All four analyzed cities fall in that category. The Ministry in charge of urban and spatial planning supports urban planning, by means of co-finance, based on open competition between cities. In 2014 subsidies for planning were available for local municipalities/cities which have ensured part of the finance from their resources for the urban plans for which they applied and justified the earlier donated funds for the development of urban plans. However, when it comes to detailed regulatory plans, investor can order new plan according to his/her needs and influence development of the area.

Planning documents can be developed by public company, or other organization established by local government unit for conducting spatial and urban planning, as well as companies or other legal entities, which are registered for performing spatial and urban planning and preparation of planning documents (Law, Article 36). However, as analyzed plans suggest and considering anecdotal evidence, urban planning process is still prominently conducted within public institutions and initiate by them.

Legislative framework in Serbia have a unique methodology for spatial and urban planning (Law). The Law and ordinance define planning procedures and textual and graphical content of the plan. Planning institution firstly develop conceptual version of the general plan. Before the public review, draft planning document is subjected to expert review of the Planning Committee, established by local government. The President and members of Planning Committee shall be appointed from professionals from within the field of urban planning and other sectors important for the performance of professional activities in the field of spatial planning and construction (e.g. water management, forestry), while one third of the members shall be appointed on the proposal of the minister responsible for spatial planning and urban development (Law, Article 52). Committee review all aspects of the plan, but in practice the focus remains on regulatory aspects of the plan, which is visible in analyzed documents. After public review, ministry for spatial and urban planning give a final word on acceptance of the plan, based on its consistency with plans of a higher order. Afterwards, the assembly of the local self-government adopt or reject the plan, based on the consensus of majority.

The planning institution define development trajectories and specific priorities itself, however, analysis points to collaboration of planning authorities with external institution and organization (mainly from public realm). Those institutions are usually public utility companies which considers environmental protection, water management, the protection of cultural heritage, general sanitary conditions, and relevant hydro-meteorological and seismological services, or institutions for fire protection. Collaboration mainly considers provision or establishment of specific requirements for the environmental protection, urban design and a construction of buildings. Mentioned institutions are obliged to deliver technical assistance and documents to main planning institution free of charge (Law, Article 46). During the planning process, the institutions which develop urban plan cooperate with departments for its implementation in terms of providing comments and suggestions which will improve implementation process. Also, often in collaboration with City Planning departments, it organizes meetings with institutions and companies that are responsible for specific sectors on specific issues and priorities of the plan.

The planning procedure rely on sectorial studies relevant for particular plan, which inform planning decisions about existing conditions, terms of use and development plans of the public companies whose activities juxtapose/overlap with urban planning process (e.g. relevant utility institutions for traffic and other technical infrastructure; organizations, agencies and companies for environmental protection, and for the protection of waterways; relevant hydro-meteorological and seismological institutes). Some of the studies are done for the purpose of the plan, while others are used as input for defining planning solutions. Sectors which plans in practice take into account, but which are not by name defined in the legislation, considers following: demographic development, economy (agriculture, forestry, industry, trade, tourism etc.), public services, housing, utilities, green areas, traffic, infrastructure, environmental protection, protection against natural disasters, natural and technical disasters. However, plans did not give priority to specific sectors. Legislative framework allows the institute for urbanism (or other urban planning authorities) to order particular study for planning purposes from the relevant institutions (Law, Article 45). Besides the public utility companies already mentioned, analyzed plans does not point to collaboration with other expert institutions in the relevant fields, e.g. university, chamber of commerce, research institutes etc., for this purposes.

Furthermore, plans do not recognize collaboration between the institution responsible for development and implementation of the plan (urban planning department, city planning office and city construction inspection) in terms of feedback from the implementation to planning level. During the implementation of the plan, the authority recognized areas where, due to certain circumstances, is not possible to implement the plan, which is the starting point for changes to the planning document.

The law stipulates that the GUP/MP contains a general urbanistic land use plans which predominantly consider construction area and the general directions and corridors for transport, energy, water, waste disposal and other infrastructure, as well as general conditions and measures for human life and health protection, and protection from fire, natural disasters, technological disasters, and war (Law and Regulations).

The GUP/MP plans somewhat considers sectors sensitive to climate change. They include (by Law) general requirements and measures for protection from fire, natural disasters, technological disasters, and conditions and measures for the protection of the natural heritage, the environment and human life and health (Law, Article. 30 and Ordinance). However, analyzed plans have different interpretation of those requirements in respect to local context and priorities. They all threat mentioned sectors in terms of measures, framed between recommendation and objective (see Table 2).

Table 2:

Sectors	**Measures by plan**			
	GUP Niš 2010-2020	MP Novi Sad 2021	GUP Kragujevac 2015	MP Subotica-Palić 2020
Agriculture	- afforestation of degraded agricultural land - barren land greening - land reclamation and flood protection	-retention of wetlands and setting green shelterbelts (networking space) in order to protect from wind, snow, raising dust and others.	-ban of conversion of agricultural into construction land, except the facilities exclusively for the agricultural production	-
Forestry	- prevention of forest degradation - afforestation - intensive care and protection of existing forests - connect all green areas in a unique system of green		- establishment of forests with priority protection function -afforestation base on indigenous species.	-

Erosion and landslides	-reforestation or conversion of landslides into pastures and meadows - ban on clear-cutting of forests on the landsides - construction of retention basins - ban the construction on the erosive land	- ban the construction on the erosive land - ban of the removal of vegetation cover, deforestation - construction of anti-erosion and reclamation systems - the construction of groynes - the regulation of streams, landscaping and reforestation	-examination and assessment of stability - protective infrastructure, reducing the degree of development and special technical and urban planning measures - corrective, and above all preventive measures to protect the restoration and planting new vegetation, drainage field etc. - Protective green belt and green lands -coastal protection from abrasion and erosion	-continuous green belt with water and soil protective function - coastal protection from abrasion and erosion
Flood	-construction of a common protective embankment - ban the exploitation of gravel and sand on the river-shore. -deepening the river- bed -implementation of slow embankment	-construction of a common protective embankment - ban planting trees in the protective zone of the embankment - street open ducts for surface water drains	-The City Assembly adopted medium-term and annual plans for flood protection.	- street open ducts for surface water drains

GUP / MP lack monitoring procedures and evaluation of the extent and quality of implementation. Although, monitoring of urban plans is not defined by law and is not part of the plan, in practice, preliminary plans are starting points for new plans. Planners analyze the current plan, the level of implementation, parts of plan that have been realized, analysis of the situation on the ground (uses, types of building, transport corridors), the conditions that have changed since the previous plan etc.

Risk management procedure present in the plans are related to the strategic assessment of the environmental impact. The assessment is parallel process with the development plan and is exposed to public scrutiny along with the plan. Strategic Environmental Assessment of the Plan considers the environmental problems of the plan and the possibility of influencing: air; water; land; climate; flora and fauna; habitats and biodiversity; protected areas; population and health; cities and other settlements; cultural and historical heritage; infrastructure, industrial and other facilities; other created value (Law on Strategic Environmental Impact Assessment, from hereon called LSEIA). It is carried out for particular plans or programs within the urban planning (LSEIA, Article 5). It describes, evaluate and assess the likely significant environmental effects that may result from implementation of the plan and determine measures to reduce negative impacts on the environment. Decision on a strategic assessment shall be made by the authority responsible for the preparation of plans and programs (LSEIA, Article 9). The authority responsible for the preparation of plans and programs choose the institution/company which will conduct strategic assessment, any company registered register for conducting spatial planning and the preparation of planning documents and urban planning and urban development plans (LSEIA, Article 10).

CONCLUDING REMARKS AND RECOMMENDATIONS

In line with our main research question - whether we have to rethink existing urban planning framework in the context of climate change – discussion above points to potentials for incorporation of CCA policies into process of urban planning, but underscored that current planning framework have to be enhanced in order to ensure that they better account for the climate sensitive sectors in order to promote a more adaptive and strategic urban planning approach.

Particular strength is seen in legislative framework which provide unique urban planning methodology at the national level and obligatory planning for all urban settlements (GRP and GUP / MP). Such framework may help consistency in integration of adaptation policies/regulation/requirements (e.g. unique set of measures, indicators or planning procedures). However, the reviewed plans seem to emphasize spatial component through regulations and requirements, rather than quality criteria for the process of planning, which may hinder long term perspective in urban planning necessary for dealing with uncertainty of CC.

In contrast to strategic planning, which involve external funds and expert organization in planning process (see Milutinovic and Zivkovic, 2014), based on analyzed plans, urban planning relay on local budget and state support. In circumstances of unstable economies, local plans financing, which rely on state transfers, can have adverse effects on CCA in particular, since other strategic priorities (e.g. unemployment, education) and related short-term risks can overweight CCA due to its uncertain nature.

Even though multi-stakeholder involvement and the participation in the planning process exist, legislative frameworks prioritize more top-down oriented process, with a decisive role of local politicians for adoption of GUP / MP, and more passive participation of local community and non-governmental sector. This trend strengthen the role of local politicians in decision making process, which may help or hinder CCA, deepens of political interests and local economy. As Wilson (2006) argue, problem burdening local level is relatively short mandate of elected decision makers, which diminishes their interest in long-term effects of planning. Thus, more effective bottom-up communication is needed, with involvement of diverse stakeholders involved directly or indirectly in CCA issues to enforce long-term and strategic perspective in urban planning and development.

As analysis reveals, and going back to our first sub-question, cross-sector collaboration is integrated in urban planning process, and it is enforced by law. This planning practice is essential for CCA, since it recognize importance of cross-cutting issues across sectors while planning. Legislative framework allows flexibility to the municipality/city to give additional attention to sectors which are of their particular interests (besides the compulsory ones). However, collaboration is very formalized and narrowed down to regulations and requirements rather than on strategic collaboration, and remains within the circle of public institution.

In regard to our second sub-question, analyzed plans recognize some sectors or planning elements, which are vulnerable to climate change, e.g. agriculture, forestry, water management (floods), or land sliding. Since the development of particular plans for sectors presented in Table 2, are not defined strictly by law, related measures are defined in terms of suggestions, regulations or recommendation, and differ case-by-case. They imply the physical and spatial adjustments in particular space or area, ranging from short term intervention such as consolidation of riverbanks, to long term strategic measures such as afforestation or setting of green wind-protection shelterbelts. This clearly shows awareness and will of local planning institution to deal with uncertainties, which may help integration of CCA policies. However, a higher level of uncertainty calls for more climate sensitive planning strategies and normative definition of measures in terms of objectives.

Considering our third sub-question, analyzed plans lack monitoring procedure/manuals for the implementation of plan (e.g. annual monitoring report, monitoring units/indicators). The Concept of master plan contains an analysis and assessment of the existing situation, which is not necessarily an inventory that reflects previous plan. Since the adaptation measures are context sensitive and challenged by dynamic changes of local conditions, and thus, consider flexibility, lack of monitoring (feedback) mechanism prevents timely intervention and adaptation to changing conditions and potential risks. When it comes to risk management planning framework envisage strategic environmental assessment, for each part of the plan which may have potential adverse environmental effect, which can be solid platform for incorporation of climate related risks into planning process.

However, the analysis of the GUP / MP draws attention to some implications regarding urban planning process, which may improve urban planning framework for more effective integration of CCA policies. Some adjustments could have the following features: 1) uniquely defined sectors in the plans that are sensitive to climate change; 2) more studies related to climate sensitive sectors that preceded the development of plans; 3) the encouragement of active participation of the private and civil sectors in the development of planning documents; 4) the improvement of horizontal coordination between sectorial departments; 5) - The introduction of procedures for monitoring the implementation of plans (e.g. annual implementation report, indicators for implementation).

REFERENCES

Baxter, P.J., Moller, I., Spencer, T., Spence, R.J., Tapsell, S. (2002). Flooding and climate change, in Baxter, P., Haines, A., Hulme, M., Kovats, R.S., Maynard, R., Rogers, D.J., Wilkinson, P. (eds.) Health Effects of Climate Change in the UK. London: Department of Health.

Birkmann, J., Garschagen, M., Kraas, F., Quang, N., 2010. Adaptive urban governance: new challenges for the second generation of urban adaptation strategies to climate change. Sustain. Sci. 5 (2), 185–206. http://dx.doi.org/10.1007/s11625-010-0111-3.

Centre for European Policy Studies (CEPS) (2008) Adaptation to climate change: Why is it needed and how can it be implemented? CEPS Center for European Policy Studies CEPS Policy Briefs No 161 May. http://www.ceps. eu/system/files/book/1667.pdf

EU Cities Adapt Survey Report (2012). Available from: http://eucities-adapt.eu/cms/assets/NewFolder/Appendix-3-Survey-v1-AEA.pdf.

IPCC (2013). Summary for Policymakers. In Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA

ICLEI (Local Governments for Sustainability, European Secretariat) and CEPS (Centre for European Policy Studies) (2013). Climate change adaptation: Empowerment of local and regional authorities, with a focus on their involvement in monitoring and policy design (report)

Hallegatte, S. (2009) “Strategies to adapt to an uncertain future.” Global Environmental Change doi:10.1016/j.gloenvcha.2008.12.003.

J. Carter, A. Connelly, J. Handley and S. Lindley (2012) European Cities in a Changing Climate: Exploring climate change hazards, impacts and vulnerabilities, The University of Manchester

Larsen, J., (2003). Record heatwave in Europe takes 35,000 lives. Eco-Economy Update.Washington DC: Earth Policy Institute.

Milutinovic, S. and Zivkovic, S. (2014). Planning local sustainable development in Western Balkans, Management of Environmental Quality: An International Journal Vol. 25 No. 1, pp. 19-29

MŽSPP - Ministarstvo Zivotne Sredine i Prostornog Planiranja, Republicka agencija za prostorno planiranje (2010) Prostorni plan republike Srbije 2010-2014-2021

OECD (2009). The Economics of Climate Change Mitigation: Policies and Options for Global Action beyond 2012, OECD, Paris.

OECD (2010). Cities and Climate Change, OECD Publishing.

Reacher, M., McKenzie, K., Lane, C., Nichols, T., Kedge, I., Iversen, A., Hepple, P., Walter, T., Laxton, C., Simpson, J. (2004) Health impacts of flooding in Lewes: a comparison of reported gastrointestinal and other illness and mental health in flooded and non-flooded households. Communicable Disease and Public Health, 7(1), pp. 1–8.

Rodriguez, S.R. (2009). Understanding and Improving Urban Responses to Climate Change. Reflection for an Operational Approach for Adaptation in Low and Middle-Income Countries, Fifth Urban Research Symposium, World bank Marseille, France, June 2009

Romero Lankao, P., Qin, H., (2011). Conceptualizing urban vulnerability to global climate and environmental change. Curr. Opin. Environ. Sustainability 3, 142–149. http://dx.doi.org/10.1016/j.cosust.2010.12.016.

Sekulic, G. Dimovic, D. Krnajski, Z. Jovic, Todorovic, N. (2012). Procena Ranjivosti na klimatske promene - Srbija-WWF: Beograd

Solecki, W., Leichenko, R., O’Brien, K., (2011). Climate change adaptation strategies and disaster risk reduction in cities: connections, contentions, and synergies. Curr. Opin. Environ. Sustainability 3 (3), 135–141. http://dx.doi.org/10.1016/j.cosust.2011.03.001.

Wilson, E. (2006) Adapting to climate change at the local level: the spatial planning response. Local Environment 11(6), pp.609-625.

ECONOMICS OF SUSTAINABLE DEVELOPMENT OF URBAN AREAS

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USE OF WASTE ENERGY OF AIR-CONDITIONING SYSTEM

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ABSTRACT

Decreasing energy resources of the Earth and enhanced energy consumption are typical of our life. However, one of the basic conditions to survive is that the amount of the energy used every day should be reduced. This article presents a solution to the problem. The energy used to air-condition a room and the possible use of secondary energies generated by the air-conditioning is studied in the research. The heat energy distracted by a heat pump out of the room is not let outside as heat loss, but it is used for making domestic hot water. The efficiency of the heat pump is examined with varied air parameters inside.

Keywords: *Heat pump, air-conditioning, effectiveness, coefficient of performance (COP), domestic hot water supply.*

INTRODUCTION

In general, the purpose of air-conditioning is to generate temperature lower than the ambient temperature and keeping it constant inside the room to air-condition [8]. In practice, heat pumps driven by an electric compressor are generally used. The ratio of the heat energy egressed by the heat pump and the energy taken from the electric supply for driving the compressor (and the fans) is called the coefficient of performance of the cycle. The higher the coefficient of performance of a heat pump is the more economic it is, it varies between 2 and 5 according to the structure of the heat pump, the ambient temperature outside and the way of application. See the schematic diagram of a heat pump in Figure 1.

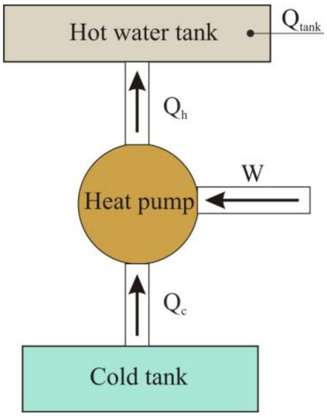


Figure 1. Schematic diagram of a heat pump

The following relation can be described between the energies in Figure 1:

$$Q_h = Q_c + W \tag{1}$$

where:

Q_c the heat distracted from the room [*J*],

Q_h the quantity of heat egressed to the hot water tank [*J*],
W electric energy taken by the heat pump [*J*].

Theoretical coefficient of performance of the heat pump [1-6]:

$$COP = \frac{Q_h}{W} = \frac{Q_c + W}{W} \tag{2}$$

where:

COP coefficient of performance of the heat pump [-].

The heat energy stored in the hot water tank of the heat pump as hot water:

$$Q_{\mathrm{tank}} = m_w c_w \Delta T_w \tag{3}$$

where:

Q_{tank} heat energy stored in a hot water tank [*J*],
m_w mass of the heated water [*kg*],
c_w specific heat of the water, $(4.2\, kJ/kg^{\circ}C)$ [$kJ/kg^{\circ}C$],
ΔT_w difference of the mean temperature at the bottom and on the top of the water tank [$^{\circ}C$].

As a result of the losses of the system:

$$Q_h > Q_{\mathrm{tank}}. \tag{4}$$

The heat loss on the condenser side:

$$Q_{loss} = Q_h - Q_{\mathrm{tank}} \tag{5}$$

where:

Q_{loss} loss generated in the heat exchanger (condenser) [J].

Thus the relation of the actual and theoretical coefficients of performance can be written on the operation of the heat pump, using relation (3):

$$COP > COP_{\mathrm{actual}} = \frac{Q_{\mathrm{tank}}}{W} = \frac{m_w c_w \Delta T_w}{W}. \tag{6}$$

The heat pump system is a cycle that consists of two heat exchangers (evaporator, condenser), a compressor and a butterfly valve [7]. Each element is joined by a pipe filled with transfer medium. The operation of the heat pump is illustrated in Figure 2.

1 The compressor condenses the gaseous transfer medium (R134a) using electric energy (which heats) and circulates it in the system permanently.

2 The heat of the hot gas inside the fan-coil unit - through a water heat exchanger - is used for making hot water, while the medium cools down, precipitate and turned into fluid again.

3 The liquid medium flows to a space of bigger cross section, through an expansion valve, to the evaporator. The pressure declined hereby makes the medium, which expands and strongly cools accordingly, gaseous again.

4 By utilizing hundreds of cubic meters of air sucked through the evaporator, heat is distracted from the surroundings, which makes the air cool down in the room. Then this hotter vapor is condensed again starting from the first step.

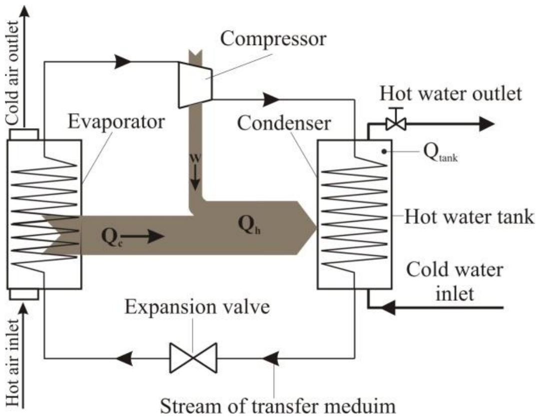


Figure 2. Working process of the heat pump cycle

Heat pumps are heat engines of reverse operation. The thermodynamic cycle can be followed on the temperature-entropy (T-s) diagram (Figure 3). The process starts from point 1, where the medium at p_i pressure and T_i temperature occurs as saturated vapor. Processes 1 and 2 are adiabatic compressions that happen in the compressor. Normally, this change of state is indicated in the diagram as a vertical line (isentropic compression), but in reality the change of state is irreversible, entropy permanently increases, thus the curve slightly bends to the right. Processes 2 to 5 happen in the condenser: processes 2 and 3 are the distraction of overheating heat, in point 3 the vapor reaches saturated state at pressure p_f. In processes 3 and 4 the temperature does not change, more and more vapor precipitates and the liquid state emerges in point 4. Processes 4 and 5 in the condenser is the possible after-cooling of the fluid medium, then processes 5 and 6 is the thermodynamic process, which results in sudden fall of the pressure, at the end of which the medium expands to p_f pressure and T_f temperature, the liquid partly (approximately half of it) evaporates suddenly and the medium turns into wet, vapor state. This is an isenthalpic process, i.e. during the process the enthalpy does not change. Finally, in processes 6-1, the medium takes heat in the evaporator from the space to cool at permanent temperature and pressure, while the moisture content of the vapor declines gradually. Then the medium returns to the starting point of the cycle, to state 1, and the process starts again. Naturally, all mentioned above apply to an ideal medium, the processes rather differ in deed [10].

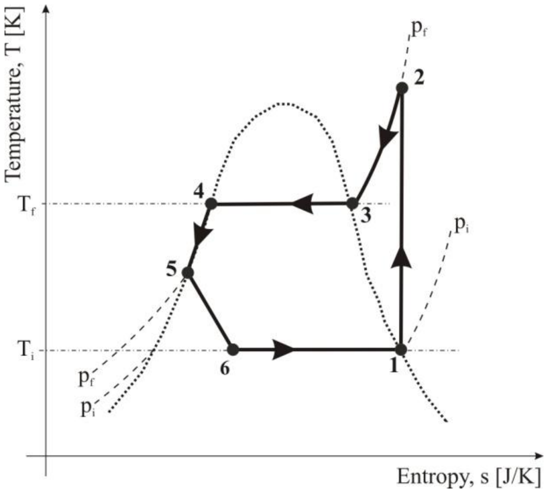
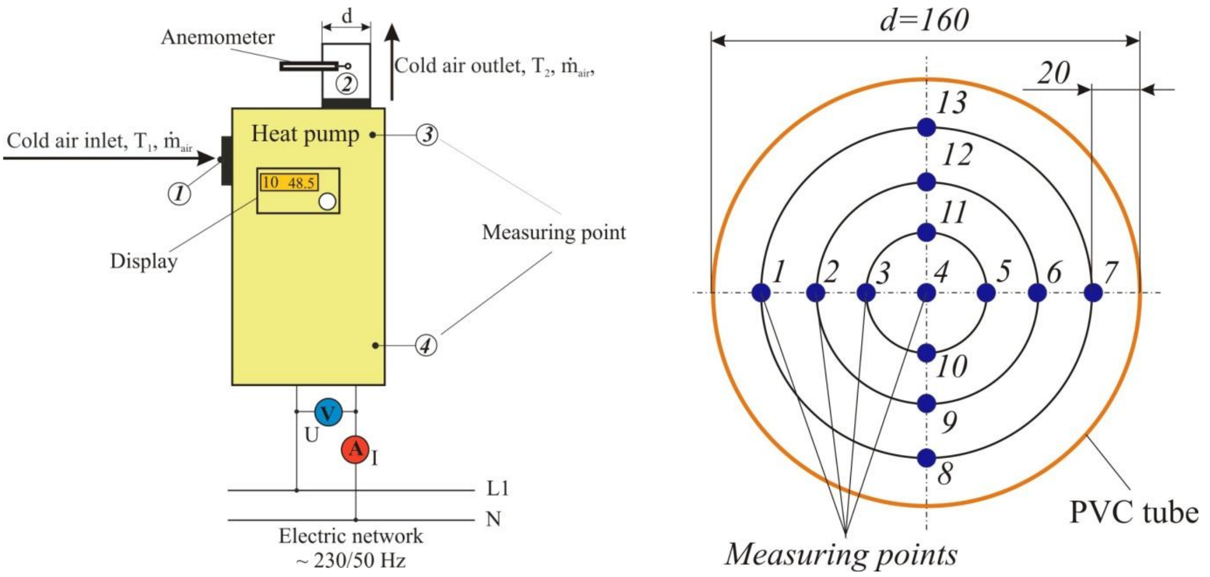


Figure 3. Cycle of the vapor-compression refrigerator on the temperature-entropy diagram

MEASURING SYSTEM AND MEASURING METHOD

A heat pump installed in one of the rooms of the site of Óbuda University in Doberdó Street is examined focusing on the economy of air-conditioning. The examination is performed depending on the measuring order illustrated in Figure 4a.



(a) (b)

Figure 4. Measuring order of a heat pump

The measuring system consists of the following main elements:

- air-water heat pump to examine,
- anemometer type testo 435,
- ammeter and voltmeter,
- thermometers built in the heat pump.

MEASURING AND RESULTS

The temperatures of the air let in and out of the pump are measured at the measuring points 1 and 2 as illustrated on Figure 4. At point 2 the air flows out of the pump through a pipe end of 160 mm diameter. The speed of the air let out of the pump is measured with an anemometer (as shown in Figure 4b), type testo 435, the average of which is: $v_{air} = 3.3\,ms^{-1}$. During the time of warming up ($t = 242 \min \approx 4\,h$) the volume flow rate of the air blown out is 237.6 m^3/h. The outcoming values relating to the measuring time are illustrated in Microsoft Excel. Afterwards, the trend lines are defined by using regression, indicating the determinant coefficients R^2.

Table I: Temperature measuring results

Measuring time, t [min]	Inlet air temperature, $T_1\,[^\circ C]$	Outlet air temperature, $T_2\,[^\circ C]$	Hot water temperature up, $T_3\,[^\circ C]$	Hot water temperature down, $T_4\,[^\circ C]$
0	24.2	22.5	26.9	26.4
5	24.2	17	27	26.4
10	23.5	13.2	27.6	26.4
15	23.1	12.5	28.2	26.4
30	22.6	12.1	30	26.4
45	22.5	11.4	31.6	26.5
60	22.4	11.1	33.2	26.5
75	22.3	10.9	34.7	26.6
105	22.2	10.9	37.5	26.7
135	22.2	11.1	40.3	27
165	22	11.1	43.1	27.4
195	21.8	11.2	45.8	27.9
225	21.7	11.3	48.5	28.5
242	21.7	11.2	50	29.8

Figures 5 and 6 illustrate the inlet and outlet temperatures of air listed in Table I.

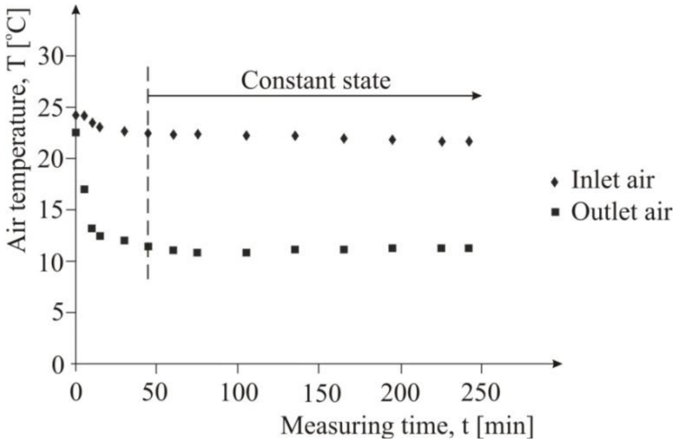


Figure 5. The temperatures of inlet and outlet air during the operation of the heat pump

Figure 6 indicates the regressive approach of the air let in and out, also marking the determinant coefficients.

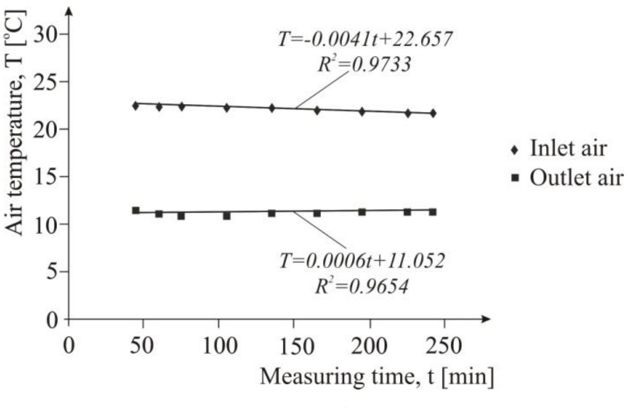


Figure 6. The temperatures and regression of inlet and outlet air in the constant state

At measuring point 3 in Figure 4, the temperature is measured at the top of the hot water tank, and at point 4, the temperature is measured at the bottom of the tank. Table I contains the measuring results. Figure 7 shows the temperatures of the hot water tank.

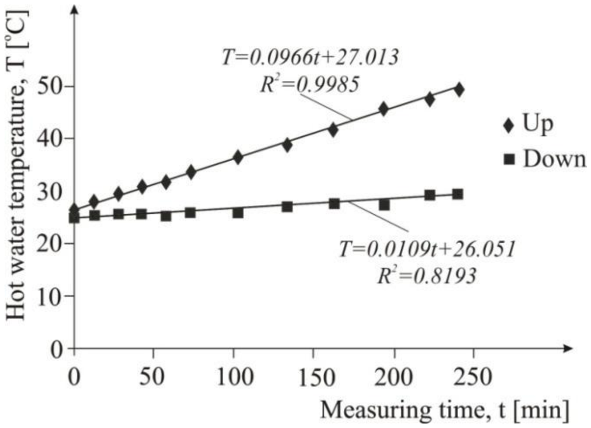


Figure 7. The temperatures of the hot water tank up and down

Figure 8 indicates the temperatures of the evaporator.

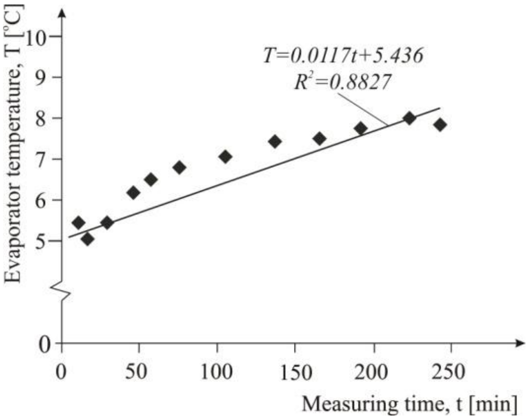


Figure 8. Temperature ranges of the evaporator

Figure 9 presents the current consumption of the heat pump with constantly $U = 224V$ alternating voltage, the graph indicates increasing current consumption. The value of the power factor during the operation of the heat pump is $\cos\varphi = 0.9$.

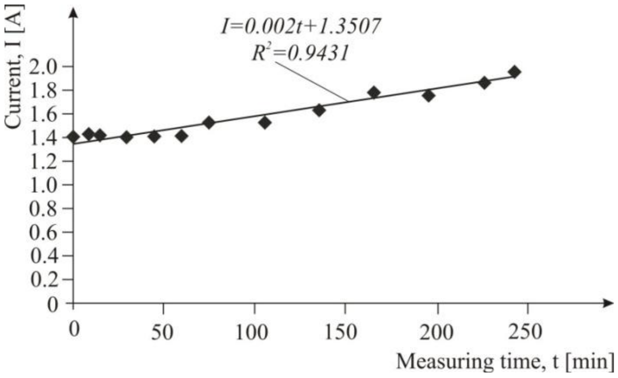


Figure 9. Current consumption of the heat pump

Rewriting relation (6) to performances:

$$COP_{actual} = \frac{Q_{\text{tank}}}{W} = \frac{P_{\text{tank}} \cdot t}{P_e \cdot t} = \frac{P_{\text{tank}}}{P_e} \tag{7}$$

where

P_{tank}	heat power of the hot water tank	$[kW]$,
P_e	electric power taken by the heat pump	$[kW]$.

Taken electric power based on the measured data:

$$P_e = U\bar{I}\cos\varphi = 224 \cdot 1.53 \cdot 0.9 = 308.5\,W \approx 0.3\,kW. \tag{8}$$

where

U	effective value of the alternating voltage	$[V]$,
$\bar{I}$	average of the measured currents (based on the data of Figure 9).	

Volume flow rate of the inlet and outlet air:

$$\dot{V}_{air} = A\bar{v}_{air} = \frac{d^2\pi}{4}\bar{v}_{air} = \frac{0.16^2\pi}{2}3.3 = 0.02 \cdot 3.3 = 0.066\,m^3/s = 237.6\,m^3/h. \tag{9}$$

where:

A	cross section of the and air pipe end in and out	$[m^2]$,
d	diameter of the air pipe end in and out (Figure 4)	$[m]$,
$\bar{v}_{air}$	the average speed of the air outlet in the cross section out	$[m/s]$.

The mass flow of the inlet air:

$$\dot{m}_{air} = \dot{V}_{air}\rho_{air} = 0.066 \cdot 1.2 = 0.0792 \approx 0.08\,kg/s = 288\,kg/h. \tag{10}$$

where:

ρ_{air}	density of the air ($\rho_{air} = 1.2\,\text{kg/m}^3$)	$[\text{kg/m}^3]$.

Heat power extracted from the air:

$$\dot{Q}_c = \dot{Q}_{air} = \dot{m}_{air}c_{air}\Delta T_{air} = \dot{m}_{air} \cdot c_{air}\left(\overline{T}_1 - \overline{T}_2\right) = 0.08 \cdot 1 \cdot (22.6 - 11) = 0.928 \approx 0.93\,kW. \tag{11}$$

where

c_{air}	specific heat of the air at constant pressure ($c_{air} \approx 1\,kJ/kg^\circ C$)	$[kJ/kg^\circ C]$,
ΔT_{air}	difference of the mean temperatures of the inlet and outlet air	$[^\circ C]$.

Quantity of the heat of the hot water based on (3) and Figure 10:

$$Q_{\text{tank}} = m_w c_w \Delta T_w = m_w c_w \left(\overline{T}_{34f} - \overline{T}_{34i}\right) = 290 \cdot 4.2(40.0 - 26.65) = 16260.3\,\text{kJ} \approx 16.26\,MJ. \tag{12}$$

where

$\overline{T}_{34i}$	the mean temperature of the water tank at the beginning of measuring (Fig. 10)	$[^\circ C]$,
$\overline{T}_{34f}$	the mean temperature of the water tank at the end of measuring (Fig. 10)	$[^\circ C]$.

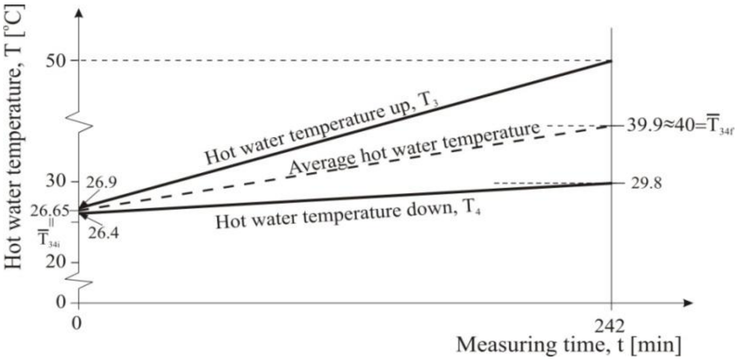


Figure 10. Temperature ranges of the hot water tank depending on measuring time

Heat power:

$$P_{\mathrm{tank}} = \dot{Q}_{\mathrm{tank}} = \frac{Q_{\mathrm{tank}}}{t} = \frac{16.26 \cdot 10^6}{14.52 \cdot 10^3} = 1.119 \approx 1.12\,kW. \tag{13}$$

where

t measuring time (warming up time) [s].

Applying this factor the result is relation (7), i.e. the actual coefficient of performance of the heat pump:

$$COP_{actual} = \frac{P_{\mathrm{tank}}}{P_e} = \frac{1.12}{0.3} = 3.73 \approx 3.7. \tag{14}$$

CONCLUSION

The value of the coefficient of performance, while examining the heat pump energetically, is $COP = 3.7,$ which corresponds to the value defined in the technical literature.

At present, concerning air intake air conditioners, the heat energy taken from the space to air-condition is generally let outside the room. In our research a system is established that enables the heat energy that has been managed as loss so far, to be utilized for making domestic hot water. This energy decreases the amount of electricity taken for making domestic hot water. Thus the efficiency of the system (air-conditioning and making domestic hot water), having been examined, is nearly 100%.

The time of the static return of investment of the system may be defined by the following relation [9].

$$\text{Time of return of investment} = \frac{\text{Invested sum of money}}{\text{Savings annually}}. \tag{15}$$

Return of investment of this system may be expected within 5 years.

REFERENCES

M. S. Kumar,”Experimental Investigation of Heat Pump for Domestic and Light Commercial Market”. International Journal of Engineering Science and Technology (IJEST), Vol. 4 No.09, 2012, pp. 4130-4138.

S. M. Al-Zahrani, F. L. Tan and F. H. Choo, „A TRNSYS Simulation Case Study on Utilization of Heat Pump for Both Heating and Cooling”. Energy Science and Technology, Vol. 3, No. 2 2012, pp. 84-92.

J. D. Munk, M. R. Ally, V. D. Baxter, “Measured Impact on Space Conditioning Energy Use in a Residence Due to Operating a Heat Pump Water Heater inside the Conditioned Space”. 2012 ASHRAE, SA-12-C004, pp. 28-29.

F. Busato, R. M. Lazzarin and M. Noro, “Energy and economic analysis of different heat pump systems for space heating”. International Journal of Low-Carbon Technologies 2012, 7, p. 105.

J. Bush, R. Domitrovic, A. Amarnath, “Low Outdoor Temperature Heat Pump Applications to Reduce Electric Resistance Second Stage Heat”. 2012 ASHRAE, CH-12-C079, p. 629.

C. C. Shen, J. H. Lu and W. H.Chuo, ”Water Management of Heat Pump System for Hot Water Supply in a Medium Size Hospital”. PROCEEDINGS OF WORLD ACADEMY OF SCIENCE, ENGINEERING AND TECHNOLOGY VOLUME 41 MAY 2009 ISSN: 2070-3740, p. 390.

Y. Udagawa, K. Sekiguchi and all, ”Development of an Outdoor Air Cooling-Type Air-Cooled Package Air Conditioner for Data Centers”. 2013 ASHRAE, DA-13-015, p. 2.

I. Patkó, Műszaki ábrázolás és gépszerkezetek II. Budapest, 1991. p. 145.

B. Béres, „A hőszivattyúk üzemeltetési és beruházási költsége”. Magyar Installateur, 2008/7. pp. 34-35.

hu.wikipedia.org/wiki/Hőszivattyú

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THE RELATIONS BETWEEN SOCIO-SPATIAL MOBILITY AND URBAN-RELATED IDENTITY: A COMPARATIVE ANALYSIS OF INTERNAL MIGRANTS AND HOST CULTURE MEMBERS IN SIX BIG CITIES OF TURKEY

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ABSTRACT

As a result of high and rapid urbanization in Turkey internal migration becomes an important component which affects the economic, social and spatial structures of the country. The aim of this research was to compare urban-related identity, satisfaction with several life domains and the extent of socio-spatial mobility of ethnically different (Turks and Kurds) internal migrants from different regions of country who resettled in Izmir, Ankara, Istanbul, Bursa, Gaziantep, Diyarbakir and the host culture members of these cities. The sample consisted of 866 host culture members and 871 internal migrants. The mean age of the whole sample was 38,96 years (range = 18-80; SD = 13,21). According to the findings, host culture members were found to be more attached to their city than the migrants. Moreover significant disparities were found to be in access to several social services within groups. The migrants in Izmir were found to access more easily for the health services in the city core and the level of social mobility were the highest compared to other cities. The results indicated that the unjust social and environmental structures significantly associated with the level of socio-spatial mobility, urban attachment and life satisfaction.

Key words: *internal migration, urban-related identity, life satisfaction, host culture, Turkey.*

INTRODUCTION

Urbanization and modernization in many countries have led to internal movement of people from rural areas into urban areas. Tas and Lightfoot (2005) stated that “the direction of rural migration to cities has been from the poor and less developed mountainous sections in the east and northeast toward the more developed, industrialized, and fertile areas in the west and Mediterranean region” in Turkey (p.267). “In the 1950s onwards internal migration gathered speed and transformed Turkey from a predominantly rural country to a mainly urban one in less than half a century” (Eryurt and Koc, 2012, p. 1). However, starting from the end of 1970s, urban-to-urban migration became the major direction of migration flow (Tekeli, 2007). After 1980s, a new kind of migration wave, internal displacement (forced migration) began due to political and social conflict in the country. As a result of these high and rapid internal movements, Turkey has been experiencing a fundamental transformation in its settlement pattern (Keles, 1976). Sonmez (2007) reported that “Istanbul, Izmir and Ankara are the largest metropolitan cities in population growth although some other cities have had an increasing level of economic development trend since recent decades” (p.324).

In environmental psychology, the issues of place attachment and place identity become more critical when we talk about migration or displacement experiences. From the view point of migrants and displaced people, they leave their home and they have to adapt to a new culture and moreover they try to maintain their own customs and other cultural practices. Especially in last decade researchers focused on disruptions in place attachment (e.g. Bogac, 2009; Brown and Perkins, 1992; Dixon and Durrheim, 2000; 2004; Fried, 1963) highlighted the salience of these place bonds. Brown and Perkins (1992) offered that examination of distruptions is important for understanding “place attachments holistic, multifaceted and multiscale nature. According to these authors “when place attachments are disrupted, individuals struggle to define their losses in order to identify what types of connections will provide them with a meaningful relationship to the world” (p.280). Moreover Dixon and Durrheim (2000) stated that “place identity is sometimes defined as a psychological structure of which people are only partially conscious. Often, it is only when established person-setting relations break down that one can recognize its full significance” (p.36). In this context we may argue that spatial integration is an important aspect of migrant groups’ experiences. Thus, the current study aims to examine the spatial integration issue within a multi-cultural context formed by different cultural groups including internal migrants and host culture members in Turkey.

THEORETICAL FRAMEWORK

The theoretical framework of the current research is outlined below.

Place attachment and place identity

Within the past several decades, the issue of “place attachment” has been improved by an interdisciplinary approach with various studies from diverse perspectives such as social anthropology (Low and Altman, 1992; Pellow, 1992), human geography (Relph, 1976; Tuan, 1977), sociology (Gustafson, 2001) and urban planning (Beatly, 2004) besides psychology. Different viewpoints lead to different conceptualizations (e.g. place attachment, place identity, place dependence, sense of place, sense of community etc.) and we may assert that the most apparent conceptual discussion is on how place attachment and place identity are connected. While several authors do not make any distinction between these concepts, several authors offer that these two concepts are two different constructs which are related with each other (Hidalgo and Hernandez, 2001; Lewicka, 2008). In other aspects place attachment is defined as a sub dimension of place identity (e.g. Lalli, 1992) or these two concepts are conceptualized as sub dimensions of a broader concept: sense of place (e.g. Hay, 1998). Despite these varied formulations, researchers (e.g. Hidalgo and Hernandez, 2001; Lewicka, 2008, 2010; Low and Altman, 1992) seem to reach a consensus in the widest sense: place attachment is defined as the affective/emotional bond that people develop with certain places whereas place identity is conceptualised as by linking with self-identity (Proshansky et al., 1983; William and Vaske, 2003).
Place identity can be related to spaces at different levels. There is a continuum ranging from a micro-spatial level (e.g. home) to the macro-space of a whole continent or even the world. Lalli (1992) offered the term of “urban identity” to stress the emotional bond between human and the town. The town as a whole fulfills a more global function, which is not only directly derived from action or locomotion in the environment. Urban-related identity, as an aspect of an individual’s more comprehensive self-identity, is the result of a complex association between self and urban environment. The town becomes the general symbol of an individual’s wealth of personal experiences. The second central function of urban-related identity is to differentiate residents from other individuals. This sense of belongingness does not only lead to the perception of “being different”, but it also imbues an individual with specific attributes which are associated with the town in question.

Social and political dimension in place identity

Several authors have criticized the individualistic view of place identity. For instance Dixon and Durrheim (2000) attracted attention to a common problem related to individualistic emphasis on place identity formulations. According to these authors “this emphasis obscures the collective nature of the relations between persons, identities and material settings” (p.29). ‘‘Place attachment may contribute to the formation, maintenance, and preservation of the identity of a person, group, or culture” (Low and Altman, 1992, p.10). Fried (2000) underlined the role of socio-cultural context on spatial identity. For Fried “spatial identity designates the physical/geographic dimension within which houses, streets, even whole communities can bound, intensify, and provide a spatial locus for identification and community attachment linked to social group identity” (p.197). Relations with others, social identities, and moreover ethnic back ground affect where we feel “at home” and “out of place”, where we may move to, or avoid where we allow others to be and where we ourselves want to be (Hopkins and

Dixon, 2006). The sense of place and place identity become more essential when we are talking about immigrants and also ethnic minorities. Dovidio and Esses (2001) proposed that the act of leaving one's native country and settling in another country has immediate and long-term consequences for both immigrants and members of migration-receiving countries.

Comparison of social and physical dimensions of place attachment to different spatial levels showed that "physical and social components generally come together and become a general affective feeling toward the place of residence in its physical as well as its social dimension" (Hernandez and Hidalgo, 2001, p.279). In this respect the findings of several researches performed in Turkey also showed the impact of sociopolitical processes regard to use of space. For instance Karakuş and Göregenli (2008) showed that urban-related identity was significantly associated with the social identity orientation and spaital usage. This study was performed in Çeşme which is one of the touristic towns of Izmir. Çeşme received migrations from Greece and Yugoslavia due to population exchange in 1920s. In present time, the second and third generations of these immigrants live in this town. Moreover this town has been receiving internal migration from other regions of the country, as well. Findings revealed that the level of spatial usage of the town centre and the attachment to town were significantly correlated. Another important outcome of this study was the interaction between social identity orientation and the type of migrant group. The internal migrants who had least level of social identity orientation had least level of place attachment when they were compared with other groups who had higher level of social identity orientation. Social identity orientation was found to be an important determinant of place attachment. Another research in Turkey (Göregenli et al., 2013) revealed relational outcomes between several socio-demographic variables (place of birth, gender, length of residence) and place attachment. This research was held in Selçuk. This town has been receiving migration from western countries since the establishment of Turkish Republic. In 1980s a new kind of migration, internal migration wave has began and a considerable number of people migrated to this town from different regions of country. Within semi-structured interviews the participants living in Selçuk were asked to report their opinions related to several issues such as "migration to Selçuk, social and cultural life in Selçuk and etc." through their own perceptions and memories. The results revealed that participants who were born out of Selçuk reported lower place attachment than the participants who were born in Selçuk. Moreover the migrant group reported that they use public areas less than the local group. Migrants were found to be more attached to their neighborhood and their spatial usage was usually limited by their neighborhood boundaries. On the other hand the host culture members had negative attitudes towards the internal migrants in Selçuk. These findings were in line with other studies in Turkey (e.g. Göregenli, 2013; Göregenli et al., 2009; 2014; Karakuş, 2007; 2014) and also in other countries (e.g. Hernandez et al., 2007).

On the base of this theoretical back ground the aim of this research was to determine the attitudes of internal migrants and host majority members towards integration to city in terms of satisfaction with several life domains and place identity. Thus the present research examined the urban related identity and satisfaction with several life domains (e.g.life in general, life in the city, life in the neighborhood etc.) of host society members and ethnically different internal migrants from different regions of the country who resettled in six cities of Turkey.

METHOD

A field research was conducted in Istanbul, Ankara, Izmir, Bursa, Gaziantep and Diyarbakir with 1809 adult participants. Two separate questionnaires were prepared for host culture members and internal migrants. Along with socio-demographic questions, Satisfaction with Several Life Domains Scale (Karakuş & Göregenli, 2008), Urban-Identity Scale (Lalli, 1992) and Socio-Spatial Mobility Scale (Karakuş & Göregenli, 2008) were conducted with both samples.

Sample

Specifically we performed a comprehensive field research including 1737 adult participants from the provinces of Izmir (300); Ankara (298); Istanbul (309); Bursa (302); Gaziantep (300); Diyarbakir (228). The mean age of participants was 38,96 years (range = 18-80, *SD*= 13.21). 49,9 % of the participants were host culture members and 50,1 % were from the migrant group. In terms of ethnicity, 63,5 % of the sample was ethnically Turkish, 33,3 % was Kurdish and 3,2 % was from other ethnic groups (e.g. Yugoslavian, Romanian, Bulgarian etc.). The members of host culture have relatively higher income than the internal migrants in all cities.

Materials and Procedure

In this study a questionnaire was used including socio-demographic variables and attitude scales. The subsections of the questionnaire are described next.

Socio-demographic variables. Questions about gender, age, education level, income level, place of birth and length of residence in the neighborhood and in the city were included.

Satisfaction with several domains of daily life All participants were asked to rate their satisfaction with several domains of their daily life such as: “living in the neighborhood; with social life in the neighborhood/living with neighbours; the street life”. The response scale ranges from “Not satisfied at all” (1) to “Very satisfied” (5). The internal reliability alpha score in this study was 0.74. This scale had sufficiently high reliability and good validity in Turkish culture (Karakuş and Göregenli, 2008). The internal reliability alpha score in this study was 0.82.

Urban-related identity scale (URI): A version of the 20-item Urban Related Identity Scale (Lalli, 1992) was used. Sample items include “Izmir is like a part of myself; I am looking forward to witnessing Izmirs’ future development; I have had so many experiences in this city that I have become intimately bound up with this place; Lots of things in Izmir remind me of my own past”. Participants indicated their agreement with each statement on a 5-point scale where (1) is “Strongly disagree” and (5) is “Strongly agree”. The higher points indicate higher level of urban-related identity. This scale had sufficiently high reliability and good validity to justify its use as a measurement of attitudes in Turkish culture (Göregenli, 2013). The internal reliability alpha score in this study was 0.84.

Socio-spatial mobility scale All participants were asked to mention for which activities (e.g. work, health, education, social meetings, shopping) they mostly use their home, neighborhood and the city. The items were based on the scale which was used in previous studies (e.g. Karakuş and Göregenli, 2008) in Turkey. In this scale the responses are measured by a frequency analysis and percentage values are calculated.

FINDINGS

In the first part of this section, we will provide the results of principal component analysis of “Satisfaction with several domains of daily life” scale. In the second part the group differences concerning satisfaction with several domains of daily life, urban-related identity in terms of several socio-demographic variables and the results of regression analysis will be demonstrated. Finally in the last part the findings related to socio-spatial mobility in six cities will be evaluated.

Satisfaction with several domains of daily life

A principal component analysis of “Satisfaction with several domains of daily life” scale yielded four factors that explained 84,87 % of the total variance. The first factor that included two items accounted for 31,59 % of the variance and represented “satisfaction level of relations with host majority members and urban life”. The second factor that consisted of two items accounted for 21,68 % of the variance and represented “satisfaction level of relations with neighbours and neighborhood life”. The third factor included one item that accounted for 17,03 % for the variance and focused on "the life satisfaction in general". The fourth factor included one item that accounted for 14,58 % for the variances and focused on "the satisfaction level of local government policies".

Comparison of internal migrants and host culture members in terms of satisfaction with several life domains and urban-related identity

A number of independent-samples t-test was conducted to compare the responses of internal migrants and host culture members to sub-scales of satisfaction with several life domains and urban-related identity scale. According to the results host culture members had higher mean scores than the migrants on all scales except the satisfaction with local government policies. The descriptive statistics and t values are shown in Table 1.

Table 1: The results of independent-samples t-test

	Host Culture Member		Internal Migrants				
	Mean	*Sd*	Mean	*Sd*	*t*	*p*	Min-Max Scores
Satisfaction level of relations with host majority members and urban life	8,27	*1,96*	7,45	*2,29*	8,041	.000***	2-10
Satisfaction level of relations with neighbours and neighborhood life	11,49	*3,23*	11,10	*3,28*	2,511	.012*	2-10
Life satisfaction	3,67	*1,24*	3,51	*1,25*	2,697	.007**	1-5
Satisfaction with local government policies	2,88	*1,46*	2,89	*1,42*	-,064	.949	1-5
Urban-Related Identity	79,80	*13,87*	65,88	*16,27*	18,287	.000***	20-100

*p<.05; **p<.01; ***p=.000.

Other group differences in urban-related identity in whole sample

Gender: An analysis of variance was performed in order to examine the relationship between gender and the level of urban-related identity in whole sample. Male *(M =72.91, sd=16.95)* and female participants *(M =72.87, sd=16.38)* did not differ significantly on URI ($F_{(1, 1575)}$ = .002, $p > 0.05$).

City: An analysis of variance was performed in order to examine the relationship between the city and the level of urban-related identity in whole sample (see also Figure 1). The results revealed the main effect of city is significant on URI scores ($F_{(5, 1575)}$ = 27.448, p = .000). Participants who live in Istanbul reported the lowest URI scores *(M =66.64, sd=18.77)* in whole sample. The participants who live in Izmir reported higher URI scores *(M =78.57, sd=18.76)* than participants living in Ankara *(M =67.69, sd=15.41)*, Istanbul and Gaziantep *(M =71.57, sd=16.57)*. The participants who live in Bursa *(M =75.07, sd=12.08)* reported higher URI scores than the participants who live in Ankara and Istanbul. Finally the participants who live in Diyarbakir were found to be more attached to their city than the participants in Ankara, Istanbul and Gaziantep.

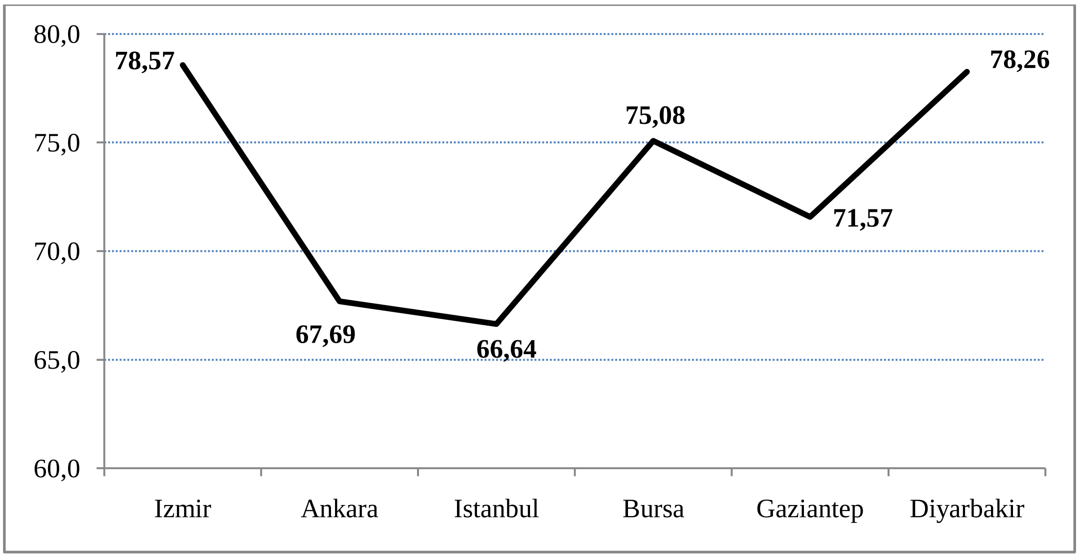

Figure 1. Urban-related identity mean scores as function of the city

Ethnicity: An analysis of variance was performed to examine the relationship between ethnicity and the level of urban-related identity in whole sample. Turkish and Kurdish participants differed significantly on URI ($F_{(1,\ 1498)}$ = 61.26, *p* = .000). The results revealed that Kurdish participants *(M =68.54, sd=17.17)* reported lower URI scores than Turkish participants *(M =75.47, sd=15.70)*. Furthermore an analysis of variance was performed to examine the relationship between migration type and the level of urban-related identity among Kurdish migrants. Although the internally displaced Kurdish migrants had lower URI scores *(M =64.18, sd=16.34)* than the voluntary migrants *(M =66.08, sd=16.00)*, the mean difference was not significant ($F_{(1,\ 679)}$ = 1.884, *p* >.05).

The predictors of urban-related identity in migrant group: Regression analysis

Multiple regression analysis with adjusted mean scores was conducted to examine the predictive power of several variables (gender, ethnicity, migration type, length of stay, satisfaction with several life domains) towards urban-related identity in internal migrant sample. Results of the regression analysis revealed that satisfaction level of relations with host majority members and urban life; length of stay and gender are the significant predictors. These values explained 33% of the total variance, $F_{(3,\ 610)}$ = 98.617 (*p =.000*), R^2 = 0.57. Three predictors had a significant beta weight in this analysis: satisfaction level of relations with host majority members and urban life: β = 0.47 (*p =.000*); length of stay β = 0.24 (*p =.000*); gender: β = 0.10 (*p =.002*). According to these results, the participants who are tied to their city life socially and physically had higher URI scores. In other words, the satisfaction level of contact with the host majority members has big impact on internal migrants' urban attachment. As the length of stay increases, the level of urban related identity increases, too. Finally, the main effect of gender is significant on internal migrants' urban related identity. Female participants reported higher level of urban-related identity than male participants did.

The socio-spatial mobility of internal migrants and host-culture members

Host culture members reported higher level of urban environment use than internal migrants. Besides the activities of host culture members in city centre were found to be more diverse than the migrant groups' activities. Especially host culture members had higher level of social integration in urban environment than the migrants. Compared to host culture members, internal migrants were found to have more activities in their neighbourhood (e.g. meeting with friends, shopping, and entertainment activities). A part from working activity, a great majority of internal migrants reported that they mostly use urban environment when they need health services. Concerning the differences in terms of city, the migrant participants living in Izmir reported highest level of accessibility to urban environment whereas the migrant participants living in Ankara reported least level of accessibility to urban areas and social mobility.

DISCUSSION

The results indicated that the unjust social and environmental structures significantly associated with the level of urban identity and several life domains' satisfaction. According to the results Kurdish participants were less satisfied with the life domains in general when they are compared to Turkish migrants. Moreover internally displaced migrants were found to be less satisfied with the life domains than voluntary migrants. Female migrants in whole sample scored higher in life satisfaction domains than the male migrants. Result of the regression analyses revealed that satisfaction level of relations with host majority members and urban life; length of stay and gender are the significant predictors.

Several explanations to this result may be suggested**;** First of all, rapid urbanization in Turkey has been the cause and the factor that further accelerated mass migrations from rural to urban areas. Associated issues of urban squatters, degraded environment, inadequate infrastructure and services, the informal economy, and poverty have emerged as major issues surrounding internal migration (Icduygu, 2004). Especially in the mid 1980s, internal displacement which was constituted mostly by the Kurdish population contributed to this urbanization rate dramatically. In cross-cultural psychology literature, Ward and Kagitcibasi (2010) emphasized the role of practical issues such as “securing employment, obtaining adequate housing and addressing economic disadvantages” can be more debilitating than intercultural contact and change. Whereas the Kurdish migrants who relocate in big cities not only face a new social and physical environment but also have to encounter and get involved in a new cultural surrounding, where a different language from their mother tongue dominates the daily activities and life. The cultural discrepancy which Turkish migrants experience upon relocating in big cities is more about adapting to the “city life”. However, for Kurdish and especially for the female migrants of the Kurdish community, the language difference and other cultural distinctions are accrued on the process of adaptation to the “city life”. A majority of the Kurdish migrants lack the necessary Turkish language skills when they relocate in the big cities; this is more evident among the female members and the pre-school age children (Goksen and Cemalcilar, 2010; Mutlu, 2009). Most of them move next to their relatives and/or fellow countryman who are already relocated in the “Kurdish districts” located in the surrounding suburbs of the big city centres and try to hold on to the city life by finding a job (Isik and Pınarcıoglu, 2002). In this respect, the integration strategy is developed out of an obligation more than in an effort for adapting to the host culture. Furthermore Gui, Berry and Zheng (2012) pointed out that rural and urban life lead to two different civic cultures in China. In a similar vein, we may argue that rural and urban culture comes into contact with each other as a result of internal migration in Turkey, as well. As Gui et al. (2012) suggested that moving to the city involves engagement in a new civic context, and this can be considered as an acculturative transition.

As a consequence of social and political inequalities, internal migrants' settlements in big cities have been largely built up in the peripherial areas (TESEV, 2008). We would argue that the location of these residential areas in the city causes these spatial units to be more disconnected with urban centres. This physical remoteness to central areas may also affect the urban experiences of migrants in a negative way. Compared to Turks, Kurds’ accessibility to central areas and functional mobility is much lower. For this reason we also examined urban-related identity which may be related to several life domains. In support of this argument, it is also notable in our study to underline how the physical and geographical characteristics of the big city which is being migrated to, affects the urban-related identity. Moreover the participants, either Turks or Kurds living in Izmir were found to have highest urban-related identity scores. Compared to other cities, the geographical features and the general urban planning principles in Izmir lead to more permeable borders between urban centre and the peripherial areas. The accessibility to public areas and social mobility in Izmir may be assumed as relatively higher than the other two cities and various social and ethnic groups have more possibility to contact with other groups in a heterogenous urban setting. These findings pointed out that the advances of environmental psychology may be helpful to understand cultural transition from rural to urban life. For this reason, it is necessary to underline the importance of reaching solid, pratical outcomes from the studies conducted on acculturation in order to improve migrants' quality of life. Based on the findings of the present study, we may argue that satisfaction with life domains and socio-spatial mobility are closely related to urban-related identity. However the geographical position, physical features of the neighborhood and the urban planning principles have impact on this interrelation.

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REFERENCES

Beatley, T. (2004). *Native to nowhere. Sustaining home and community in a global age*. Washington: Island Press.

Boğaç, C. (2009). Place attachment in a foreign settlement. *Journal of Environmental Psychology*, 29, 267-278.

Brown, B. B. & Perkins, D.D. (1992). Disruptions in place attachment. In I. Altman & S.M. Low (Eds.). *Place Attachment*. (279-304). New York & London: Plenum Press.

Dixon, J. & Durrheim, K. (2000). Displacing place-identity: A discursive approach to locating self and other. *The British Journal of Social Psychology*, 39, 27-45.

Dixon, J.; Durrheim, K. (2004). Dislocating Identity: Desegregation and the transformation of place, *Journal of Environmental Psychology*, 24, 455-473.

Dovidio, J. F. & Esses, V. M. (2001). Immigrants and immigration: Advancing the psychological perspective. *Journal of Social Issues*, 57, 375-387.

Eryurt, M.A., Koc, I. (2012). Internal migration and fertility in Turkey: Kaplan-Meier Survival Analysis. *International Journal of Population Research*, Article ID 329050, 1-11.

Fried, M. (1963). Grieving for a lost home. In L. J. Duhl (Ed.), *The urban condition* (pp. 151-171). New York: Basic Books.

Fried, M. (2000). Continuities and discontinuities of place. *Journal of Environmental Psychology*, 20, 193-205.

Goksen, F. & Cemalcilar, Z. (2010). Social capital and cultural distance as predictors of early school dropout: Implications for community action for Turkish internal migrants. *International Journal of Intercultural Relations*, 34, 163-175.

Göregenli, M. (2013). *Çevre psikolojisinde temel konular (The fundamental issues in environmental psychology)*. İstanbul: İstanbul Bilgi Üniversitesi Yayınları-2.Baskı. *(in Turkish).*

Göregenli, M., Karakuş, P., Kösten, Y.Ö. & Umuroğlu, G. İ. (2014). Mahalleye bağlılık düzeyinin yer kimliği ile ilişkisi içinde incelenmesi (A study on neighborhood attachment in relation with urban-related identity). *Türk Psikoloji Dergisi*, 29 (73), 73-85 *(in Turkish).*

Göregenli, M., Karakuş, P., Umuroğlu, İ. & Ömüriş, E. (2013). *Selçuk kent belleği: Dün, bugün ve geleceğin zihinsel temsilleri (Selçuk urban memory: The cognitive representations of past, today and future)*. İzmir, Selçuk Belediyesi: Selçuk Efes Kent Belleği Yayınları. Mediform *(in Turkish).*

Goregenli, M., Ömuris, E. & Karakus, P. (2008). Kemeraltı envanter çalışması (Kemeraltı, Inventory research of a historical bazaar in a big Turkish city). M. Göregenli (Ed.) *Kemeraltı* içinde (73-201) Izmir: İzmir Ticaret Odası Yayınları No: 166 *(in Turkish).*

Gui, Y., Berry, J. W. & Zheng, Y. (2012). Migrant workers' acculturation in China. *International Journal of Intercultural Relations*, 36, 598-610.

Gustafson, P. (2001). Roots and routes: Exploring the relationship between place attachment and mobility. *Environment and Behavior*, 33, 667-686.

Hay, R. (1998). Sense of Place in Developmental Context. *Journal of Environmental Psychology*. 18, 5-29.

Hernandez, B., Hidalgo, M.C., Salazar-Laplace, M.E. & Hess, S. (2007). Place attachment and place identity in natives and non-natives. *Journal of Environmental Psychology*, 27, 310-319.

Hidalgo, M.C. & Hernandez, B. (2001). Place Attachment: Conceptual and empirical questions. *Journal of Environmental Psychology*. 21, 273-281.

Hopkins, N. & Dixon, J. (2006). Space, place, and identity: Issues for political psychology. *Political Psychology*, 27, 173-185.

Icduygu, A. (2004). Demographic mobility and Turkey: Migration experiences and government responses. *Mediterranean Quarterly*, 15, 88-89.

Isik, O. & Pinarcioglu, M. (2008). *Nöbetleşe yoksulluk: Sultanbeyli örneği* (*Poverty by turns: The Sultanbeyli example)*. Istanbul, Turkey: Iletisim Press *(in Turkish).*

Karakuş, P. & Göregenli, M. (2008). Linking place attachment with social identity orientation: An examination of the relationship between place attachment, social identity orientation and integration to city. *International Journal of Psychology*. 43.

Karakuş, P. (2007). *İzmir Kültürpark'ının İzmirliler açısından anlamı ve Kültürpark hakkındaki temsilleri (The meanings and cognitive representations of an urban park)*. Yayınlanmamış Yüksek Lisans Tezi. Ege Universitesi, Sosyal Bilimler Enstitüsü, Izmir *(in Turkish).*

Karakuş, P. (2014). *Farklı kimlik gruplarında yer kimliği, yerin anlamları ve kültürlenme süreçleri (Place identity, meanings of place and acculturation process in multiple group identities)*. Yayınlanmamış Doktora Tezi. Ege Universitesi, Sosyal Bilimler Enstitüsü, Izmir *(in Turkish).*

Keles, R. (1976). Regional Development and Migratory Labour. In N. Abadan-Unat, R. Keles, R. Penninx, H. Van Renselaar, L. Van Velzen & L. Yenisey (Eds.). *Migration and development. A study of the effects of international labour migration on Bogazliyan district*, (pp.139-141). Ankara, Turkey: Ajans-Turkey Press.

Lalli, M. (1992). Urban-related Identity: Theory, measurement and empirical findings. *Journal of Environmental Psychology*, 12, 285-303.

Lewicka, M. (2010). What makes neighbourhood different from home and city? Effects of place scale on place attachment. *Journal of Environmental Psychology*, 30, 35-51

Lewicka, M. (2008). Place attachment, place identity, and place memory: restoring the forgotten city past. Journal of Environmental Psychology. 28, 209–231.

Low, S.M. & Altman, I. (1992). *Place attachment: Human behavior and environment. Advances in theory and research*. Vol. 12. Plenum Pres. New York & London.

Mutlu, Y. (2009). *Turkey's experience of forced migration after 1980s and Social Integration. A comparative analysis of Diyarbakir and Istanbul*. Master Thesis. Middle East Technical University, Ankara, Turkey.

Pellow, D. (1992). Spaces that teach: Attachment to the African Compound. In I. Altman and S. M. Low (Eds.). *Place attachment: Human behavior and environment. Advances in theory and research*. Vol. 12, (p.187-208). Plenum Pres. New York & London.

Proshansky, H.M., Fabian, A.K. & Kaminoff, R. (1983). Place-identity: physical world socialization of the self. *Journal of Environmental Psychology*, 3, 57-83.

Relph, E. (1976). *Place and placelessness*. London: Pion.

Sonmez, I. O. (2007). Concentrated urban poverty: The case of Izmir Inner Area, Turkey. *European Planning Studies*, 15, 319-338.

Tas, H.I. & Lightfoot, D.R. (2005). Gecekondu settlements in Turkey: Rural-Urban Migration in the developing European periphery. *Journal of Geography*, 104, 263-271.

Tekeli, İ. (2007). The different categories in Turkeys' Migration History. In A. Kaya & B. Sahin (Eds.). *The roots and paths: The migration processes in Turkey*. (pp.447-473). Istanbul, Turkey: Istanbul Bilgi University Press.

TESEV (2008). *Coming to terms with forced migration: Post-displacement restitution of citizenship rights in Turkey.* TESEV Report by D. Kurban, D. Yukseker, A.B.Celik, T. Unalan & A. Aker. Istanbul, Turkey: TESEV Publications (English edition).

Tuan, Y. F. (1980). *Rootedness versus sense of place*. Landscape. 24, 3-8.

Ward, C. & Kagitcibasi, C. (2010). Introduction to acculturation theory, research and application: Working with and for communities. *International Journal of Intercultural Relations*, 34, 97-100.

Williams, D. R., & Vaske, J. J. (2003). The measurement of place attachment: validity and generalizability of a psychometric approach. *Forest Science*, 49, 830–840 .

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PROBLEMS OF THE SUSTAINABLE DEVELOPMENT OF THE REGION TAKING INTO ACCOUNT THE INVESTMENT FACTOR

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ABSTRACT

Techniques of an estimation of investment appeal of regions that is caused by requirement for definition of an estimation of investment aspect of social and economic development of region as bases for acceptance of various administrative decisions are resulted.

Key words: *economy, competitiveness, sustainable development, region, investments.*

INTRODUCTION

In the conditions of decentralization of economic system of society, delegation of power in various fields of activity their economic independence and powers in the sphere of life support of the population sharply increased by level of regions. Increase of responsibility of the subject of regional government for effectiveness of social and economic functioning of the territory became a constituent of this tendency. The designated tendency puts subject of regional government before need of development of strategy of the economic body height as which important element increase of competitiveness of an economic complex of the region acts. This problem becomes aggravated in the conditions of need of engaging of investments into the region both internal, and investors of foreign countries.

THEORY

In the modern conditions regions become the subjects of the competition differently using capacity of characteristic territory. Depending on effectiveness of this use, they possess different ability to open, use and keep competitive advantages. All this conducts to need of development of systems of an assessment, the analysis and management of competitiveness of the region and staticizes problems of selection of key factors of increase of competitiveness in the conditions of limitation of competitive resources. In the same communication by an important problem there is a choice of spheres of the most favorable appendix of the capital. It demands detailed studying and the account, as the obshcheekonomiche-skikh of the factors defining functioning of these spheres, and specific features of exercise in them specific investment projects. From this need of synthesis of experience of development of strategy of regional investment and to development on this basis of the modern methodical approaches to definition of the priority directions of investment policy of the region follows. In the same communication by an important problem there is a choice of spheres of the most favorable appendix of the capital that demands detailed studying and the account as the all-economic factors defining functioning of these spheres, and specific features of exercise in them specific investment projects [1].

Now is available very much both domestic, and expressly adapted foreign techniques of an assessment of investment appeal of regions. Relevance of similar researches is caused by need for an integral index of an assessment of investment aspect of social and economic development of the region as bases for adoption of various administrative decisions. As the main development it is possible to allocate a technique of monitoring of social and economic climate of the Russian regions of analysts of the Kommersant magazine (1993); "Methodical recommendations about an assessment of investment appeal of subjects of the Russian Federation" [2]; the reviews of investment appeal of the economic region of Russia of agency of "Universe" allocating a resultant indicator of regional enterprise risk (1993-1995); "Technique of an assessment of investment climate of regions of

Russia" Institute of economy of the Russian Academy of Sciences; "A technique of an assessment of regional risks in Russia" Institute of perspective researches on the order of bank of Austria (1995); "Rating of investment appeal of Russia" "Expert RA" agencies (annual since 1996); "Technique of calculations of indexes of investment appeal of regions" (1996), (Russia) executed in unison by Expert institute and the Center for studying of Russia and Eastern Europe of Birmingham university (Great Britain).

FINDINGS AND DISCUSSION

Studying of available methodical approaches says about particular disagreements in definition of such categories, as "investment appeal", "investment climate", "investment potential", and their interrelations that leads to selection of different characteristics of these categories therefore "on one index it is expedient to carry the region to a zone of the favorable investment climate, and on another to a zone of the suppressed investment activity" [3]. Therefore before starting the analysis of investment appeal of the region, it is necessary to decide on analysis tools, i.e. to specify the contents and parameters of categories.

In a technique of a group of authors of Council for studying of productive forces of the Ministry of Economic Development of the Russian Federation and the Russian Academy of Sciences initial methodical concept is the concept of investment climate, and its building blocks - the investment potential, investment scratches, investment appeal and investment activity. The investment climate of the region represents the set of various social and economic, natural, ecological, political and other conditions determining scales (volume and rates) of engaging of investments into fixed capital of this region which developed for a row of years. Investment climate determine by two components of investment appeal and investment activity of the region. Investment appeal of the region is the volume of capital investments which can be attracted in its economy proceeding from the investment potential inherent in it and level of investment risks in it. Investment activity is intensity of engaging of investments into region economy. Investment potential of the region the volume of investment which can be attracted in its economy at the expense of all (internal and external) financing sources, proceeding from existence of various economic, social and natural resources, features of its geographical position and other objective prerequisites, essential to formation of investment activity in it. Authors of this technique created a set of the most investment and significant indexes who are applied to an assessment of investment appeal of the region (table 1).

Table 1: Indexes of investment potential of the region [4]

Name private indexes	Unit of measure (indexes of the state statistician)
1	2
I. Indexes of production and financial capacity of the region	
Industrial output	Volume of production of the industry per capita region
Rates of change of industrial output	Annual rate of change, proceeding from volumes in the comparable prices
Level of development of small business	Share taken at small enterprises in total number economically the fissile population
Share of the unprofitable enterprises	Specific gravity of the enterprises and organizations which finished year at a loss in total of the enterprises and organizations conducting business activity
Bulk volume of internal investment resources of the enterprises	The sum of the depreciation charges of all enterprises provided with a monetary covering and profits of the profitable enterprises per capita the region
Volume of retail commodity turnover	The volume of retail commodity turnover per capita (with adjustment on regional distinctions in level of retail prices)
Export of production to the foreign and neighboring countries	Export from the region in dollars per capita the region
II. Indexes of social capacity of the region	
Security of the population with housing	Housing (in sq.m of total area) per capita
Security of the population with cars	Number of cars in property of citizens on 1000 people of the population
Security of the region with highways with a hard coating	The total length of highways per acre the region and per capita the region determined with application of an index of E. Enggel K_e =

	D/VTH, where *D* - length of a network of highways, in km; *T* - Square of the region, in hundreds of km^2; *N* - the population of the region, in tens of thousands human
The volume of paid services for the population	Volume of paid services per capita
III. Indexes of natural and geographical capacity of the region	
Standard of living of the population of the region	Ratio of the average per capita located resources and size of a living wage
Volume of natural stocks of naphtha and gas (hydrocarbonic resources)	The volume of natural stocks of naphtha and gas, taking into account profitability of development of fields
Existence of natural stocks of mineral raw material resources except the hydrocarbonic	The volume of natural stocks of mineral raw material resources except the hydrocarbonic
Geographical position of the region (border)	The mark assessment based on objective natural and geographical signs
Share of the needy population	The population share with the monetary income is lower than the size of a living wage
Crime rate	The complex index integrating number of registered crimes (minus the heaviest) and number of the most serious crimes on 100 thousand population
Unemployment rate	The number of the unemployed in % to the number of the economically fissile population
Level of ecological impurity and climate diskomfortnost in the region	The complex index integrating ecological characteristics according to the state statistician and the mark climatic characteristic
Relation of the population of the region to processes of formation of market economy	Difference between shares (in %) votes given in the region at the last parliamentary (presidential) elections for candidates, supporting formation of market economy, and against them

Regional noncommercial investment risk probability of inexact realization of investment potential of the region in view of existence in it negative economic, social and (or) ecological conditions of the investment activity forming probability of loss of investments or the income from them and interfering those use of its investment potential. The basic building blocks of investment potential and investment climate of the region and interrelation between them are shown in table 2.

Table 2: Factors making investment appeal of the region

INVESTMENT APPEAL OF THE REGION			
Investment potential of the region		Investment climate of the region	
Investment resources	Investment infrastructure	Institutional environment	Investment scratches
raw	Credit organizations	Formal rules	economic
labor	Exchange, stock market	Informal rules	financial
financial	Funds of the relative investment		political
share (power)			social
	Insurance and leasing companies		ecological
	Structural organizations and wholesale trade in investment goods		criminal
			statutiry
	Road and transport infrastructure, communication		
LEVEL OF INVESTMENT ACTIVITY IN THE REGION			

The defined integral index is defined by a path of data of numerical values of separate indexes of investment appeal. Numerical value of an integral index of investment appeal as a whole is accepted to unit or to 100%, and values of integral indexes for regions are defined in relation to national average level. Investment activity, according to the proposal of authors of this technique, has to be measured by two private indicators: the shower volume of investment and growth rates of investments in the region. For the accounting of different degree of intensity of influence of investment appeal on each of two components of investment activity at integral measurement of investment activity weight coefficients [4] are appropriated. The main advantage of this technique, in our opinion, is possibility of definition of extent of realization of investment appeal of the region. It should be noted that appeal, in our opinion, this concept in many respects subjective, dependent both from the potential investor, and from objective characteristics of the region, and potential concept especially objective, indicating resource opportunities of the region. Really, investment appeal reflects the subjective relation of the potential investor to object of investment, unlike investment climate which reflects readiness of social, ecological and economic systems for investment [5]. Investment appeal of the region consists of investment climate, resource security and the competitive environment.

Feature of methodical approach of the Ekspert magazine is identification of interrelation of two main components of an assessment of investment appeal of regions: investment potential and investment risk. Thus investment potential consists of eight private capacities of the region: resource and raw, labor, production, innovative, institutional, infrastructure, financial and consumer. The rank of each region is defined by the quantitative assessment of its potential as shares in the cooperative capacity of all regions of the country. The investment risk characterizes probability of loss of investments and the income from them. It also consists of seven private risks: economic, financial, political, social, ecological, criminal and statutiry. The rank of each region by this or that type of risk is determined by value of an index of investment risk to the relative deviation from the average and state risk level which is taken as a unit. As a result of an assessment of all regions on indexes "potential risk" is formed a rating on which all regions are offered to be distributed on groups of a scale [2]:

maximal potential - minimum risk (1A)
high potential - moderate risk (1B)
high potential - high risk (1C)
average potential - minimum risk (2A)
average potential - moderate risk (2B)
average potential - high risk (2C)
low potential - minimum risk (3A)
under potential - moderate risk (3B1)
under potential - high risk (3C1)
slight potential - moderate risk (3B2)
slight potential - high risk (3C2)
low potential - extreme risk (3D)

This technique allows investors at a choice of subjects and objects of investment to make more efficient decisions, however does not clear up communication between various categories of an investment perspective.

CONCLUSIONS

Therefore at determination of competitiveness of the region or effectiveness of its social and economic functioning it is necessary to come from original positions of the modern theory of investments in processes of formation of competitiveness of regions, and comprehensions of that in conditions of decentralization of economy the region as the economic system possesses opportunity self-contained to develop and realize the strategy directed on increase of competitiveness by increase in the investment appeal on the basis of development of the priority directions of investment policy.

REFERENCES

Мирончик, Е.А. Анализ инновационной и научно-технической деятельности в регионах Беларуси по устойчивому развитию / Е.А. Мирончик, И.В. Акулова / Актуальные вопросы социально-экономического развития России в XXI веке: аспиранты и студенты в научном поиске // Матер. III межрегион. науч.-практ. конф. – Смоленск: ВПО «СГУ», 2009. – С. 373-379.

Гришина, И. Комплексная оценка инвестиционной привлекательности и инвестиционной активности российских регионов: методика определения и анализа взаимосвязей / И. Гришина, А. Шахназаров, И. Ройзман / Инвестиции в России, 2001. - № 4.

Дерябина, Я. Сравнительный анализ подходов к оценке инвестиционной привлекательности и инвестиционной активности российских регионов / Я. Дерябина / Инвестиции в России, 2003. - № 8. - С. 17-19.

Инвестиционный климат, стратегия и эффективность регионального управления. – Эксперт, 2003. - № 43.

Мозгоев, А. О некоторых терминах, используемых в инвестиционных процессах / А. Мозгоев / Инвестиции в России, 2002. - № 6. - С.48-49.

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ECO-CULTURAL SYSTEM PLANNING OF THE EXISTING BUILDING STOCK: THE ANALYSIS OF THE CITY OF İZMİR

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ABSTRACT

From its emergency and inclusion into the literature, the term "sustainability" is being used mostly for defining or mentioning to the physical environment. However, sustainability is more than this. It can be defined as providing the best life conditions for living creatures in modern city environments for maintaining continuity in the natural environment by protecting the historical and the cultural elements. In order to provide this continuity, the cultural sustainability has important role. The ecological culture can be identified as the soul and the source of the eco-city in which direct expression of ecological relation between the society and nature is provided. Not only adapting the ecological culture for new structures but also to existing building stock is also important for the enhancement of the city and the urban. In this research, the existing building stock of İzmir that needed to be enhanced in social and cultural terms will be analyzed. Through this analysis, the effect of individuals, the management system and the social morals over the social sustainability will be mentioned. By referring to the other examples from the world also, an eco-culture criterion is tried to be set for the existing building stock of the urban.

Key words: *eco-culture, sustainability, urban planning, existing building stock, İzmir.*

INTRODUCTION

Since its first emergency in 1980's, the term "sustainability" was used to provide the best relation between the economy, the society and the environment. Although it is that much comprehensive, sustainability is thought only as a physical issue related with its detailed aspects like material usage, daylight, ventilation or acoustical factors. Sustainable use of natural resources encompasses not only ecological and economic, but also social cultural dimensions (Throsby, 1999; Council of Europe, 2000; Hawkes, 2001; Littig and Grieβler, 2005; Forest Europe, UNECE and FAO, 2011). In addition to this, it is also thought that sustainability can only be applied to new buildings rather than the existing building stocks. However, sustainability can be defined as trying to provide the best living conditions for each and every single living creatures in built environments to resume the continuity in both the natural environment and natural resources through conserving both the historical, cultural and social elements and items.

As it is obvious, cultural sustainability has the same importance with the physical sustainability for maintaining physical, social, cultural and economic continuity. In addition to being physical beings, buildings and structures are also the cultural collective memories. Aldo Rossi in his book, The Architecture of the City, indicates that while the single building is the object of architecture in the city, the collective cultural process construct cities over time (Rossi, 1984). According to his theory, to understand the complexity of the city as an artifact a morpho-typological classification system must be used. And he defines this artifact as an evolutionary process of adapting building types over time, where old forms can take on new meaning. It is similar to the critique of modernism where form followed function. Rossi concentrates on the historical European city, and these cities' metabolism can be defined as regionally self-sufficient by means of the need for food, water and human security.

In addition to this, cultural sustainability also comprises social sustainability in terms of social relations, individuals and management factors. Rem Koolhaas, in his book entitled *Delirious New York* uses the “culture of congestion” statement that stems from modern technology and high-rise buildings of Manhattan. He offers new design models with high-density metropolitan architecture that produces new social relations, but also new problems. In his model, by using mass transportation and high-density living, it is succeeded to achieve great efficiencies in metropolitan life. In this system, the metropolis is a highly organized machine with strict social hierarchies that separate rural and urban space and people (McGrath & Pickett, 2011).

More shortly, cultural sustainability can be defined as the soul and the source of the eco-city in which direct expression of ecological relation between the society and nature is provided. Not only adapting the ecological culture for new structures but also to existing building stock is also important both for the enhancement of the city and the urban, and the cultural continuity to next generations.

In this paper, the existing building stock of İzmir that needed to be enhanced will be analyzed from the perspective of cultural and social sustainability. In the literature review part, ecological culture will be firstly defined. Afterwards, its components will be lined up and the importance of ecological culture will be mentioned. The goals of the ecological culture and its 4 principles will also be touched upon. The requirements of the enhancement from the perspective of ecological culture in exiting building stock will be listed and some important international examples will be given. In the case study part, the details and the methods of the case study will be elucidated. Through the situation analysis, the effect of individuals, the management system and the social morals over the ecological culture will be mentioned. The problems and the needs that make cultural and social sustainability enhancement required for the existing building stock of İzmir will be listed. With the proposals that will bring forward, an eco-cultural criterion will be set for the existing building stock of the urban built environment.

CULTURAL SUSTAINABILITY

Before mentioning the cultural sustainability, it is better to define what “culture” and “cultural” is. “Cultural” relates to a non-biological system of development and adaptation (Steward, 1955). Culture thus includes any kind of heritage from the past, ranging from how people interact and do things to any kind of object or environments that are a results of human constructions or use of landscape. For transferring all those heritages to new generations, cultural ecology should be provided with its every aspect. Cultural sustainability can be counted as the forth element of the sustainability after ecological, economic and social sustainability (Konuk, 2009). In other words, urban ecological culture can also be interpreted as the special expression of ecological culture on the city scale. The reason why cultural sustainability is defined as the forth element of the sustainability is its new emergency into the literature.

Although there is still no exact definition of the cultural sustainability, 2 definitions come to the forefront:

1) The duty and the responsibility of transferring the cultural values and indicators to the new generations which were obtained from the before generations through adding new ones (Cebeci & Çakılcıoğlu, 2002).
2) The composition of the true principles and the strategies for developing the protection politics to maintain the cultural values and trying to provide their usage in addition to their salt protection by also considering that the modern cultural circumstances can change (Beyhan, 2004).

Through these above 2 definitions, it can be understood that the 2 common points to provide the cultural sustainability are the provision of the required politics and the ownage of the individuals. Social and cultural sustainability criteria encompass objects and structures, such as historical remains and habitat for people and values such as sense of place, local culture and traditions (Fairclough and

Rippon, 2002; Antrop, 2003; Palang and Fry, 2003; Claval, 2004). Rather than having an exact definition, cultural sustainability is always being defined with its aims (Konuk, 2009):

1) Trying to solve global trends which effects cultural diversity in local scale

2) Guaranteeing that cultural politics are at the center or urban management politics

3) Being able to request from all the national and international facilities to improve and strengthen their point of views toward cultural sustainability

In other words, basically; ecological culture seeks to establish the core values, morality, and the ethics of harmony with nature and sustainable development of the society.

The 10 key elements for providing the cultural sustainability are as (Konuk, 2009):

1) Sustainability of the Culture: Inoculating people the sustainable life style and make them reflect their learning into every aspect of their lives.

2) Globalization: Highlighting the importance of protecting the culture being affected from the globalization.

3) Protecting the Heritage: Protecting the cultural heritages, human experiences and infrastructures away from the effects coming from the outside.

4) Space Perception: Bringing the importance of the symbols, structures and art to the forefront and trying to provide a holistic point of view in which both economic and cultural improvement can be obtained.

5) Local Information and Traditional Habits: Protecting the traditions and local properties and trying the make them sustainable.

6) Cultural Social Improvement: Highlighting the importance of the protection of the values by individuals by themselves.

7) Art, Education and Youths: Trying to impose that youths, art and education are so important in cultural sustainability.

8) Sustainable Design: The shoring of nature friendly design, recyclable structures and urban design. Also they were seen as a part of cultural sustainability.

9) Planning: How the culture can be integrated into the planning phase of the existing urban and improvement plans are important and it can be obtained through the perception of the sustainability with its whole aspects.

10) Cultural Politics and Local Government: Culture and politics should work together with integration for obtaining higher life standard.

As it was understood from the above 10 items, ecological culture can be handled through both human consciousness, idea, belief, organizational, institutional and regulatory forms of the cultural patterns. For constructing the ecological culture, 3 different categories can be classified as (Zhang, Y., & Su, Meirong, 2013):

1) Social factors: Political, economic, cultural, educational and other aspects.

2) Industries: Agriculture, industry, tourism, construction and other fields.

3) Implementing actors: Governments, enterprises, public institutions, communities, schools, families.

These all elements of these above 3 categories have different and crucial roles for obtaining an ecological culture and cultural ecology.

To improve urban ecological and cultural construction with unified guidance and operations covering a wide range of ecological and cultural construction, a cultural of an eco-cultural framework was proposed with 3 levels, 3 approaches and 4 brands (Zhang, Y., & Su, Meirong, 2013).

If all these elements can be provided, cities with high quality can be provided in cultural, scientific, educational and environmental terms. Cities according to their characteristics have to play on the basis of:

1) Rich and unique culture: Mining the city for cultural resources, combined with the city's history, culture, music, architecture, landscape and characteristics will help to integrate various cultures, ideas.

2) High-tech, environmentally friendly technology: In the process of building a material and cultural ecology, resource efficient recycling is the principle of high-tech, environmental technology and industry.

3) Advanced, green education: Public education ensures the sustainable development of urban ecological and cultural construction. Increased investment in education and construction, with an emphasis on creating green primary and secondary school environments.

4) Harmonious and friendly environment: Ecological material culture through the visual manifestation of the silent appeal of spiritual and cultural ecology and ecological protection within the institutional culture jointly create a warm, friendly environment and build a socialist material civilization, institutional civilization and spiritual civilization and the organic unity of a harmonious society and thus attract talent, capital and surrounding.

Within a holistic approach, most basically; the success of the cultural policies and ecological culture can be provided only by maintaining (Mercel, 2002):

1) Cultural vitality, diversity and conviviality;

2) Cultural access, participation and consumption;

3) Culture, lifestyle and identity

4) Culture, ethics, governance and conduct.

By interpreting all these above basic information on ecological culture and cultural ecology, some principles can be set while evaluating the existing building stock in terms of socio-cultural sustainability (Türker, 2011). Firstly, while making eco-cultural system planning into an existing building stock; it should be considered that it is not only a physical enhancement but also a semantic revolution. In addition to this, the authority making this eco-cultural system planning should be aware of the urban dynamics of the epochal. The meanings and the emotions should not also be disregarded. They are all important part of the cultural reservoirs of cities from the perspective of the individuals. Also, time is another effective dynamic over the eco-cultural system planning evaluation process. The traditions of the specific city should also be considered like their daily habits, their religious places, their social infrastructure and their ethic values.

Some important international and national examples in terms of eco-cultural system planning of the existing building stocks can be listed as (Türker, 2011):

- Cubist Casbah Housing Madrid, Spain
- 124 Apartment Block Eco-Rehabilitation Szczecin, Poland
- Germany, Berlin Kreuzberg Housing Eco-Rehabilitation
- England, London Southwark Neighborhood Eco-Rehabilitation
- Familistere Godin, Guise, France
- Denmark, Copenhagen Housing Revitalization Program
- Fener-Balat Rehabilitation Project, İstanbul, Turkey
- 37. & 42. Streets Rehabilitation Project, Tarsus, Turkey
- Turkey, Mardin Participatory Urban Rehabilitation Project

CASE STUDY

As a case study, the existing building stock of İzmir was analyzed from the perspective of eco-cultural enhancement. Firstly, the history of İzmir was divided into 3 as from Smyrna to the establishment of Turkish Republic, from the establishment of Turkish Republic to the end of 1960’s and from the starting of 1970’s to nowadays. The whole existing building stock of İzmir was categorized by referring to above periods. After periodical division, each periods’ indicator buildings were listed. Through this method, it was aimed to maintain the continuity of İzmir’s buildings which remind people the cultural and social properties of their past.

SITUATION ANALYSIS & THE NEEDS THAT MAKE CULTURAL & SOCIAL SUSTAINABILITY ENHANCEMENT REQUIRED IN THE EXISTING BUILDING STOCK OF İZMİR

İzmir as being the 3rd biggest city of Turkey, it is Turkey’s best-developed industrial cities with İstanbul, Kocaeli and Ankara. When it is looked to employment division of 2006, service sector takes the first place whereas industry sector takes the second place. As being one of the most important trade cities, İzmir still maintains this characteristic.

The followed politics that caused changings in city economics after 1980’s also changed the spatial structures. With the enlargement of service sector and increasing of productive services; there were some other centers raised up in conjunction with the housing zones besides Kemeraltı like Karşıyaka-Mavişehir and Çiğli at north, Bornova at west, Balçova and Narlıdere at south. As traditional centers, Konak, Çankaya, Basmane and Alsancak were all affected from this process and it continued in 1990’s also. In result, Konak and Kemeraltı were transliterated into places where wholesale and retail trading were rolled up. However, there was no big difference in the trading and entertainment traditions of Alsancak but the profile of inhabitants here was changed with a great impact. In addition to the decrease in the young population, in some areas; some marginal groups started to live in which resulted with security problems in some streets at nights.

When it is looked to the existing building stock of İzmir from the perspective of social and cultural values, indicators can be identified according to the important “*thresholds*” of the history of the city. In this research, they have been classified as in the following:

- 1st period: Beginning from the ancient Smyrna to the establishment of Turkish Republic
- 2nd period: From the establishment of Turkish Republic to the end of the 1960’s
- 3rd period: From the 1970’s till today

1st period: Beginning from the ancient Symrna to the establishment of Turkish Republic

The ancient city of Smyrna was the home to Roman and Byzantine civilizations following the death of Alexander the Great. Under the sovereignty of the Roman Empire after 133 B.C., the city benefited from the Acropolis at Kadifekale and the Theater that existed during the Hellenistic period. One of those still remaining rare works of buildings is the Aqueducts bridging the two sides across the Kemer River at Kızılçullu.

In the 11th century, İzmir was the central city of the first Turkish Principality founded at West Anatolian coasts. As a result of the First Crusades, the Latins occupied the harbor district and the Turks located in Kadifekale Citadel, which leads to the city being divided into two parts as Yukarı (Upper) İzmir and Aşağı (Lower) İzmir and the city maintained its dual structure till the end of the 17th century (Güner, 2005).

As the city of Izmir became a great harbour city after the second half of the 17th century, a customs building and a bedesten were built. With the rise of commercial activity the numbers of inns in the city were increased rapidly and new mosques around the Inner Port were built like the Şadırvan (1636), Kestanepazarı (1667) and Kemeraltı Mosques (1673). Additionally, Armenian and Jewish districts were established in addition to existing Rum district. After the abandoning of the residents of Kadifekale district, the dual morphological structure of the city was over.

In the late 18th century, the Levantine population of the wealthy class people began to settle in new villages which will have turn into new suburbs gradually such as Buca, Bornova, Seydiköy (Gaziemir) and Karşıyaka for summer housing and providing shelter for potential epidemics. With this decentralized settlement pattern, the city gained its metropolitan structure.

During the 19th century a number of improvements were seen in the city: International bank branches were opened, The French and Ottoman Post began to service, and consulates of 17th different countries took place. Additionally, railway constructions started and Alsancak and Basmane railway stations were built. In 1867, by the construction of Kordon road and the quay, the Levantines, merchants, the Jewish, Rum and Armenian citizens of the Ottoman began to move their offices to the coast.

Beginning from the 1913 till 1922, the period of Governor Rahmi Aslan, Bahribaba Park, and the foundations of Orphanage, National Library, National Movie and Girls’ High School were built to modernize the city with a contemporary appearance.

Indicators of the period:

- Ancient Ruins of the city: Bayraklı, Kadifekale, Agora, Tilkilik, Basmane, Yeşildere area
- Historical city center: Kemeraltı, inner port
- Historical districts that reflects cosmopolitan character of the city like Turk, Rum, Armenian, Jewish quarters.
- Levantine villages in Bornova, Buca, Karşıyaka and Seydiköy (Gaziemir)
- Significant buildings and traces (pathways, roads, squares, materials, etc.) at Kordon, Punta area, Alsancak, Konak, Varyant, Bahribaba Park, Karataş and Göztepe.
- İzmir Harbour District: Old Water Gas Factory, soap, oil, tobacco, fig treatment and cement factories and depot
- Social and cultural pattern of the inhabitants of the city

2nd period: From the establishment of Turkish Republic to the end of the 1960’s

In the year of 1922, as a result of the İzmir Fire physical, cultural and social topography of the city were ruined. Armenian, Rum and Levantine districts were affected largely and only Belle-Vue (Kordon Road) was partly rescued from these burning areas.

By the foundation of the Turkish Republic in 1923, with the improvements in all cities in Turkey, the urban reconstruction movements in İzmir had also been started with the ideology to reflect the identity of the new Turkish Republic by the help of architecture and city planning.

Indicators of the period:

- İzmir Harbour District: Electricity Factory (1928), Orient Factory (1924), Old Tile Factory, Old Sümerbank Chintz Industry, Old Tariş Alcohol Factory and Old Floor Factory
- Gazi Boulevard, Cumhuriyet Square
- Kültürpark (Culture Park)
- Modern publicity buildings: opera house and cinema
- Mimar Kemalettin Street and environs (Buildings that belong to 1st National Architectural Style period)
- Public memory buildings: museums and libraries

3rd period: From the 1970's till today

One of the most important developments in this period was the Condominium Act (1965) that intended to bring together small capitals to facilitate individuals in acquiring houses of their own. This led to the change in the scale with the building height figure of 24.8 meters (Eyüce, 2005).

1973 Master Plan of İzmir was the most important issue that determines the development tendencies around the Bay as along the axes of north-south and east-west.

After the second half of 1960's, the International Style examples were seen at the significant buildings of the city. In some administrative buildings in the city center, contemporary and liberal look were being reflected.

By the year of 1980, with the rapid and different culture of consumption, pot-modern implementations were seen in the city especially in the commercial axes of Karabağlar and suburban villages in Narlıdere.

Indicators of the period:

- International Style examples: Eski Merkez Bankası (Old Central Bank), Türk Ticaret Bankası (Turkish Bank of Trade), City Hall for the Greater Municipality of Izmir, former Grand Ephesus Hotel-current Swiss Hotel, İzmir Chamber of Commerce Local Headquarters
- Formation of commercial sub-centers: Konak Atatürk Square, The Sosyal Sigortalar Çarşısı (Bazaar of Social Insurance Institution)
- Contemporary and liberal approach: Governor's Mansion of İzmir, Yeni Merkez Bankası (New Central Bank)
- Mass housing projects: EVKA, Egekent, Atakent, Mavişehir.
- Re-generation projects: Konak Pier, Mimar Kemalettin Street

PROPOSALS

When it is looked to the existing building stock of İzmir from the perspective of eco-cultural system planning, a classification can be made as: "cultural and social sustainability" in areas where industry left, re-functioning of the historical buildings at city center, adaptive reuse of structures that can be classified as modern architecture heritage constructed after Republic, adaptive reuse of civil architecture examples and monumental structures and revitalization of the structures and lands to city back which belongs to state and private firms and located in inner-city.

Within the scope of above classification; the applied/in the process of application/planned to be applied/proposed projects are listed below which are under the subtitle of "eco-cultural system planning" of historical and cultural heritage of İzmir.

- With a project that will be composed - “Urban Readings”; different scaled, closed, semi-open and pin board like interactive information centers can be created to the regions, neighborhoods, streets, buildings and other historical areas which represents its periods through coloring each 3 different era’s with separate colors.
- With a virtual communication web that will be composed, it will become easier to make a contact between the city dwellers, move commonly and generate new ideas. For increasing participation of the citizens in the next urban transformation, tweets, blogs, community sensing and mapping projects, games for change, smart mobs, festivals, workshops, painting competitions and flash events can be organized during the year in the different parts of the city.
- With a digital information system that will be composed, it can be provided to make city dwellers access all kinds of information. Through access that provided from every place with smart phones, i-pads, laptops; “urban digital maps” can be composed which are continuously updated. This system can also be supported by using a “magnetic card” which serves not just a physical transportation network but also an information network.
- A total urban system in which historical pattern (ancient ruins, historical commercial city center, modern industrial heritage at harbour area, etc.), singular buildings, green pattern and sea become integrated can be composed in behalf of ecological and cultural sustainability.
- To reinvigorate ecological processes within the city, possible opportunities must be determined such as using vacant lots for urban parks, constructing large parcels with more green areas by combining small parcel divisions, creating more pedestrian and bicycle ways in addition to public transport system by encouraging the lower levels of car ownership.
- Within the proposed urban system, the decontamination of the vehicle traffic as much as possible can be supplied through the circulation of the pedestrians, bicycles, trolleys, metros, buses and private cars can be provided at different levels and elevations and the composition of the lower-case car parking areas next to the city center.
- Through the adaptive reuse of the existing building stock with enhancement located at the axis of Basmane-İkiçeşmelik-Kadifekale and at the harbour district (Ege Neighborhood and nearby), positive contribution to İzmir’s sustainable development will be ensured.
- If the re-handling of Culture Park can be provided also with its integration to İzmir, this place can be turned out into a 7/24 hours free public domain and it can be used as center of attraction from all ages. Also with some proposed performance activities in addition to the physical planning, it can be provided to make citizens to use this area much frequently and more efficiently.

CONCLUSION

It is possible to identify indicators and match them with verifier variables to support inclusion of social and cultural values in planning.

Because that each city’s own historical, cultural and morphological structure is different from the others, the indicators defined in the eco-cultural system that will be proposed will also be different. By referring to that reason; the communal habits which compose the historical, social pattern and cultural structure and the requests of the citizens should be deeply analyzed. Afterwards, it can be provided to permit each citizen to use the environment equally and to reinvigorate ecological processed within their boundaries in ways that benefit citizens as well as the environment.

Each neighborhoods’ and / or districts’ one of a kind structures or buildings can be protected like commerce, industry or housing or mixed usage – commercial functions at the ground floor and the housing at upper floors. For each district, different sized and typed greenery areas, pedestrian ways, pavements, building heights or building densities can be defined.

For obtaining and living a more sustainable life; specialists from different disciplines can be encouraged to work together to make planning proposals in area-city-neighborhood-district-street scale through providing some design scenarios.

In these scenarios, the regions of the city which need emergent intervention should be handled primarily and in the process of the staging, some pre-studies like questionnaire, property determination, searching for financial assistance to other areas.

REFERENCES

Axelsson, R., Angelstam, P., Degerman, E., Teitalbaum, S., Andersson, K. Elbakidze, M., & Drotz, M. K. (2013). Social and Cultural Sustainability: Criteria, Indicators, Verifier Variables for Measurement and Maps for Visualization to Support Planning. *AMBIO: A Journal of the Human Environment*, 42, 215-228.

Chiu, R. L. (2004). Socio-cultural Sustainability of Housing: A Conceptual Exploration. *Housing, Theory and Society*, 21 (2), 65-76.

Dündar, Ş. G. (2010). Cultural Policies Between the Strata. In A. E. Göksu & Ş. Gökşen Dündar (Ed.), *Urban Historical Stratum: From Smyrna to İzmir* (pp. 34-42). Turkey, İzmir: Dokuz Eylül University Faculty of Architecture Press.

Eyüce, Ö. *Architecture in İzmir, İzmir Architectural Guide 2005*, İzmir Branch of Chamber of Architects, 2005, pp.8-19.

Gottmann, J. *The Urbanized Northeastern Seaboard of the United States*; The Twentieth Century Fund: New York, NY, USA, 1961.

Güner, D. *Urban History of İzmir*, İzmir Architectural Guide 2005, İzmir Branch of Chamber of Architects, 2005.

Konuk, S. (2009). *A Road of Approach for Planning: Cultural Sustainability, Case of Kumkapı* (Unpublished master dissertation). İstanbul Technical University, İstanbul.

McGrath, B. & Pickett, S.T. “The Metacity: A Conceptual Framework for Integrating Ecology and Urban Design”, *Challanges*, 2011, 2, 55-72.

Rossi, A. *The Architecture of the City*; MIT Press: Cambridge, MA, USA, 1984.

Roy, A., & Goll, I. (2014). Predictors of Various Facets of Sustainability of Nations: The Role of Cultural and Economic Factors. *International Business Review*, 23 (5), 849-861.

Sharifi, A., & Murayama, A. (2013). Changes in the Traditional Urban Form and the Social Sustainability of Contemporary Cities: A Case Study of Iranian Cities. *Habitat International*, 38, 126-134.

Soini, K., & Birkeland, I. (2014). Exploring the Science Discourse on Cultural Sustainability. *Geoforum*, 51, 213-223.

Tavernor, R. (2007). Visual and Cultural Sustainability: The Impact of Tall Buildings on London. *Landscape and Urban Planning*, 83, 2-12.

Türker, C. (2011). *The Analysation of Afordable Residential Stocks According to Eco-Rehabilitation in terms of Social Cultural Perspective* (Unpublished master dissertation). Mimar Sinan University of Fine Arts, İstanbul.

US Commission Grant. 7. Ecological Culture of Citizens. 196-220.

Vallance, S., Perkins, H. C., & Dixon, J. E. (2011). What is Social Sustainability? A Clarification of Concepts. *Geoforum*, 42, 342-348.

Zhang, Y., & Su, Meirong. (2013). Eco-Habitat and Eco-Cultural System Planning. In Z. Yang (Ed.), *Eco-Cities* (pp.195-227). USA, NY: CRC Press.

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CLEAN ENERGY PRODUCTION USING BIOFUELS

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ABSTRACT

The paper focuses on the necessity of environmental protection through modern combustion facilities that assure the thermal and electrical energy for small applications such as: greenhouses, small farms, or food production facilities. It is known that air quality is depending on such pollutant sources, as well, especially because the exhaust source is at low level over the soil, and the dispersion of the pollutants is reduced. Using biofuels instead of fossil fuels, in special designed technologies such as cogeneration, assures the reduction of the CO2 in the flue gases, supplementary other advantages such as regional energy independence, cost, local utilization of waste energy resources, sustainability of the existing and new business and also creating jobs, etc. Of course disadvantages are also notable. The author's summaries their experience achieved on pilot plant using as biofuel: diesel and butanol.

Key words: *environment, pollution, cogeneration plant, CO2 reduction, concentration, butanol*.

INTRODUCTION

The present paper analyzes the possibility of using alternative fuels in a cogeneration plant developed at the University Politehnica Timisoara, outlining in a comparison study, the use as primary energy source fossil fuel and bio-fuel, the advantages from the energetic and environmental point of view.

Reduction of CO2 emissions translates into reduction of the fuel consumption. A solution to reduce fuel consumption, when electric energy and heat is produced in cogeneration, is by using internal combustion engines integrated into the system. The most common reciprocating internal combustion engines used in cogeneration systems are diesel engines. (Russ et.al, 2008) In comparison with other internal combustion engines the diesel can be driven with pure bio-fuels and also mixtures of bio-fuels and fossil. (Ionel et.al, 2009) Experiments were conducted on the pilot combined heat and power plant (CHP) at the University Politehnica from Timisoara, where the primary fuel was replaced by a concentration by volume of 10 % butanol and the rest diesel. Butanol (C4H10O) is a alcohol that has a high calorific value compared with other alcohols. It has the inferior calorific power of 33.1 Mj/kg. Butanol can be produced chemically and trough fermentation using bacteria from the Clostridium family. When in produced from biomass, it is called bio-butanol.

The primary mover of the CHP it's a single cylinder (406 cc), air cooled, direct injection diesel engine. The heat recovery system is made from a heat exchanger mounted in a closed divergent –convergent nozzle, connected to the exhaust gas delivery pipe of the engine.

EXPERIMENTAL

The paper introduces to a technology that is not novel but should by more applied in order to demonstrate the advantages and disadvantages, from different points of view (environmental, energetically) of using blended fuels (fossil diesel with butanol, in different percentage by volume parts) and at different loads. The pilot plant is working in cogeneration (figure 1), thus assuring the optimum energy flow.

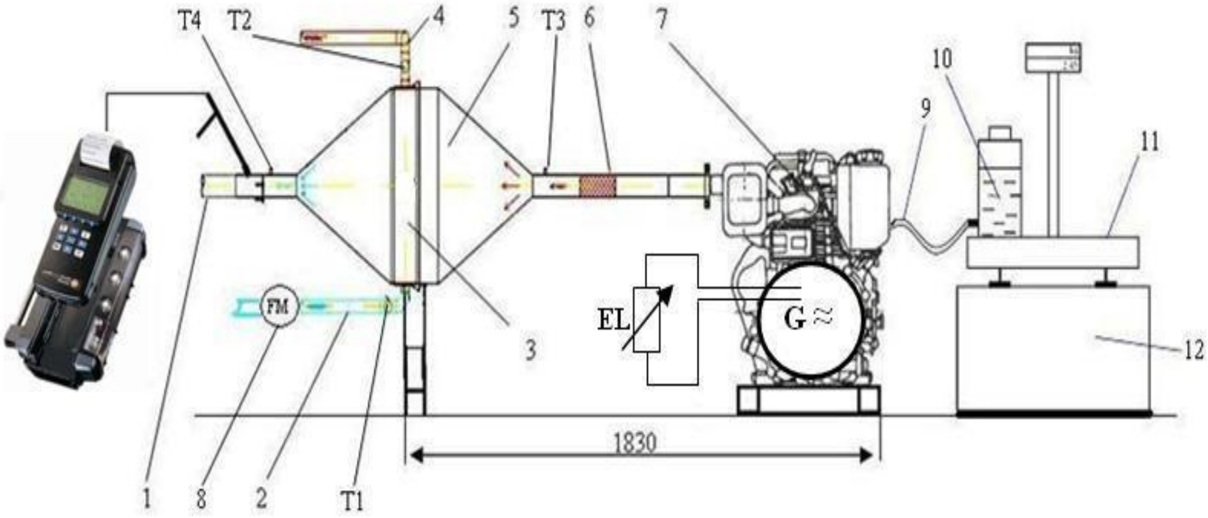

Figure 1. Pilot cogeneration plant with diesel engine
1- Exhaust gas outlet, 2- Water inlet (cold), 3- Heat exchanger, 4- Water outlet (warm), 5-Nozzle, 6- Engine vibration absorber, 7- Diesel engine, 8- Water flow meter, 9- Fuel pipe, 10- Additional fuel tank, 11- Electronic weightier, 12- Weightier frame, G- electric generator, 13- Electric load, T1,T2- Thermocouples for water, T3,T4- Thermocouples for exhaust gases.

One will focus on the CO2 reduction potential, as well on the efficiency variation, by blending into diesel the butanol, by volume (10 %).

Cogeneration is a well-known technology to perform efficiency improvement, in addition to pollutant diminution, but not always in the exhaust gases. At the University Politehnica Timisoara, tests were performed on a cogeneration plant using a small four stroke air cooled diesel engine, with one cylinder, with the capacity of 406 cc, and 5.5 kW power. The first step of the study was measuring the parameters of the cogeneration plant, using pure diesel, establishing in this way the reference parameters. Later on is showed the differences from the energetic and environmental point of view, when the fossil fuel is replaced with blends of butanol and diesel, by volume parts.

RESULTS AND DISCUSSIONS

In figure 2, is presented the calculation for the total efficiency of the cogeneration plant, when it was used as primary fuel diesel at full percentage. In order to observe better the advantages of the cogeneration system, the pilot plant was loaded in tree steps with the help of an electric rheostat as is presented in figure 1.

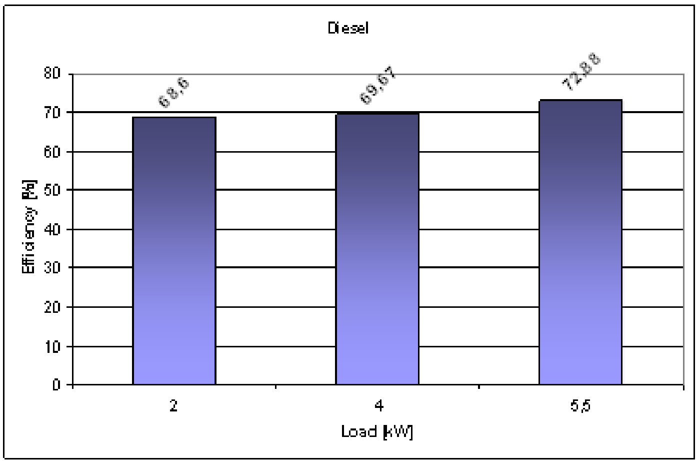

Figure 2. Co-generation plant efficiency, for diesel used as primary fuel

The electric load dictates the total efficiency of the plant. A primary conclusion from this figure is drowned, that the highest efficiency of the cogeneration system is determined at the maximum load.

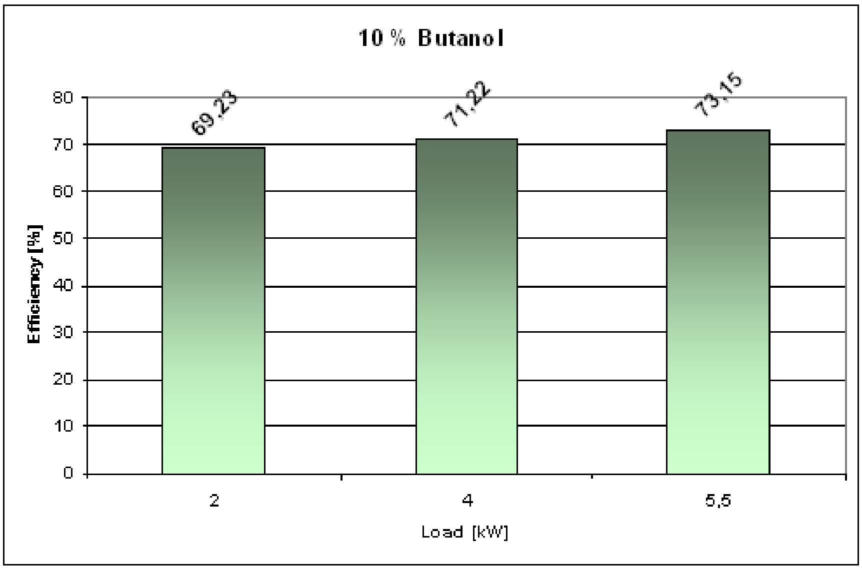

Figure 3. Co-generation plant efficiency for 10 % butanol concentration by volume parts in diesel

The increase in the efficiency is considered to be a result due to the improvement of heat transfer from the exhaust gases to water, through the heat exchanger, but also through a slight change of fuel consumption, obtaining in this way a better electrical efficiency. (Russ at.al, 2008)

Other experiments revealed that adding butanol in diesel, by volume parts, largely does not modify significantly the level of emission.

The values have been obtained after adjusting to the reference oxygen of 5 % (Popescu et.al, 2007), the recorded values with the TESTO 350 X/ML gas analyzer. (Popescu et.al, 2009) It can be noticed that along with the increase of the power of engine, the concentration value of CO2 emission rises (figure 4).

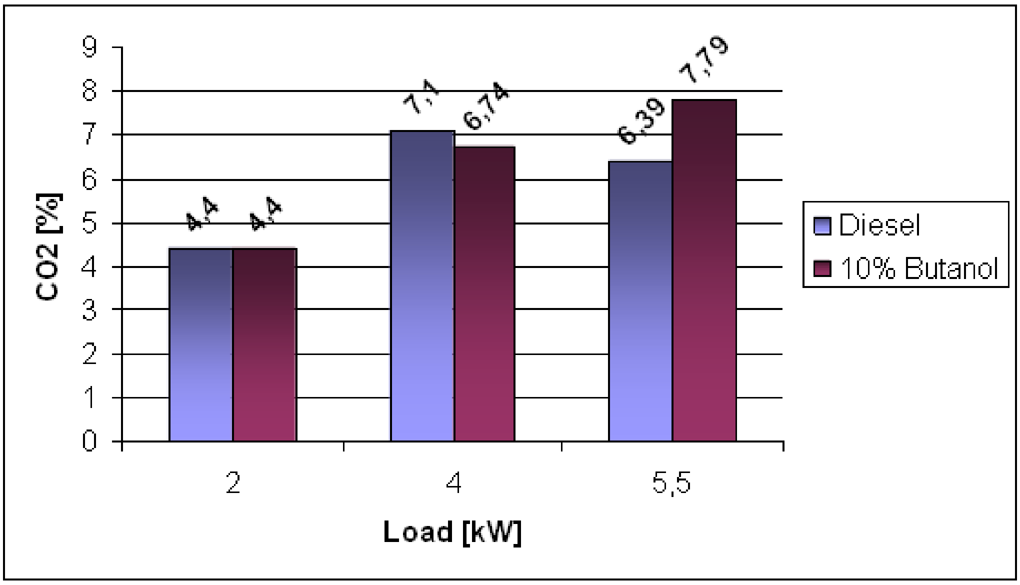

Figure 4. Load versus CO_2 concentration

Next, based on the same principal, the concentration of CO_2 was determined by replacing the diesel fuel with the mixture (10 % butanol by volume parts). Figure 4 presents the CO_2 concentration variation with the engine loading and the butanol concentration. With the same type of fuel and a constant loading, increasing the butanol concentration in diesel determines enhance of the emission, in dependence to the load applied (Figure 4). Because of the physical and chemical properties of butanol, that is due to the increased time of the vaporization process. The result may be by the residence time of the oxygen molecule that increases, in combustion areas with higher temperatures.

For the 5,5 kW loading step it can be observed an increase of over 2 units for this „emission”. This increase of the carbon dioxide is due to the fact that the engine is not technically adapted for this type of fuel. Regarding the carbon dioxide, the maximum butanol concentration reached, leads to the 5,5kW power.

For the lower loading steps (especially at 4 kW load) it can be observed a decrease of the emission when the bio fuel is used as primary fuel but, it is not profitable from the fuel cost point of view for a cogeneration plant to operate at a loading below the maximum capacity.

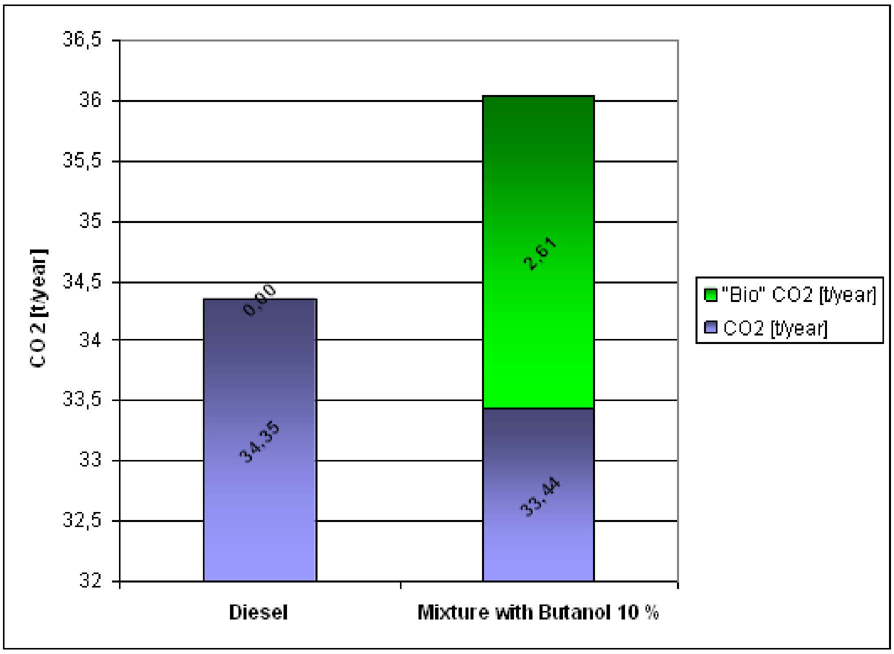

Figure 5. Nov.2013 – Feb.2014 comparative results for BTX concentrations

The data analysis from figure 5 shows that by generalizing the researched cogeneration solution can be obtained significant reductions of CO2 emitted from fossil sources. The interpretation is based on calculated values of the CO2 emission, for the maximum fuel flow, and takes into consideration the material balance of carbon (introduced with assimilated diesel as C18H32 and butanol with the formula C4H100). It is assumed that the combustion is perfect (no CO, CnHm in the flue gases).

The CO2 emission reduction, of fossil origin, is explained by the increase of „bio” fuel percentage in the fuel mixture. Basically, the annual reduction is 2,61 t of CO2 (the case of maximum load and using 10 % butanol by volume percentage in the fuel mixture). This value is determined by the „bio” presence, so it is stated as a neutral emission and is considered to have no worsening influences on the greenhouse effect.

CONCLUSIONS

A cogeneration plant system has the highest efficiency at maximum load. Thus it is necessary to focus on this loading step regarding the CO2 concentration. When the concentration of butanol in diesel was raised at 10 % by volume parts, for this specific load, it was measured a higher concentration of CO2 in the exhaust gases. Others also experienced this when the percentage of butanol by volume part in diesel was raised (al. Hasan et.al., 2008). The present study wishes to highlight the advantages or disadvantages of using mixtures of butanol and diesel in the primary fuel. The most profitable mixture in this case is the concentration of 10 % by volume parts butanol in diesel, for all loadings.

In conclusion the paper demonstrates by theoretical and experimental research advantages of cogeneration, using blends of butanol with fossil diesel fuel in the generator powered by a diesel engine. Conclusions regarding the best practice related to cogeneration with diesel engines, mostly based on experiments, are presented. It is demonstrated the critical advantages and limits, when biofuels used in blends with diesel are use as a primary fuels on small power generators operating in cogeneration and based on diesel engines.

As presented, one demonstrated that if one uses 10 % butanol by volume parts in diesel a rising of the efficiency and a preservation of the fuel consumption is experienced. The result showed that when using 10 % butanol by volume parts in diesel it is a gain from the economic and environmental point of view when is used to produce simultaneously power and heat, in cogeneration (Praetorius et. al, 2006).

REFERENCES

Lontis Nicolae, (2008), Cercetări teoretice şi experimentale privind cogeneratea cu motor m.a.i., funcționând cu biocombustibil – PhD thesis, Ed. Politehnica, Timisoara, ISBN – 978-973-625-766-71;

Lontis N, Ioana I, Popescu F, Constantin C., (2009), Results concerning the co-combustion of fossil and bio-fuels in a cogeneration plant, using internal combustion diesel engines, SIXTH MEDITERRANEAN COMBUSTION SYMPOSIUM Porticcio – Ajaccio, Corsica, France, June 7-11

N. Alasfour (2006), Butanol-a single cylinder engine study:eingine performance. International Journalo of Energy, vol 21, pp 21-30;

Russ W., Meyer-Pittroff R., Dobjanshi A., Lachenmaier-Kolch, (2008), Usability of food industry waste oils as fuel for diesel engines . Journal of environmental management ISSN 0301-4797 CODEN JEVMAW, vol. 86, no3, pp. 427-434

Popescu F., Ionel I., Meyer-Pittroff R., (2007), Alternative Fuel for Internal Combustion Engines. Biodiesel, Transesterification of Animal Fats with High FFA .Proceedings of the 15th European Biomass European Conference - From Research to Market Deployment,Berlin, Germany, 7 - 11 May, ISBN 978-88-89407-59-X , ISBN 3-936338-21-3, pp 2031 – 2034;

Ionel I., Popescu F., Lontis N., Tordai G.T., Russ W., (2009), Co-combustion of fossil fuel with biofuel in small cogeneration systems, between necessity and achievements, 11th WSEAS International Conference on Sustainablility in Science Engineering (SSE 09) Timisoara, ROMANIA, MAY 27-29,

Al-Hasan M. I., Al-Momany M., (2008), The Effect of Iso-butanol-Diesel Blends on Engine Performance., Transport, vol 24, pp 306-310.

Popescu F., Ionel I., Ungureanu C., (2009), Air quality monitoring in the city of Timisoara, Journal of Environmental Protection and Ecology, paper reference number 1151/26.07.06, book 1, vol. 10, pag. 1-13, ISSN 1311-5065.

Praetorius B., Schneider L., (2006), Micro cogeneration: towards a decentralized and sustainable german energy system? 29th IAEE International Conference, Potsdam, 7-10 June, 579.

http://www.raeco.com/products/emissions/man_testo350_132.pdf.

IV International Conference
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PERVAPORATION OF BIOETHANOL PRODUCED FROM APPLE POMACE

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ABSTRACT

The limited availability of fossil fuels has encouraged the development of various fermentation processes for large scale bioethanol production using recombinant microbial sources. In this study, bioethanol production was performed in 5 L stirred tank reactor using apple pomace as a substrate for bioethanol production by Escherichia coli KO11. Cell-free fermentation broth was transferred to pervaporation unit. Produced bioethanol was concentrated at two different temperatures and the success of pervaporation was compared in terms of membrane selectivity and ethanol flux. In this study produced ethanol concentration was 16.72 g/L at 48 h. Ethanol concentration was decreased to 0.03 and 0.05 g/L at the end of the pervaporation period at 65°C and 70 °C, respectively. The fluxes of the fermentation broth and ethanol were 3499.27 g/m2/h and 1.05 g/m2/h at 70 °C, respectively. From an economic perspective this work suggests that waste apple pomace offers a promising potential as a substrate for bioethanol production. From an industrial perspective, pervaporation can be considered as an alternative method for the purification of bioethanol with high selectivity and also it reduces the downstream processing steps with high product yields and low process cost.

Key words: *Apple pomace, bioethanol production, Escherichia coli KO11, membrane selectivity, pervaporation.*

INTRODUCTION

Bioconversion of biomass into ethanol has been studied by researchers as it is safe, sustainable, and CO_2-emission-free. In order to promote bioethanol production and utilization, reducing the production cost using agroindustrial wastes is required. The largest source of the economic development in Turkey is agriculture, and apple is widely cultivated as a commercial crop for juice industry. About 70 million tons of apples were grown worldwide in 2010, and Turkey is the third producer with an amount of 2600 million tons, followed by China and the USA (Turkish Statistical Institute, 2010). Cemeroglu et al. (2001) reported that the apple pomace, as an agro-industrial waste of juice industry, can directly used as a substrate for biological conversion without any pretreatment due to the availability of the sugars. It was reported that apple pomace was composed of glucose, fructose and sucrose up to 99% in dry bases (Cemeroglu et al., 2001). Several studies also reported the utilization of the apple pomace without pretreatment process for the bioconversion of value-added bioproducts (Hang et al., 1982; Ngadi and Correia, 1992). In our previous study we also showed that quince pomace which is also an agro-industrial waste, could be used for bioethanol production by *E. coli* KO11 (Deniz et al., 2014). This strain has been employed as a promising biocatalyst for the bioconversion of fructose, sucrose and glucose into ethanol. The strain was proved to show high product yield of 0.4 g/L under unaerated conditions (Ingram et al., 1998). A successful study must also include the separation of produced ethanol from fermentation broth using less purification units with more efficiency. According to Gaykawad et al. (2013), one of the ways to improve ethanol productivity and reduce the overall production costs is to modify the configuration of the process. The conventional recovery of ethanol is handled by distillation which is a challenge because of the high costs, less efficiency and energy expenditure required (Bello et al., 2014). Thus, membrane based separation technologies such as pervaporation have been used. Pervaporation normally fulfills the criteria for sustainability and energy efficiency as it is environmentally friendly. In pervaporation, a liquid mixture is fed through a membrane where the components permeate selectively through and vaporize on the other side of it at low pressures. In brief, there is a selective removal of organic compounds from dilute aqueous solutions. There are several studies regarding ethanol pervaporation and they relate mainly to the use of different membranes (Gaykawad, et al. 2013). Studies on pervaporation of produced bioethanol have not used apple pomce for ethanol production. Hence the aim of this research is to evaluate if apple pomace can be used as a substrate for ethanol production and to investigate the effects of operating variables for the recovery of ethanol by using pervaporation using hydrophilic membrane. To our knowledge, this is also the first report on the successful utilization of apple pomace for bioethanol production on the lab scale fermentation by *E. coli* KO11.

METHODS

Growth Conditions

Recombinant *E.coli* KO11 (pLOI 1910) strain was supplied by Professor L.O. Ingram from University of Florida. Stock cultures were stored in 20% glycerol at –86 °C. For inoculation, cells from fresh 3 colonies were transferred into 500 ml flasks containing 150 ml LB medium supplemented with 60 g/L glucose. Seed cultures were incubated under static conditions for 16 h at 30 °C.

Substrate

Apple pomace was used as substrate for ethanol production instead of glucose. Apples were pressed and dried to constant weight at 70°C in pasteur oven to remove bound-water (Memmert, Germany). Dried pomace was grinded to 0.1 mm in size.

Reactor Conditions

Fermentations were carried out in 5 L (Sartorius A plus stat.) bioreactor with working volume of 3 L. LB (without glucose) containing apple pomace was used as substrate. Apple pomace and the basal media were autoclaved at 121°C for 30 min. The fermentation was carried out at pH 6 and 35 °C. All experiments were carried out in duplicate.

Pervaporation

The cells were separated via a centrifuge (5000 rpm, 5 min) and the supernatant was filtered through a membrane with a pore diameter of 0.22 μm. The filtrate was used for pervaporation.

The pervaporation unit (Sulzer Co.) used consisted of a hydrophilic polyacrylonitrile membrane (PERVAP^{TM} 1201, Sulze Co.) with a crosslinked structure. The pore diameter of membrane is 2 μm with a thickness of 0.2 mm and an effective surface area of 172 cm^2. The cell-free fermentation supernatant was supplied at a flow rate of 100 L/h with the aid of a gear pump from a reservoir positioned upstream from the membrane. A vacuum pump coupled to the permeate side of the assembly provided the pressure drop (7 mbar) for vaporization of ethanol. The permeate vapor was directed to a condensation bath refrigerated with liquid nitrogen. The liquid retentate was recirculated to the feed tank. Two different condensation temperatures of 65 and 70°C were studied for the optimization of pervaporation. The tests were carried out in duplicate, and the results presented here were consistent with the average of the same. Feed and permeate samples (upon reaching the steady-state condition), were collected for 30 or 60 min during each test to quantify the concentrations of ethanol with a gas chromatograph (GC, 6890N Agilent Technologies Network GC System).

PARAMETERS FROM THE PROCESS EVALUATION

The performance of the process of pervaporation has been expressed in terms of separation factor of the membrane (selectivity, α), the total permeate flux (J_{tot}), the ethanol permeate flux (J_{etoh}) and enrichment factor (β) according to (1), (2), (3) and (4), respectively (Bello et al., 2014).

$$\alpha_i = \frac{y_i/y_j}{x_i/x_j} \tag{1}$$

$$J_{tot} = \frac{W}{At} \tag{2}$$

$$J_{EtOH,p} = \frac{W_i}{At} \tag{3}$$

$$\beta_i = \frac{y_i}{x_i} \tag{4}$$

where y_i and y_j are the weight fractions of ethanol and water in the permeate, respectively, and x_i and x_j are the weight fractions of ethanol and water in the feed, W and W_i is the mass (g) of the permeate and ethanol, respectively, A is the effective area (m^2) of the membrane, and t is the time interval (h) for pervaporation.

Reynolds number was calculated according to Schnabel et al. (1998). It was considered an aqueous solution, and because of this, viscosity and density used was the values described by the authors with temperature of 298 K (25 °C).

Analytical Measurements

Fermentation broth viscosity was measured twice at the beginning and at the end of the fermentation period by a rotational viscometer (Brookfield model DV-E, USA) with LVtype spring torque using LV1-61 spindle and determined by Poiseuille Equation (5). Average viscosity of 1.36×10^{-6} m^2/s was used in the equations.

$$\frac{dV_L}{dt} = \frac{\pi D_C}{8\ \eta} \frac{dP}{L} \tag{5}$$

The density of the fermentation broth was measured by 25 mL pycnometer (Isolab, Germany) at the beginning and at the end of the fermentation and an average density value was used in the study (1043 kg/m).

Total reducing sugar content of apple pomace was determined using dinitrosalicylic acid (DNS) method where the absorbance was measured at 540 nm (Miller, 1959).

Ethanol concentrations were measured using a Gas Chromatograph (6890N Agilent Technologies Network GC System) equipped with a flame ionization detector and a DB-FFAP 30 m × 0.32 mm × 0.25 mm capillary column (J&W Scientific) (Azbar et al., 2009).

Statistical Analyses

Statistical analyses of the data were performed by one-way analysis of variance (ANOVA). A probability value of $p<0.05$ was considered to denote a statistically significant difference of two batches. Data are presented as mean values ± SEM (standard error of the mean).

FINDINGS AND DISCUSSION

In this study 16.72 g/L bioethanol was produced using apple pomace corresponding to a remaining sugar content of 4.2 g/L (see also Figure 1). This result shows that apple pomace has the potential to be used in bioethanol production by E. coli KO11. In our previous study we proved the utilization of another agroindustrial waste from fruit juice industry, quince pomace, for bioethanol production (Deniz et al., 2014).

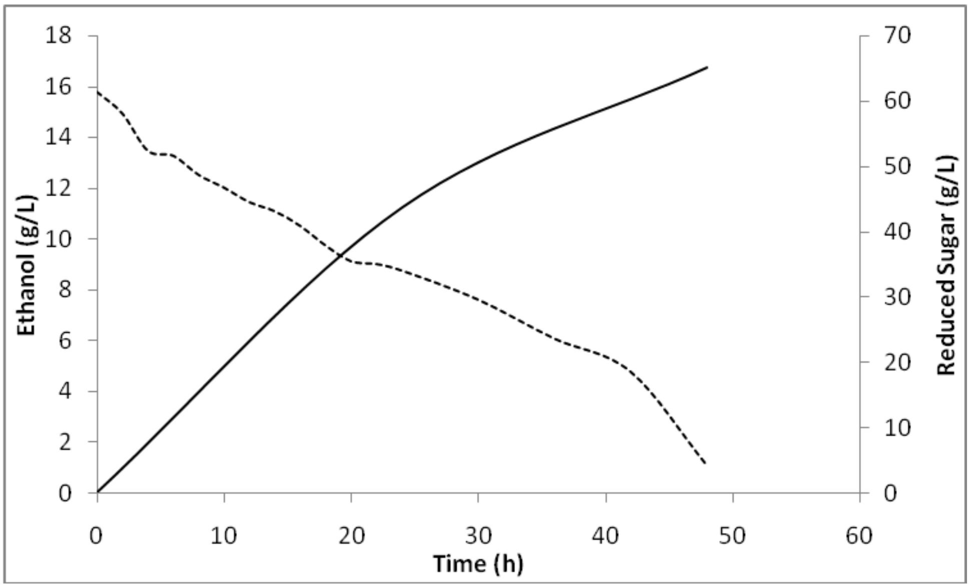

Figure 1. Produced bioethanol (-) and remaining sugar (---) concentrations (g/L) at 400 rpm in bioreactor

In this study, the cell-free supernatant was further used for pervaporation in order to separate ethanol efficiently. The final goal of the study was to investigate the appropriate separation conditions for ethanol. The theory of the pervaporation process used in the study was based on the permeate flow of hydrophilic compounds through a membrane via driving force of pressure difference between two sides of membrane, whereas ethanol was concentrated on retentate phase.

The calculated Re number was 4885.19, indicated that the flow was turbulent during the process. Aroujalian and Raisi, (2009) reported that pervaporation efficiency was optimum in turbulent regime where the hydrophobic membrane selectivity was 2.25.

In this study as the membrane was hydrophilic, the ethanol was concentrated in retentate phase which implied that lower membrane selectivity (α) showed a better separation. As seen in Table 1, after 10 h the α value was 0.005 and 0.011, at 65°C and 70°C, respectively. Moreover, the ethanol content in permeate decreased to 0.03 g at 70°C, whereas the ethanol concentration in permeate was 0.05 g at 65°C in 10 h. Nonetheless the ethanol weight fraction in retentate was concentrated from 1.6% to 4.11% at 7 mbar. Chovau et al. (2011) showed that the ethanol was concentrated from 5% to 30.7% at 3 mbar for 12 h which indicated the importance of pressure drop that was used. As seen in Table 1 and Figure 2, the α value was in trend of decreasing for both temperatures, however the decline was higher at 70°C that at 65°C (p<0,05).

Table 1: The summary of the pervaporation results for 65°C and 70°C in 10 h

	Permeate				Retentate		
	M_{tot} (g)	J_{tot} ($g/m^2/h$)	J_{EtOH} ($g/m^2/h$)	C_{EtOH} (% g/g)	α	β	C_{EtOH} (% g/g)
65°C	353,24±0,1	2744,67	1,31	0,05±0,1	0,011	0,011	4,11
70°C	425,91±0,2	3499,27	1,05	0,03±0,1	0,005	0,006	5,30

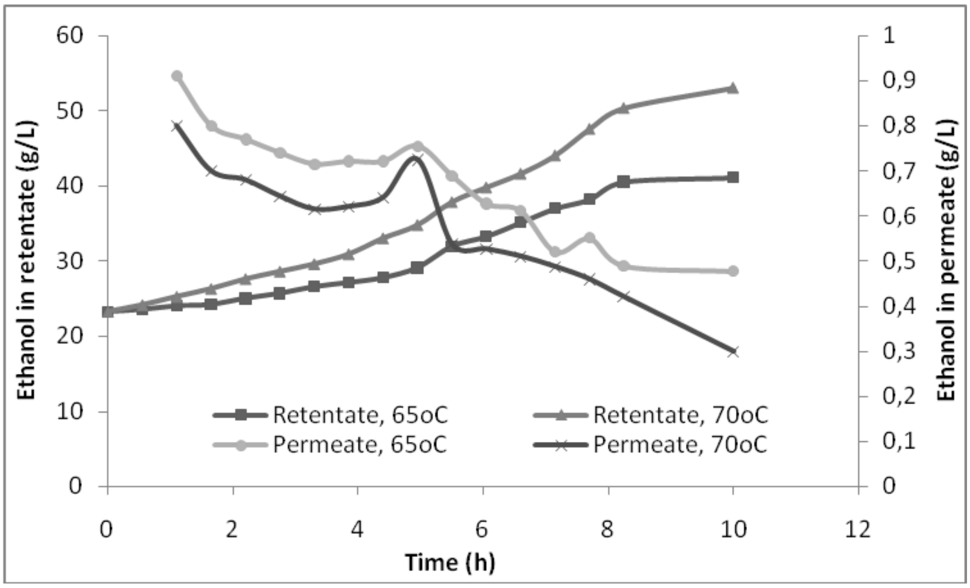

Figure 2. The ethanol concentration in retentate and permeate phases at 65°C and 70°C

The flux value has an important role on the kinetic model for ethanol separation (Staniszewski et al., 2007; Wang et al., 2010). In this study, the total fluxes declined for both temperature values and reached steady state in 7 h (see also Figure 3). The total flux reached in 10 h was 27.5% higher at 70°C than 65°C. Moreover the ethanol flux decreased at both 70°C and 65°C after the first 5 h and reached steady state in 7 h. Chen et al. (2001) reported that at higher temperatures than 50 °C, the total flux of hydrophilic membrane increased and β value decreased due to the membrane swelling (Table 1). The decrease in β value may be resulted from the increased movement of molecules owing to the rise in temperature. Wang et al. (2010) reported that the best separation was carried out at 70°C and Thongsukmak and Sirkar (2009) emphasized that at higher temperatures near 70°C, flux values increased. In this paper, as the ethanol concentration in retentate phase increased, α value decreased (see also Figure 4). This study is in good agreement with Kaseno et al. (1998).

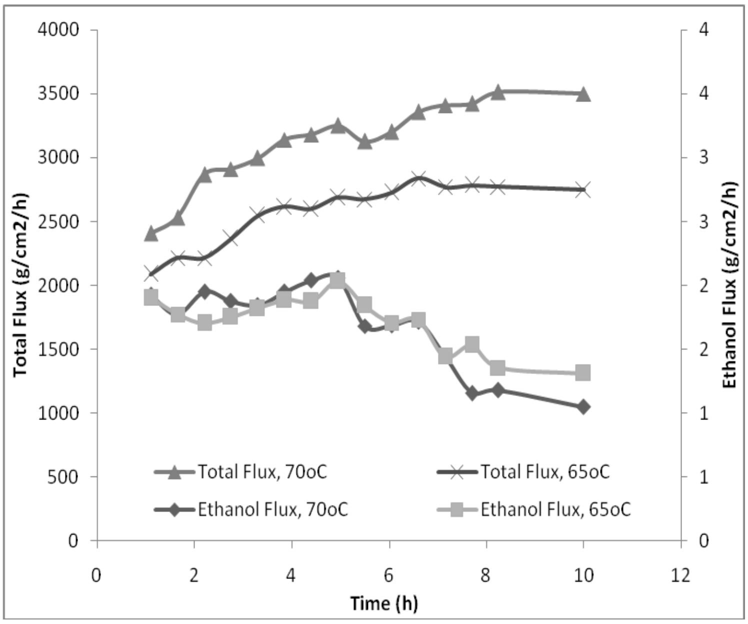

Figure 3. Total and ethanol flux values at different temperatures

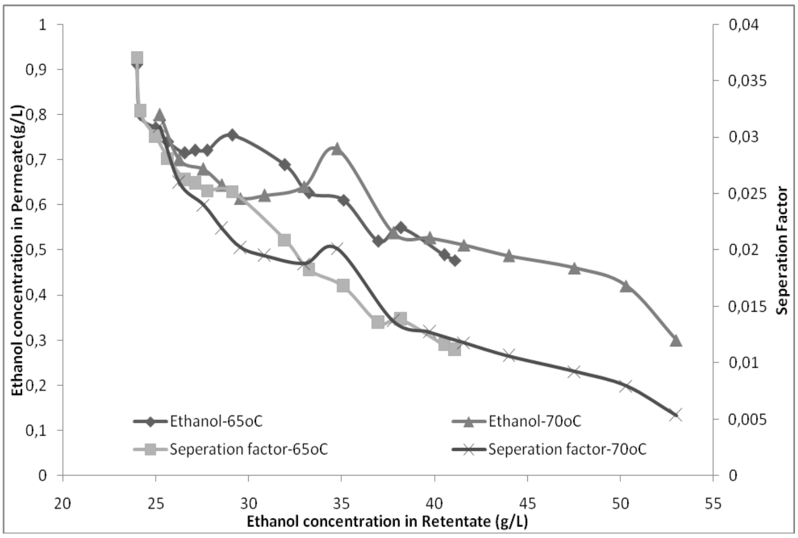

Figure 4. Ethanol concentration in retentate and permeate phase versus seperation factor

CONCLUSIONS

In this study, the bioethanol production and pervaporation of produced ethanol were carried out in lab scale bioreactors. Results showed that, 16.72 g/L ethanol was produced from apple pomace in 48 h. Ethanol concentration was decreased to 0.03 and 0.05 g/L at the end of the pervaporation period at 65°C and 70 °C, respectively. The fluxes of the fermentation broth and ethanol were 3499.27 g/m^2/h and 1.05 g/m2/h at 70 °C, respectively. Thus, 70 °C was chosen as an appropriate temperature value for the separation via pervaporation. From an economic perspective this work suggests that waste apple pomace offers a promising potential as a substrate for bioethanol production. From an industrial perspective, pervaporation can be considered as an alternative method for the purification of bioethanol with high selectivity and also it reduces the downstream processing steps with high product yields and low process cost.

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REFERENCES

Azbar, N., Tutuk, F., & Keskin, T. (2009). Effect of organic loading rate on the performance of an up-flow anaerobic sludge blanket reactor treating olive mill effluent, *Biotechnology and Bioprocess Engineering*, 14, 99-104.

Aroujalian, A., & Raisi, A. (2009). Pervaporation as a means of recovering ethanol from lignocellulosic bioconversions, *Desalination*, 247, 509–517.

Bello, R. H., Linzmeyer, P., Franco, C. M. B., Souza, O., Sellin, N., Medeiros, S. H. W., & Marangoni, C. (2014). Pervaporation of ethanol produced from banana waste, *Waste Management*, 34, 1501–1509.

Cemeroglu, B., Karadeniz, F., & Özkan, M. (2001). *Fruit-Vegetable Process Technologies-II* (Turkish). Turkey, Food Technologies Publications.

Chen, S., H., Liou, R., M., Hsu, C., S., Chang, D., J., Yu, K., C., Chang, C., Y., 2001, Pervaporation separation water/ethanol mixture through lithiated polysulfone membrane, *Journal of Membrane Science*, 193: 59–67pp.

Chovau, S., Gaykawad, S., Straathof, A., J., J., & Bruggen, B. (2011). Influence of fermentation by-products on the purification of ethanol from water using pervaporation, *Bioresource Technology*, 102 (2), 1669-1674.

Deniz, I., Imamoglu, E., & Vardar Sukan, F. (2014). Aeration-enhanced bioethanol production. *Biochemical Engineering Journal*, (In press: DOI: 10.1016/j.bej.2014.05.011).

Gaykawad, S. S., van der Wielen, L. A. M., & Straathof, A. J. J. (2013). Effects of yeast originating polymeric compounds on ethanol pervaporation. *Bioresource Technology*, 116, 9–14.

Hang, Y., Lee, C., & Woodams, E. (1982). A solid state fermentation system for production of ethanol from apple pomace. *Journal of Food Science*, 47, 1851-1852.

Ingram, P., Gomez, X., Lai, M., Moniruzzaman, B., Wood, L., & Yomano, S. (1998). Metabolic engineering of bacteria for ethanol production. *Biotechnology and Bioengineering*, 58, 204–214.

Kaseno, Miyazawa, I., Kokugan, T. (1999). Effect of product removal by a pervaporation on ethanol fermentation, *Journal of Fermentation and Bioengineering*, 86 (5), 488–493.

Miller, G. L. (1959). Use of dinitrosalicylic acid reagent for determination of reducing sugar, *Analitic Chemistry*, 31, 426-428.

Ngadi, M., & Correia, L. (1992). Kinetics of solid-state ethanol fermentation from apple pomace, *Journal of Food Engineering*, 17, 97-116.

Schnabel, S., Moulin, P., Nguyen, Q. T., Roizard, D., & Aptel, P. (1998). Removal of volatile organic components (VOCs) from water by pervaporation: separation improvement by Dean vortices, *Journal of Membrane Science*, 142, 129–141.

Staniszewski, M., Kujawski, W., & Lewandowska, M. (2007). Ethanol production from whey in bioreactor with co-immobilized enzyme and yeast cells followed by pervaporative recovery of product – Kinetic model predictions, *Journal of Food Engineering,* 82 (4), 618–625.

Thongsukmak, A., & Sirkar, K., K. (2009). Extractive pervaporation to separate ethanol from its dilute aqueous solutions characteristic of ethanol-producing fermentation processes, *Journal of Membrane Science*, 329, 119–129.

Turkish Statistical Institute (2010). For tea Rize Trade Market and General Directorate of Tea Establisments, for other products, Ministry of Food, Agriculture and Livestock, Production of fruits, beverage and spice crops (For selected products), internet source: http://www.tuik.gov.tr/UstMenu.do?metod=temelist

Wang, J., Ma, Y., & Tsuru, T. (2010). Prediction of pervaporation performance of aqueous ethanol solutions by nanopermporometry characterization, *Separation and Purification Technology*, 74, 310–317.

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CORPORATE SOCIAL RESPONSIBILITY AND SUSTAINABLE DEVELOPMENT

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ABSTRACT

The main objective of modern business is achievement of business excellence and world-class of products and services. Companies which actively and continuously apply modern management methods and techniques have significantly better chance to strengthen their competitive capability on global market and to assume stable market position with perspective for further market development. Modern business philosophy implies that organization has to be responsible for its actions and steps and towards all stakeholders in environment. Attaining of business excellence goals of an organization presupposes built corporate social responsibility. One of the most important segment of implementation and improvement of corporate social responsibility is environmental management.

Key words: *social responsibility, competitiveness, quality, business excellence, sustainable development.*

INTRODUCTION

In modern business there is an urgent need for prestructions of business functions. From traditional understanding directed to linear way of thinking, where all business functions were equally important companies have to turn to proactive thinking which implies understanding and creating of changes, as well as giving importance to those business functions which enable a company to create, maintain and improve competitive position on the global market. Functions which are strategically important for doing business inside a company are:

- research and development (which is a basic switch for development of a business company),
- quality (which enables the constant improvement of business processes) and
- marketing (which enables forming of a market picture and directs the business activity of a company due to spotted need and expressed customer`s demands, connecting all other functions in the company in order to gain firm market position)

Business changes in its base under the circumstances of global economy. Today, business organisation became aware of the fact that the way they do business has influence on the society as well. This acknowledgement has greater consequences. Implementation of principles of corporative ethics has a global character. The public interest is a primary interest of organisation, which has to incorporate into the business politics of the organisation and business politics of an organisation has to conduct completely in doing business.

Globalization, economic dynamism and social progress, sustainability and competitiveness go hand-in-hand. Competitiveness should be underpinned by a broad vision for the economy and society. Therefore, “Sustainable competitiveness” in the context of globalisation is becoming the subject of the research focusing on how sustainable development and competitiveness interact (Balkyte and Tvaronavičiene, 2010).

CORPORATE SOCIAL RESPONSIBILITY AND BUSINESS EXCELLENCE

Achieving of business excellence is not the job of only one business function, or one organizational unit of a company, it is the result of synchronous action of all functions within the company, according to precisely defined business objectives. In modern business, emphasis is put on macro-environment instead on specific market. The focus is no longer on the consumer only, but also on the entire society. New business conditions require adjustment of business entities and building of organizational structure based on new postulates. This is particularly important for companies from countries in transition – ultimate goal of building of new organization is for it to become extremely flexible and innovative, i.e. to be able to meet the growing customer demands in shorter timeframe and to form competitive advantage which must encompass the emotional component as well. In order to achieve business excellence, a company needs to permanently improve its business. Business improvement obtains the feature of continuous business quality improvement. In that sense, the main aspects of business quality are the following:

- marketing aspect,
- business aspect and
- social aspect.

Market aspect of quality improvement refers to satisfying customer’s needs, user-friendliness, and market positioning and achieving competitive advantage. Business aspect of business quality improvement refers to improvement of quality of internal organization economy – improvement of efficiency, cost reduction, work and knowledge productivity increase, profit increase. Social aspect of business quality improvement of an organization implies the improvement of social welfare in respect of life quality improvement: human health care, safety and health care of employees, protection and safety of consumers, protection and improvement of environment, preservation of natural resources, safety of entire society, business in line with regulations. Social aspect of quality management compiles business and market quality aspect, enabling the realization of synergy effect in relation to the competitive position of the company. Successful company management, which should result in achieving, maintaining and improving of competitive market position, presupposes the implementation of principle of social responsibility into the company organizational structure. Nowadays, business organizations became aware of the fact that the method in which they perform business influences the society as well. This finding has far-reaching consequences. According to Tisen at all (2006), if a company is aware of its possible influence on society, providing business, jobs, guaranteeing stable economy, then its focus must be shifted to reflect this radical view. The principles “*exist to compete”* shall have to cede position to the principle *exist to last.*

Total Quality Management is business philosophy which emerged as logical and historical reaction of entrepreneurs to demands set by modern society. Achievement of goals of business excellence of an organization presupposes built Corporate Social Responsibility (CSR). It represents determination for improvement of community welfare through discretion business practices and contributions at the expense of company resources (Kotler and Lee 2007). Key word of this definition is discretion. It is a voluntary determination of an organization and its decision to choose and apply business practices which give contributions. Some of the reasons for application and development of corporate social responsibility are the following: increase in market share, strengthening of trade mark position, strengthening of corporate image, improvement of capability for attraction and motivation of employees, business cost reduction, increased attractiveness for investors.

Once it was enough for a company to meet basic economic goals – profit, as a basis for attaining of growth and development goals. Since 1970s, business goal which implies meeting consumer demands gains significance – informed consumers become the first and the last link in the economic chain. The company must first identify consumers’ demands, and then define ways for meeting them. The 1990s have brought along the necessity to meet general social interests – therefore, in addition to consumers and asset owners, a company in modern business has to meet wider range of interests reigning in its social environment.

According to some views (Kotler and Lee 2007), six social initiatives acting in the field of corporate social responsibility can be identified today: promotion of social objectives, marketing related to social objectives, corporate social marketing, corporate philanthropy, voluntary work for community, socially responsible business practice. Promotion of social objectives implies that companies provide funds, donations in kind, or other resources in order to raise awareness of a particular social objective, or to collect funds for this social objective. Marketing related to social objectives implies that a company obliges to donate certain percentage of revenue generated from sales of products or services for a particular social objective. Corporate social marketing implies that company assists in development and/or conducting of campaign for change of behaviour in order to improve health, safety, environment or community prosperity. Corporate philanthropy is a practice where a company directly gives donations for a charitable or social action, most often as a grant funds in cash or in kind. Voluntary work for community implies that a company supports and encourages its employees, as well as employees of partner organizations to hold through voluntary work the local social organizations and actions. Socially responsible business practice implies the situation when a company at its sole discretion adopts and implements business practice which supports a social objective, which is to improve the life in community and to protect environment.

The concept of Corporate Social Responsibility nowadays is a standard and is a constituent part of integrated management systems. Review of standardized management systems is shown in table 1.

Table 1: Standardized management systems

No	Name	Mark	Interested party
1.	**Q**uality **M**anagement **S**ystem – QMS	ISO 9001:2000	User
2.	**E**nvironmental **M**anagement **S**ystem – EMS	ISO 14001:1996	Community
3.	**O**ccupational **H**ealth and **S**afety **M**anagement **S**ystem - OH&SMS	OHSAS 18001:1999	Employee
4.	**C**orporate **S**ocial **R**esponsibility **M**anagement **S**ystem – CSRMS	SA 8000	Society

Source: *Đorđević and Ćoćkalo D. (2007a), p. 14*

Each of these standards contains one of assumptions of corporate social responsibility concept, and SA 8000 standard is directly connected to development of this principle. Principles of SA 8000 can be applied by all companies disregarding thereof size and structure, but who wish to have socially responsible working place anywhere in the world. Companies can certify their locations, and can select special specific plants for certification. Thanks to application of SA 8000, a company can properly maintain working conditions through supply chain. Social Accountability 8000 (SA 8000) represents new international and inter-industrial standard created in 1997, and revised in 2001. Standard SA 8000 is based on ISO 9000, but its goal is improvement of working conditions in factories worldwide. The difference between these two standards is that SA 8000 includes the characteristics of requirements in supplement of system. Namely, SA 8000 requires the employer to give to employees the salaries which are sufficient for their needs, to provide safe working environment, not to employ children or engage force labour, and does not require from employees to work more than 48 hours a week. SA 8000 is based on nine components, as follows: children labour, forced labour, health and safety, free association and right to collective agreement, discrimination, discipline, working hours, compensation, and management system. Application of SA 8000 standard is important for all market factors: employees, unions, non-governmental organizations, buyers and investors, as well as company itself. Some of the most significant advantages of this standard are as follows: high motivation of employees which results in better working conditions, incentive for humane working conditions may lead to high quality product, raising public awareness that the company supported the protection of employee rights, improves trade mark and company reputation, differentiates the company compared to competition, the company is more attractive for new buyers. The major users of this standard are companies from the fields of textile, footwear, clothes, food, toys, cosmetics and electronic products. Service and agricultural sector are still learning the advantages of their application and especially in the area of retail, fast food, export agencies and high level crop production.

The application of the SA 8000 standard has been in constant expansion since 1998, when its original version was created. According to data from the Social Accountability Accreditation Services - SAAS (2013), this standard is applied in 72 countries of the world, where there is a total of 3,258 certified facilities. It is applied by 65 industries, with a total of 2,020,234 employees. The majority of facilities (65%) are medium-sized (51-250 employees) and small (1-50 employees) enterprises. The largest number of certified facilities is in Italy (1,068), India (733), China (522), Romania (231), with the largest total number of facility employees in India (482.191).

International Standardization Organization published standard ISO 26000 providing guidelines for social responsibility (SR). Standard ISO 26000 is addressed to all types of companies, both in public and private sector, in developed and developing courtiers. ISO 26000 represents the added value of the existing initiative for SR by providing harmonization; adequate global guidelines based on international consensus of main representatives of expert group stakeholders and thus encourage the application of best practices of SR worldwide. This standard is important not only for its relation towards the company products and services and customer satisfaction, but also for socially responsible business operation.

CORPORATE SOCIAL RESPONSIBILITY AND SUSTAINABLE DEVELOPMENT

Although terminologically and conceptually defined earlier, CSR and sustainable development and their interconnections and interactions, became the subject of wider analysis only in the first decade of the 21st century. Increasing number of authors devoted their attention to the impact of CSR on the concept of sustainable development, and internationalization of business in this regard. Particularly interesting are the works by Van Marrewijk (2003), Herrmann (2004), Moon (2007) and Kolk and Van Tulder (2010).

The contradictions of CSR and sustainable development terms (which are often used vaguely and even interchangeably) are based on the assumptions that organizations are not capable of social responsibility as well as that environmental issues and economic growth are not compatible. What is the meaning of these two terms and how are they interconnected are the increasingly raising questions because they are appraisive, internally complex and openly defined concepts which rules or principles of the application cannot be easily codified.

CSR has developed as a concept from basic philanthropy by business leaders to a facet of modern business and management itself. The definition of CSR contains the word “sustainable” indicating the development by delivering economic, social and environmental benefits for all stakeholders. They have all shown an intention to attempt to define CSR as they seek to support, encourage or criticize its practical manifestations. In European business education, ‘sustainable development’ (24%) was the most popular generic label of CSR programmes (Moon, 2007), followed by ‘business ethics’ (22%), ‘ecological/environmental management’, ‘business and society’ and ‘corporate social responsibility’ itself (all 16%). Similarly, ‘sustainable development’ was a popular research area for European scholars in CSR (18%) compared with the most popular areas of ‘business ethics’ (36%), ‘ecological/environmental management’ (21%), ‘business and society’ and corporate social responsibility’ itself (20%). When it comes to the definition of sustainable development, there are a lot of discussions among scientists about it.

Both these terms are highly related to the temporal and societal context within which they are set, and very different in terms of national, social, economic, governance and environmental systems in which they are located because what is seen as business responsibility in one country may be considered as a governmental, societal or individual responsibility in another country. This leads us to the conclusion that considering the fact that these two concepts are highly contested then they should be rejected. But, that is not the case, since CSR and sustainable development address very important issues. They cannot be easily set aside because companies, organizations and business entities have increasing social, environmental and ethical impacts on the livelihoods of people and societies, and development frequently absorbs, changes and undermines the human and environmental resources on which future development depends.

COMPETITIVENESS OF SERBIAN ECONOMY AND SUSTAINABLE DEVELOPMENT

Competitive position of Serbian companies in respect of reputation on global market is extremely bad. According to the list of the World Economic Forum for 2013, Serbia ranked 101st place out of 148 countries that were analyzed. Serbia was on the 95th place on the list in 2011 and in 2012 which means that there is movement in competitiveness, but in a negative sense. Table 2 provides a ranking of the countries of the Western Balkans in 2009-2013. Only Serbia and Slovenia were down on the list.

Table 2: Ranking of the country of the Western Balkans towards competitiveness in 2009-2013

Country	Rank in 2009.	Rank in 2010.	Rank in 2011.	Rank in 2012.	Rank in 2013.
Slovenia	37	45	57	56	62
Montenegro	62	48	60	72	67
Croatia	72	77	76	81	75
Macedonia	84	79	79	80	74
Serbia	93	96	95	95	101
Bosnia and Herzegovina	109	102	100	88	87

Source: *The Global Competitiveness Report 2013-2014*, World economic forum 2013.

The World Economic Forum provides an analysis in the field of sustainable development, from the aspect of social sustainability and viability of protection of environment (Table 3 for the Western Balkan countries). The main pillars of the social indices of sustainable development are: income, youth unemployment, access to sanitation, access to potable water, access to health services, social services, the share of informal economy, social mobility, and the overall unemployment rate. The main pillars of the index in Accounting for just protecting the environment include: the power of legislation, the protection of land, the number of ratified international protocols and agreements, the availability of water for agriculture, emission exposure to carbon dioxide ratio for fishing, the concentration of particles in the air quality of the environment.

Table 3: Ranking the Western Balkan countries by factor analysis of sustainable development in 2013

Country	Ranking by social sustainability	Ranking by sustainability in the field of environment	Change in relation to previous period
Slovenia	4.68	4.60	Slight increase
Montenegro	4.13	4.13	Stagnation
Croatia	4.09	4.13	Stagnation
Macedonia	3.99	3.83	Stagnation
Serbia	3.58	3.74	Stagnation
Bosnia and Herzegovina	3.66	3.44	Slight decrease

Source: *The Global Competitiveness Report 2013-2014*, World economic forum 2013.

When it comes to number of certified organizations in the domestic market in the field of quality management, Serbia is the leading country of the region of Western Balkans. On the other hand, the number of certified organizations in Serbia is not nearly satisfactory compared to other SEE countries, such as Hungary, Romania, Bulgaria and Greece. Table 4 provides information on the number of certified companies in Western Balkans countries compared to neighbouring countries (the entire Balkans) in 2012. These data about the implementation of integrated management systems are the best indicators of the level of the Western Balkans companies' organizational development. The SAI (Social Accountability International) data from 2013 on the implementation and certification according to the requirements of SA 8000 are used. This table indicates that among the countries listed, Romania and Hungary lead in the number of certified companies. Also, Romanian and Bulgarian companies have the most implemented ISO 14001:2004 and SA 8000 standards.

Table 4: Number of certificates organizations in 2012 (for SA 8000 in 2013)

Country	**ISO 9001**	**ISO 14001**	**SA 8000**
Slovenia	1,614	420	1
Croatia	2,614	760	3
Bosnia and Herzegovina	1,239	174	0
Serbia	3,066	817	1
Montenegro	102	16	0
Macedonia	482	204	0
Albania	154	19	1
Hungary	7,266	1,718	0
Romania	18,399	8,633	231
Bulgaria	6,090	1,395	94
Greece	4,873	657	15

Source: *The ISO Survey 2012 and SA8000 Certified Facilities: As of September 30, 2013.*

Disregarding the growing trend in the number of organizations which introduced quality management system and development of quality movement in domestic economy, overall results are still under the satisfactory level. The majority of companies which introduced quality management system belong to the group of large companies. The major problems of domestic companies are: business based on outdated management principles, inertia and lack of capability to adjust to the market changes, failure to accept integral management concept, failure to accept marketing logic, inadequate treatment of investing in knowledge, failure to acknowledge foreign experiences. One of certainly most important problems of domestic economy, which significantly causes the poor international market entry of our companies, is the inadequate use of knowledge, which primarily implies knowledge necessary for efficient company management.

Modern understanding of competitiveness implies constant struggle for work and knowledge productivity improvement. The main streams of action in the field of education of domestic managers should be:

- Education for new operation conditions, based on market mechanism, private property and productivity as a factor of competitiveness,
- Promotion of new concept – necessity of struggle for productivity, as basis for survival on market, market development and development of specific companies,
- Permanent learning from experience of others – continuous application of benchmarking with a view to achieve business excellence.
- Application of corporate social responsibility concept in domestic companies - setting up of conditions for more successful market entry and achieving competitive capability of domestic companies.

CONCLUSION

The majority of organizations being market leaders in different fields have become socially responsible, whereby this is reflected in particular through achieving consumer satisfaction. Corporate social responsibility represents one of the pillars of business excellence of an organization. The other two pillars of business excellence are meeting customer needs and improving business productivity (Đorđević and Bogetić, 2008). Application of IMS concept can be very important for companies from countries in transition. For a company that wishes to achieve business excellence goals at the current development level, it is completely justified that it determines to integrate certain management systems defined by individual standards.

Business organizations from transitional countries are faced with numerous problems, the biggest of which are those related to improving knowledge and organization, the implementation of new technologies and providing financial resources. Ecological consciousness could not be developed and modern achievements implemented on the domestic market because of long-lasting economic crisis, especially when financing such projects by the EU was in question. Application of corporate social responsibility concept in domestic companies should enable setting up of conditions for more successful market entry and achieving competitive capability of domestic companies, as well as achieving of sustainable development goals.

REFERENCES

Balkyte, A., & Tvaronavičiene, M. (2010). Perception of competitiveness in the context of sustainable development: facets of “Sustainable competitiveness”. *Journal of Business Economics and Management, 11*(2), 341-365.

Đorđević, D., & Bogetić, S. (2008). Role of Corporate Social Responsibility in Modern Business. *Megatrend Review, 5*(1), 151-165.

Đorđević, D., & Ćoćkalo, D. (2007a). *Business ethics and low*. Zrenjanin, SRB: TF Mihajlo Pupin.

Đorđević, D., & Ćoćkalo, D. (2007b). *Quality management.* Zrenjanin, SRB: TF Mihajlo Pupin.

Herrmann, K. K. (2004). Corporate social responsibility and sustainable development: the European Union initiative as a case study. *Indiana Journal of Global Legal Studies*, *11*(2), 205-232.

Kolk, A., & Van Tulder, R. (2010). International business, corporate social responsibility and sustainable development. *International Business Review*, *19*(2), 119-125.

Kotler, F., & Li N. (2007). *Corporate Social Responsibility*. Belgrade, SRB: Čigoja štampa.

Moon, J. (2007). The contribution of corporate social responsibility to sustainable development. *Sustainable Development*, *15*(5), 296-306.

SA8000 Certified Facilities: As of September 30, 2013. (2013). Retrieved 23.6.2014 from SAI. http://www.saasaccreditation.org/certfacilitieslist.htm.

The Global Competitivness Report 2013-2014. (2013) Retrieved 15.5.2014 from World Economic Forum.

The ISO Survey 2012. (2013). Retrieved 23.6.2014 from ISO www.iso.org

Tissen R., Andriesen D., Deprez, F.L. (2006). *Knowledge Dividend***.** Novi Sad, SRB: Adižes.

Van Marrewijk, M. (2003). Concepts and definitions of CSR and corporate sustainability: between agency and communion. *Journal of business ethics*, *44*(2-3), 95-105.

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AWARENESS ON ENVIRONMENTAL PROTECTION IN THE CITY OF ZRENJANIN

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ABSTRACT

City of Zrenjanin, like many in Serbia is faced with great difficulties in its development that occurred as a result of decades of impoverishment, lack of resources and lack of investment in development. Environmental protection is one of the most important segments of the sustainable development of a city. Protection of the environment affects the conservation of natural resources and providing people better quality of life. Therefore, this work aims to influence the residents to perceive the importance of environmental protection for the City of Zrenjanin.

Key words: *Environmental protection, Sustainable development, Zrenjanin, resources.*

INTRODUCTION

City of Zrenjanin, like many in Serbia is faced with major problems in its development that have arisen as a result of underdeveloped infrastructure, and bad habits and lack of concern for the environment. Protection of the environment directly affects the quality of life of people, positively affect the flora and fauna of a community. Improves the health of the citizens and create better conditions of life for present and future generations. Protecting the environment involves a set of different actions and measures to prevent environmental degradation in order to preserve the biological balance. Environmental defense is a multidisciplinary and should be a continuing obligation of all members of society. Its multidisciplinary approach stems from the fact that the health, environment and social conditions are a complex area and the problems that are in constant interaction. Therefore, every impairment of the environment leads to environmental disorders and social relations, which are interconnected and interdependent. Under the protection of the environment is not just about protecting the lives and health of people but also the preservation of plant vegetation and wildlife. "The universal declaration of human rights with article 31 states:" Every human being has the right to maintain the ecological balance in their environment, they share with all other living beings, plants and animals, whose survival as a guarantee for the survival should be ensured. "(Ninković, M., 2005)

Only by raising awareness at all in terms of realization and realization of the rights of every person to a healthy environment can be expected initial success in this struggle, which ensue brings into question the survival of the human race in general. (Vančina F., 1982) Because the risk of accidental threats to the environment represents an expansive phenomenon that knows no borders between peoples, countries, and continents, it is logical that the international community had early noted the need for a unique insight into the ways, methods and conditions for the installation of a comprehensive, complete, efficient and high quality care, regulation and improvement of the environment as a whole or its individual segments. (Ninković, M., 2004) On the other hand, the international community has correctly noted the risk of various forms and types of injuries or endanger the environment. (Komadinić P., et al, 2002) Based on today in the international framework set uniform basis towards the establishment of 'sustainable development' of the environment in accordance with the economic and social needs. (Crbnobrnja M., 1984). In fact, it is a new social attitude towards the environment, space and natural resources, with full awareness of existence of responsibility before the future generations. (Šundalić A., 2007) Therefore, the international community has adopted a series of measures, procedures and resources in order to eliminate, prevent or reduce the sources of threats to the environment. (Hedemann M. Robinson, 2007) Since this is a global problem that threatens large areas, it is logical concern of the international community to protect the environment. For Serbia, which is in the process of thorough reforms, not only social, political, but also the legal system, it is particularly important question harmonization of national legislation with international regulations, primarily with European regulations and European legal standards. (Todić D., Vukasović V., 2002)

MATERIAL AND METHODS

The empirical investigation is based on a survey conducted among the residents of the City Zrenjanjin. Research methodology is based on the formulation of the survey on environmental protection (Table 1). Questions were also formulated to incorporate awareness of respondents about the problem, basic claims and findings and incorporate respondents' opinions on various segments of the topics explored. Part of the survey are further sub-target students Technical Faculty "Mihajlo Pupin" in Zrenjanin, in order to comprehend the consciousness and awareness of young educated people. The second part of the survey were randomly divided in order to look into the minds of people with different levels of educational attainment and of different ages. Information based on data from surveys are basically quantification type, with elements of qualitative type in a few questions. Data were statistically processed, after which the results are displayed on a graph for better visibility. The objectives of this study were: 1.Consideration of public awareness of the City of Zrenjanin environmental protection. 2. Determining the attitude of the citizens on whether they find it in a proper way affect the protection of the environment. 3. Determine what actions and the actions people take about environmental issues. 4. Analysis of the awareness of the citizens in the segments of the environment. 5. by detecting bottlenecks and find solutions that would affect the environment in the City of Zrenjanin to a higher level.

Hypotheses set out in this research are:
The main hypothesis: Awareness of citizens of the City of Zrenjanin on environmental protection is not high enough.
Auxiliary hypothesis: Awareness of respondents about the relevant authorities of Environmental Protection.

Table 1: Survey, "Environmental Protection" (M. Zakin, 2013)

Dear Sir / Madam, This survey is carried out for the writing of student work at the university. The survey is anonymous and the data from it in any way will not be misused. Please carefully fill out the survey. Thank you for your cooperation and for your time. * Note: The possible responses are regulated by the numbering so that by rounding the number one giving complete denial of the question, and by rounding the number up to 5 confirming question. For example: 1 - no, 2 - way, three - maybe four - a 5 - to (descriptions offered numbers are adjustable in accordance with the set question).		
Environmental protection		
Serial number	Questions	Answers
1.	*Have you heard of the term "environment protection"?*	*1 2 3 4 5*
2.	*If the first question is given an affirmative answer, to bring out what you represent this concept.*	
3.	*Are you informed that in the municipality of Zrenjanin exists a competent authority for environmental protection?*	*1 2 3 4 5*
4.	*Do you know who is in charge of environmental protection in the City of Zrenjanin?*	*1 2 3 4 5*
5.	*Did you know that each individual is responsible for the protection of the environment?*	*1 2 3 4 5*
6.	*Do you think that the state is the most responsible for the protection of the environment?*	*1 2 3 4 5*
7.	*Do you think we should put more emphasis on environmental protection in the municipality of Zrenjanin?*	*1 2 3 4 5*
8.	*In your opinion, who is the main culprit for environmental damage?*	
9.	*Is awareness of environmental protection sufficiently developed among the citizens?*	*1 2 3 4 5*

RESULTS AND DISCUSSION

The following data will show the results of research, which are based on survey of environmental protection awareness. The following table (table 2.) gives us an insight into the social characteristics of respondents in the number of citizen who underwent a survey on environmental protection.

Table 2: Social characteristics of survey respondents "Environmental Protection"

Social characteristics of respondents					*Total*
What is your gender?	*M*	*F*			
	45	*27*			
How old are you?	*15-30*	*30-45*	*>45*		
	31	*17*	*24*		
The level of education?	*PS*	*SSS*	*HS*	*VSS*	
	7	*44*	*8*	*13*	*72*

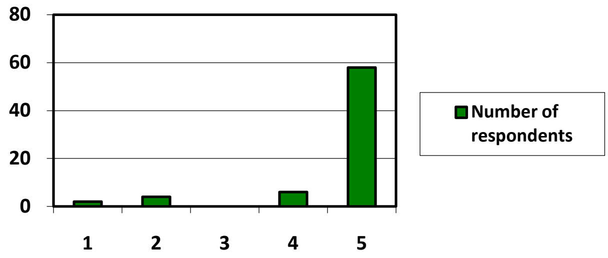

Figure 1. Informing citizens about the term "Environmental protection"

Based on the observed citizen information about environment protection (Fig.1), it can be concluded that the majority of respondents know what term environmental protection means, while a smaller number agrees with the fact that they are familiar with the term, but not sufficiently informed. Citizen awareness of given term is on high level, so further education of citizens should be continued.

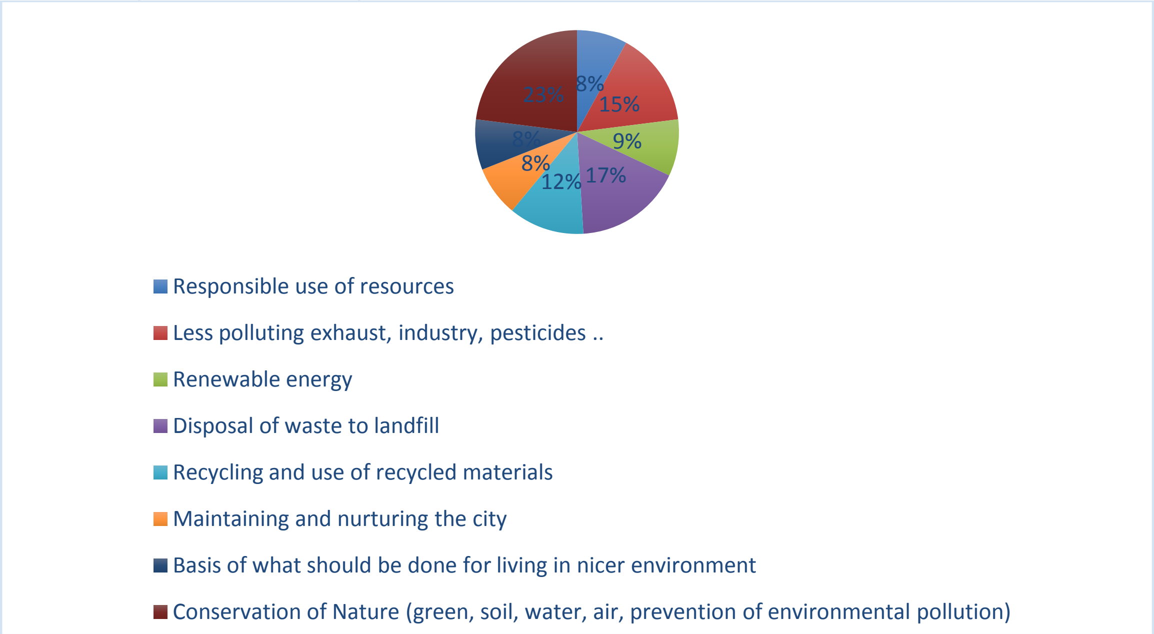

Figure 2. The meaning of the term "Environment protection"

Additionally, based on respondents opinions about the meaning of the term "Environment protection" (Fig. 2), it can be concluded that the answers given are matching the meaning of term, which represents a good awareness of respondents.

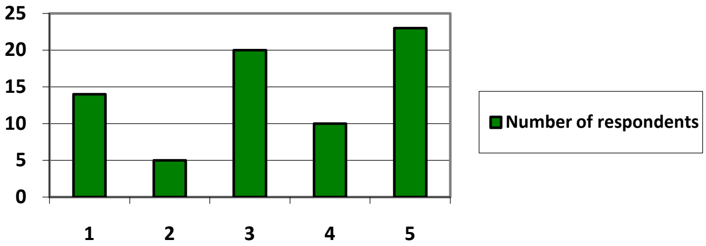

Figure 3. Being informed that there is a competent authority which is responsible for environmental protection

Based on the perceived awareness of citizens (Fig. 3), it can be concluded that the respondents are divided equally. The slightly higher percentage have reported that they are aware there is the competent authority in charge of environmental protection. Citizens should be addressed to the competent authority responsible for environmental protection and informed about the duties performed by the competent authority, and to present which help or information can be retrieved.

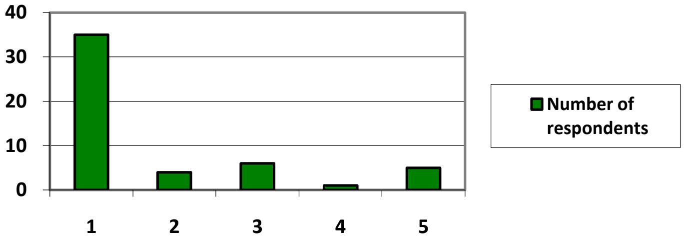

Figure 4. Familiarity of citizens who has authority in Zrenjanin for environmental protection.

Based on the answers from the survey of citizens (Fig. 4), it can be concluded that the respondents in most cases wasn’t informed about which authority responsible for environmental protection. When we look at the previous question, which was: "Are you informed that in the municipality of Zrenjanin exists a competent authority for environmental protection?", in which the participants were divided almost equally, with a slightly higher percentage that are informed, awareness in question of who is responsible authority for environment protection have dropped significantly when compared to the results of the last questions. Major number of respondents who answered that they aware about competent authority in this matter, in this question have answered that they were not informed who exactly is in charge. Citizens should be addressed to the competent authority responsible for environmental protection and the duties performed by the given body, and present what help or information can they receive.

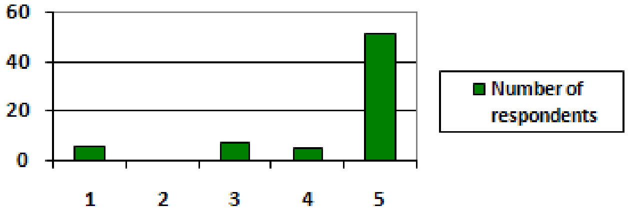

Figure 5. Familiarity that each individual is responsible for the protection of the environment

Based on the perceived information of respondents (Fig. 5), it can be concluded that majority is aware that each individual is responsible for the protection of the environment. An affirmative answer in such a large percentage is the outstanding result, so it is only necessary to motivate citizens to direct their activities so that they are for the benefit of the environment. It is necessary to present to people how they can influence and be responsible for the protection of the environment, in what way can they contribute to the preservation of the environment and what actions can have a negative effect on her.

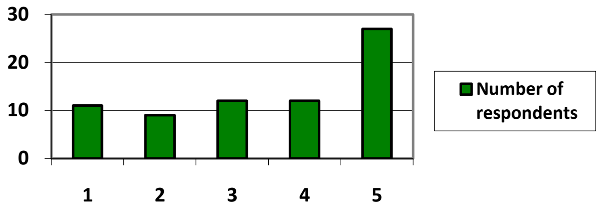

Figure 6. Public opinion that the country most responsible for environmental protection

Opinion of citizens that the state is most responsible for environmental protection (Fig.6), the highest percentage of answers were positive, while the remaining respondent’s answers were divided. State influence on the environment is very important, it is the state that makes the laws, implemented various actions that have a positive effect on the environment, and through its competent authorities for the environment prevents a negative effect on her.

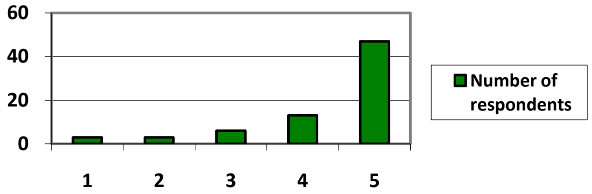

Figure 7. The need to place greater emphasis on environmental protection in the City of Zrenjanin

Additionally, based on respondents’ opinions (Fig.6), it can be concluded that the majority of respondents agreed that greater emphasis should be placed on environmental protection. Therefore, they should be able to participate in various activities to contribute to given issues and instruct on how they can contribute to the environment.

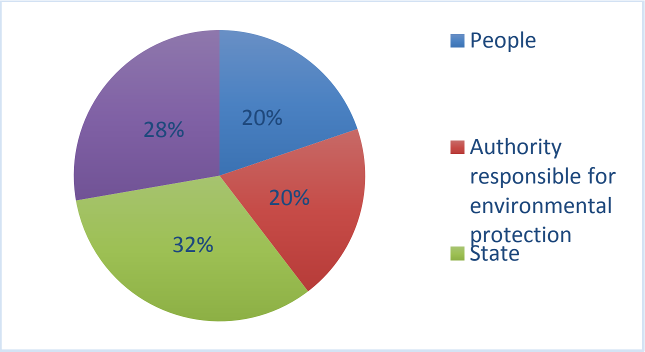

Figure 8. The main culprits of environmental degradation

To the question "In your opinion, who is the main culprit for environmental damage?" (Fig.8), the respondents answered that as the main culprit for environmental degradation experience: people, authority responsible for environmental protection, industry and state.

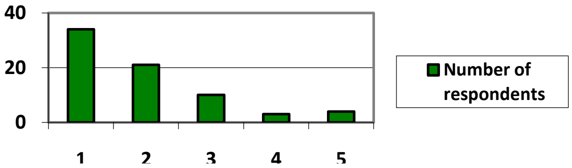

Figure 9. The awareness of people about the environment protection

When asked whether the awareness of environmental protection is underdeveloped (Fig.9), the opinion of the respondents was that it is not sufficiently developed. Given that citizens are aware that the level of awareness about the problem is low, there is need to utilize and implement a variety of actions that specifically promote the awareness of citizens.

Summary based on the survey of environmental protection:

- Citizens are informed what the protection of the environment is but are not sufficiently knowledgeable that there are bodies in charge of that area.
- Based on the survey results, the citizens believe that the state is most responsible for environmental protection and that there is need to put greater emphasis on its protection in the City of Zrenjanin.
- Also notice that the awareness of environmental protection is not sufficiently developed among the citizens, therefore it is necessary that various actions and adequate education further emphasize the importance of preserving the environment with the help and support of the state and to raise awareness that every individual in his activities can contribute to the environment.

CONCLUSIONS

Based on the research it can be concluded that the opinion of the respondents is that people's awareness of environmental protection is not fully developed, which confirmed the main hypothesis. Respondents were not sufficiently informed of who exactly is in charge of the environment and that authorities are taking the necessary measures for the benefit of the environment. Insufficient knowledge of the respondents in charge of caring for the environment, confirms auxiliary hypothesis. It should be emphasized that it is necessary not only to change the habits that negatively affect the environment, but must lead to a change of consciousness in the fields of environmental protection. If environmental protection is taken seriously, result would be drastic changes that will lead to a better functioning of the local community in many areas. Bringing awareness of environmental protection in the City of Zrenjanin to a higher level, and therefore in the Republic of Serbia would directly impact on the conservation of natural resources and raising the standards of the population which would result in improved quality of life.

REFERENCES

Ninković, M., Expert Opinions, Lex Forum, May-August 2005.

F. Vančina, the environment, Zagreb, 1982, p. 76-89.

M. Ninković, protection of the environment and environmental litigation in the United States, Belgrade, 2004, p. 112-123.

PW Birnie, International Law and the Environmental, Oxford, 2002, p. 153-168; P. Komadinić, M. Markovčić, Ž. Kiperoš, "Application of international standards of maritime safety and environmental protection in the Republic of Croatia", Naval Proceedings, Zagreb, 2002, p. 23-34

International Environmental Law, Hague, 1995, p. 89-121. M. Crbnobrnja, man, environment and economic development, Belgrade, 1984, p. 113-132.

A. Šundalić, "Environmental awareness among the youth for sustainable development and TEHNOCENTRISM, Social Ecology", Zagreb, 2007, No. 4, p. 279-296

M. Hedemann Robinson, Enforcement of European Union Environmental Law, London, New York, 2007, p. 216-231.

D. Todić, V. Vukasović, ecological crisis in the world and the response of the international community, Belgrade, 2002, p. 118-134.

Zakin M., Petkanić I., Litričin Lj., seminar "Sustainable Development in the municipality of Zrenjanin", 2013

ELECTRO AND ELECTRO-MAGNETIC POLLUTION IN URBAN AREAS

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MEASUREMENT AND ANALYSIS OF STATIC AND ELECTROMAGNETIC FIELDS OF VERY LOW FREQUENCY

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ABSTRACT

The sources and characteristics of static and electromagnetic fields of very low frequency (VLF) are presented at the beginning . Different sources of VLF fields are found in environment, houses and the workplace. Measurement and analysis of static and electromagnetic fields of very low frequency is the main topic of the paper. Some devices for measuring static and electromagnetic fields of very low frequencies are represented.

Key words: *Electromagnetic Radiation, Sources of static and VLF, Measurment of static and VLF.*

INTRODUCTION

Static electric and magnetic fields arise from both natural and man-made sources, whereas electric and magnetic fields in the VLF range (3–3000 Hz) are mostly associated with man-made sources. These are numerous and include electric power systems, electric and electronic appliances and industrial devices. Environmental levels of ELF fields are very low. Exposure levels for the general population are typically 5–50 V/m for electric fields and 0.01–0.2μT for magnetic fields.

Considerably higher exposure occurs for shorter durations and in some occupational settings. It should be noted that the earth’s magnetic field (25–65μT, from equator to poles) is a static field to which everyone is exposed. Measurements of electric and magnetic fields are used to characterize sources and levels of exposure to humans. The capabilities of instruments to measure such fields have advanced in recent years, particularly for magnetic fields. In addition to simple, easy-to-use hand-held survey instruments, there are now portable personal exposure meters capable of recording and describing the statistical, threshold, frequency and waveform characteristics of magnetic field exposure. The limiting factor in exposure assessment is not instrumentation but the lack of a consensus as to what exposure characteristics should be measured that are biologically relevant. Computational methods are available to calculate fields and their parameters for instrument calibration, laboratory exposure systems and certain categories of indoor and outdoor sources.

SOURCES UNIDIRECTIONAL AND VLF ELECTRIC AND MAGNETIC FIELDS

Electric fields caused by direct current (DC) are known as static fields, because they do not change over time. Their frequency is equal to zero and the wavelength of the atom. In this case, the circuit transmits all the energy and does not radiate at all. Therefore, we have only field. Since the field is static, there is no excitation of surrounding molecules and there is no heating. The electromagnetic field produced by direct current can cause a burning sensation when standing close to the source or high voltage source straightened hair[1]. The Earth produces an electromagnetic field, which is almost static. This field makes the Earth with its magnetism, Solar activity and atmospheric discharges in the form of electrical and lightning storm. Earth's static electric field depends on the conditions in the atmosphere. During the calm and clear weather conditions, the field has a strength of about 150-300 V / m, but during an electrical storm may reach a value over 10.000V/m.

Intensity of the magnetic field ranges from 30μT to 70 μT depending on latitude and composition of the Earth's crust (magnetically conductive ore or local mountains). The volume density of the Earth's magnetic field at latitude of 50° is 58 μT, and on the equator (0 ° latitude) is 31 μT. The average volume density of Earth's magnetic field is 45 μT(K. Dervić, S. Janković, Ž. Despotović, V. Šinik, V. Kerleta**,)**.

It is interesting to note that human movements within the Earth's magnetic field caused by induced electric field inside its body. For example, a quick run around 8 m / s creates an internal electric field of 400 μV / m. Such strength of the electric field can induce a low frequency magnetic field magnetic flux density of 20μT(K. Dervić, S. Janković, Ž. Despotović, V. Šinik, V. Kerleta**,)**.

Time-varying electromagnetic fields generated by time varying AC (Alternating Current) electricity during transmission, distribution and use of electricity. The main sources of time varying electric fields in the work area are electric cables. The strength of these fields is in the range from 1 to 100 V/m. Flow of electrical current through a conductor produces a magnetic field. These fields always form a closed loop around the conductor which caused them. As the basic unit of magnetic flux density Tesla [T] is very large, it is the practice of using smaller units: microtesla [μT] and nanotesla [nT]. Under normal conditions in the workplace time-varying magnetic fields caused by electric grid ranging from 10 nT to 1 mT.

Frequency of a VLF field depends on the field sources. Although the dominant frequency of 50 Hz and 60, people are generally exposed to a mixture of frequencies, some of which may be much larger. For example, the frequency of certain parts of electronic equipment or TV monitor can go up to 120 kHz.

Electric power system

Electrical energy produced in power plants is distributed to consumer areas via high voltage power lines from 35 kV to 400 kV. The voltage is reduced by transformers to 400/230 V for local distribution. The general population is exposed to magnetic fields at the network frequency, 50 Hz in as, via three individual sources: high voltage transmission power lines, the local system for the distribution and low voltage electricity at home and at work, and electrical household appliances. The first two sources create basic, so-called background magnetic radiation, known as the magnetic flux density of the environment.

Overhead power lines

Transmission and distribution lines can be called by one name - power lines. Overhead power lines are the less expensive way to transfer electricity. Usually consist of parallel conductors, which carry most of the energy with very few losses or small radiated energy. Field between the conductors is intense, but it is usually closed between them. The strength of the magnetic field line is determined by the rate of electricity, the proximity of the transmission line, the transmission line height above ground, distance between phases, column geometry and distance from other lines.

Highest levels of electric and magnetic field lines are located in the area where the conductors are closest to the earth, and it is midway between the two pillars. Because of the ambient temperature, the height of the lowest conductor was flying lower and higher in the winter, because the levels of the fields in the area flying higher and lower in winter.

All over the world there are vast energy network. That means that almost complete human populations exposed to various fields of power system components. The only difference is in the degree of exposure that varies in the day, days in the week, the season, and depending on the ambient temperature. Most fields are usually located beneath high voltage transmission lines, however, the field strength depends on the strength of the current.

Transformer stations

Transformer stations are one of the most important parts of the energy system, which is used to change the voltage level, and perform other functions in the transfer of control and flow of electrical energy. There are several ways to build substations in order to achieve a reliable electricity system. In essence, they are complex equipment such as circuit breakers, high voltage switches, grounding, transformers intended course with the changing voltage control. Since the substations are often located near schools and homes, must be considered as sources close to the electric and magnetic fields.

Transformers are sources of strong magnetic fields because their principle of operation is based on a time-varying magnetic fields. The problem of the magnetic field near cells is more complex, since the current entering or leaving the station, in the general case are not symmetric. Field produced by equipment weaks with distance and do not spread outside the physical boundaries stations. However, the magnetic field near the station is stronger than in other parts.

Transformer as standalone devices found in rural areas (Column transformers), and in urban areas, mostly inside residential buildings. Transformers in buildings adversely affect the people in the apartments above them. These transformers, create an extremely strong electric and magnetic fields. Unfortunately, to enable lower expenses of their installation, they are frequently installed in the buildings. That is not in line with technical recommendation which allowed that kind of installation in exceptional cases, only. This radiation is stronger than transmission radiation.

Electrical installations

Average value of the magnetic fields in homes which are away from power lines and transformer stations is small. The mean value of the magnetic fields in the houses in major cities is around 0.1 µT. Values in the smaller towns and villages are of half of noted value. In cities, about 10% of homes have at least one room where a field value exceeds 0.2 µT. If a house is near power lines and substations strength magnetic fields are even greater. It was found that 0.5% of houses have values of magnetic fields in excess of 0.2 µT. For commercial buildings, transformers and distribution boxes are placed in separate rooms in the buildings. Field values in areas around such premises or buildings have a value from 1 µT to 10 mT.

Vehicles on electric power

Electric trams and trains are also sources of static and VLF fields. For traction they somewhere use direct current somewhere alternating current. Near the coaches floor the static magnetic fields can reach 0.2 mT, and time-varying magnetic fields can reach several hundred µT. At the headquarters of passengers, electric fields can reach up to 300 V / m and magnetic field reaches values of a few tens µT.

Values are highly dependent on the level of design and location of electrical equipment and machinery within the train composition. Traction motors and equipment are often placed under the floors in the coach. They create a ver intense fields in the area of the floor below which they are located. Passengers were further exposed to magnetic fields from sources that are close to the tracks

INSTRUMENTS FOR THE MEASUREMENT OF STATIC FIELDS

In Figure 1 is shown an instrument ETM-1.Due to its specific characteristics (frequency range O Hz), only used to measure electrostatic magnetic fields.

Directional characteristic . . . . isotropic, three dimensional
Meas. range . . . . automatic ranging, three ranges
Temperature range. . . . . 0 to +40^{0}C
Sensor type . . . . magnetic field(H)
Frequency range . . . . static; 0 Hz
Specified measuring range . . . . 19.99, 199.9 and 1999 mT
Accuracy. . . . . +2% of measured value
Drift . . . .+0.05%/ëC starting at +25^{0}C
Ambient field for device with battery 0.1T
Ambient field for device
without battery (a.c. line power) 1.5T
Dimensions in mm
Weight . . . . 250 g

Figure 1. The meter of static magnetic field and its features

Applications

The probe is designed for use in measuring constant magnetic fields, as occur with medical equipment (magnetic resonance imaging, MRI), metal production and railway systems.

Features

The ETM-1 extends the EFA-1 to EFA-3 family of low-frequency field analyzers to cover measurement of constant fields. The device has automatic ranging, or one of three ranges can be selected manually (19.99 mT, 199.9 mTand 1999 mT). Results have units of mT in the 31/2 digit LC display. All three axes can be evaluated, or just one of the three (x, y, z). The probe is connected via a 1.5 m shielded cable to the test instrument. The small size of the probe (dimensions: 126126100 mm) enables measurements in tight places.

Calibration

The device is factory-calibrated. Recalibration is recommended every two years. Calibration data are traceable to national/international standards. The specified confirmation interval is only a recommendation. Users can choose a confirmation interval to suit their needs, based on the type of application and ambient conditions.

Rugged design

The rugged mechanical and electrical design of the device destines it for field use. The ETM-1 runs for about 15 hours on a standard 9 V lithium battery. The ETM-1 can also be powered from an a.c. line unit (included).

Functional principle

The probe uses three separate sensors. Hall probes are used as sensor elements for the magnetic field. The three channels are realized separately and evaluated in the mainframe. This assures display of the RMS value across a wide measuring range. Usage of these detector elements guarantees excellent overload protection, making it practically impossible to destroy the sensors through everyday usage. For remote control, the ETM-1 has an RS232 interface. The device can be remotely controlled via the supplied cable and the serial interface of a PC. This allows users to control the device from a remote site while it measures very powerful fields.

INSTRUMENTS FOR THE MEASUREMENT OF VLF

Magnetic fields are present in production areas, public places and the everyday environment. Measurements are often made in these areas to ensure that people are not exposed to fields that could cause injuries. Global efforts to provide effective protection have resulted in a range of national and international guidelines and standards in recent years, which specify reference limit values for field strengths for various frequency ranges and signal shapes. In practice, simple equipment must be used to determine the fields that occur and to check that the limit values are not exceeded. The ELT-400 is a completely new type of tester for workplace and public area exposure to magnetic radiation. It was developed specially for the above areas, for use by health and safety representatives in industry, insurers, and service providers.

Production areas The ELT-400 is particularly suitable for applications involving production plant, including welding, smelting and heating, as well as most magnetic stirring equipment. It can handle special requirements such as the pulsed signals or phase control encountered in resistance welding without problems. **Everyday environment** Magnetic fields occur everywhere in the everyday environment, being produced by everything from power supply plant through to medical equipment. For example, the electromagnetic and magneto-acoustic security systems used in department stores also operate within the frequency range of the ELT-400.

EMC test laboratory The ELT-400 is ideal for investigating the magnetic fields produced by household equipment or other electrical devices. The reference test method described in the latest product standards such as EN 50366 and prEN 50392 is implemented precisely in this instrument. **Instrument description** The ELT-400 is extremely easy to operate using just 6 buttons and can be used practically anywhere. **Exposure STD mode** Exposure STD mode is suitable for particularly simple and reliable measurements on all signal shapes (single or multiple frequency fields, pulsed fields). The level of the magnetic field is displayed directly as a percentage of the reference limit value, regardless of the signal shape and frequency. The evaluation schemes specified by the relevant safety standards are implemented in the instrument. The numerical result therefore clearly expresses the actual situation and indicates the available safety margin. **Field strength mode** The ELT-400 has a flat frequency response over a very wide frequency range. Detectors for RMS and peak value measurements can be used for broadband measurements. The results of field strength measurements are displayed in µT or mT. **Active probe** The ELT-400 can be connected to an oscilloscope or FFT analyzer for more in-depth analysis. The signal voltages from all three field probes (isotropic coil configuration) are output with proper phase. The amplified voltage can be input directly to the oscilloscope or FFT analyzer.

EMR-20C and EMR-21C, E-Field Measurement Systems

The EMR-20C and –21C are complete systems that consist of a meter and probe, along with a charging system for the NiCad batteries. The EMR-20C and EMR-21C are supplied with a cali- brated Type 8 probe that provides coverage for many industrial systems operating at 915 and 2450 MHz, as well as measuring extremely low field levels. Users appreciate the wide measurement range and extreme ruggedness of this multipurpose survey system. The EMR-20C and -21C have even been designed to withstand drops from two meters directly on the sensor head! Operation of this series of survey systems could not be any easier. All you need to do is connect the probe and turn on the meter. The system automatically detects the probe and auto-zero’s the system – even while immersed in an RF field environment. Electric field readings are displayed in units of V/m, W/m2 and mW/cm2 , with over 62 dB of measurement range, without touching a button! Both the EMR-20C and -21C feature a bi-directional fiber-optic link. With the optional software and cables, real-time readings can be displayed on a personal computer.

Figure 2. The meter of the magnetic field ELT-400 and E-electric field measurement systems EMR-20C, EMR-21C

MEASUREMENT OF STATIC ELEKTROMAGNETSKILI FIELDS (O Hz)

This type of measurement is particularly suitable for later distribution planning in areas (places to sleep and stay longer) in order to avoid long exposure to elevated values of static electromagnetic radiation. The measurements were carried out at a height of 1 m above the floor with isotropic probe, which accounts resultant measured components of static electromagnetic fields and is not sensitive to the position of the hand. Values were read after 10 sec. of stabilization and each node. After the measurements, and electronic processing of measurement results obtained are the results for the entire apartment. In order to gain better insight and analysis of the measured values of the static electromagnetic fields and Figure 3 shows the 3D look at the measured results.

In areas that are facing rgema street, measured been slightly increased radiation density of the static magnetic field with respect and natural magnetism of the country (the magnetic flux density of the earth's natural magnetism varies from 0.4 to 0.85 mT).

The assumption that the cause of communal infrastructure, and natural water flows along the street. At two places is also registered slight increased emissions due to influence of the speaker.

Although the radiation is within acceptable limits, the observed higher intensities of radiation in the bedrooms and living rooms along the north wall.

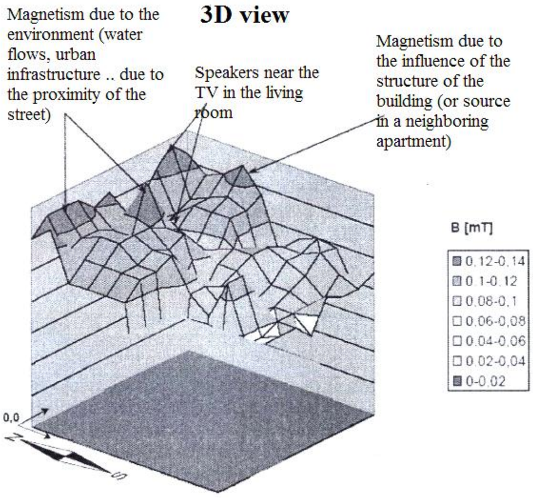

Figure 3. An example of the results and analysis of measurements of static EM fields

MEASUREMENT OF LOW-FREQUENCY ELECTROMAGNETIC FIELDS

Since the spectral analysis showed radiation power grid as the most dominant component of low frequency spectrum measured density the magnetic flux in the room. The electrical field strength was not measured in this way because of the possible distortions due to the proximity of the field of furniture and walls.

After the measurements in all the rooms and the electronic processing of the measurement results, the obtained results for the entire apartment. In order to gain better insight and analysis of the measured values of the electromagnetic fields of low frequencies in Figure 4 shows the 3D view of the measured results. The room measured maximum magnetic flux density is relatively low to moderately high intensity. Jumps occur and 4 places: the TV, the computer, the area with the kitchen cabinets and a source of radiation in the bathroom wall.

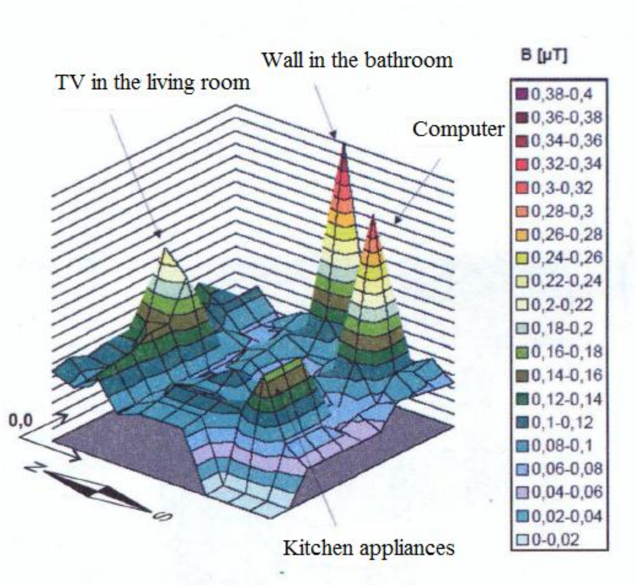

Figure 4. Example analysis of low frequency electromagnetic fields in the flat

CONCLUSION

Following the results of the analysis of exposure to electromagnetic radiation apartment in Figures 3 and 4, we can see that it recorded a slight increase in the static magnetism in the northern areas, it is in the living room and bedroom, near the road, and also in one of the eastern wall of the bedroom. As the cause of the said radiation usually impact the Earth's natural magnetism, natural waterways, the geological structure of the soil, municipal infrastructure, etc. .., you can see that the position of the apartment on the 3rd floor contributed to the reduced intensity of radiation electromagnetic static fields.

The measured radiation have a not greater impact on the body of people who reside in the specified area. Although the radiation is far below the allowed limit values, however, the intensity in some areas twice the size of Earth's natural magnetism. For some people, there was an increased sensitivity, the greater the difference in relation to the natural magnetism may, after long-term exposure (these are the years), due to the accumulating effect, lead to sleep disturbances, minor fluctuations in the cardiovascular system and the like.

As the most radiation may accumulate during sleep (average of 7 hours per day in the same place), the recommendation is to set protective coverings on the bed frame.

Also, as one might expect increased low-frequency radiation and electrical fields magnetskili near electrical devices fed voltage grid (50 Hz and 220 V), so close to the TV and the computer may notice more radiation on average distance of half to one meter. Although the aforementioned radiation of low intensity and within the permitted limit values, to avoid prolonged stay in their vicinity.

As tenants do not stay a long time in the bathroom there mentioned radiation and will have no adverse effect. However, it should be borne in mind that the radiation of low frequency and stronger intensity, due to its characteristics, it has significant negative effects on the human body (among other things, it is assumed that promotes the creation of cancerous cells).

REFERENCES

K. Dervić, S. Janković, Ž. Despotović, V. Šinik, V. Kerleta, *THE RADIATION OF ELECTROMAGNETIC FIELDS OF VERY LOW FREQUENCY,* II International Conference „ECOLOGY OF URBAN AREAS“ 2012

Instructions for the construction and use of non-ionizing radiation, the *Ministry of Environment and Spatial-Planning Department for the control and supervision*, Belgrade, May 2010.

International Commision on Non-Ionising Radiation Protection (ICNIRP) Guidelines: Guidelines for Limiting Exposure to Time Varying Electric, *Magnetic and Electromagnetic Fields (up to 300 GHz), Health Physics,* Vol. 74,4 (1998) 494-522

Directive 2004/40/EC of the European Parliament and of the Council of 29 April 2004 on the minimum health and safety requirements regarding the exposure of workers to the risks arising from physical agents (electromagnetic fields),*Official Journal of the European Union* L 159 of 30 April 2004

Council Directive *98/34/EC of 22 June 1998, laying down a procedure for the provision of information in the field of technical standards and regulations (Official Journal L 204 of 21.07.98) (former Directive 83/189/EEC).*

Kemal Dervic“ Man in the Middle radio frequency field“ *Transparency Montenegro, Podgorica*,2008

http://www.foti.co.rs/

http://www.123rf.com/photo_10872365_big-television-and-radio-tower-with-several-parabolic-antenna-

https://www.google.rs/search?q=Radio+and+TV+transmitters+fig&sa=N&tbm=isch&tbo=u&source=univ

http://en.wikipedia.org/wiki/Radar

http://www.mmust.elimu.net/BSC%28ELEC_COMM%29/Year_5/ELC-544E

http://www.who.int/peh-emf/publications/facts/fs226/en/

http://en.wikipedia.org/wiki/Transmitter

http://www.mikroe.com/old/books/rrbook/chapter2/chapter2.htm

http://www.radartutorial.eu/01.basics/rb04.en.html

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MEASUREMENT AND ANALYSIS OF ELECTROMAGNETIC FIELDS OF VERY HIGH FREQUENCY

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ABSTRACT

The sources and characteristics of very high frequency (VHF) are presented at the beginning. Different sources of VHF fields are found in environment, houses and the workplace. Measurement and analysis of electromagnetic fields of very high frequency is the main topic of the paper. Some devices for measuring electromagnetic fields of very high frequencies are represented.

Key words: *Electromagnetic Radiation, Sources of VHF, Measurment of VHF.*

INTRODUCTION

Electromagnetic radiation (EMR) is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter. The electric and magnetic fields come at right angles to each other and combined wave moves perpendicular to both magnetic and electric oscillating fields thus the disturbance. Electron radiation is released as photons, which are bundles of light energy that travel at the speed of light as quantized harmonic waves. This energy is then grouped into categories based on its wavelength into the electromagnetic spectrum. These electric and magnetic waves travel perpendicular to each other and have certain characteristics, including amplitude, wavelength, and frequency.

Electromagnetic radiation consists of waves of electric and magnetic energy moving together (that is, radiating) through space at the speed of light (Figure 1).

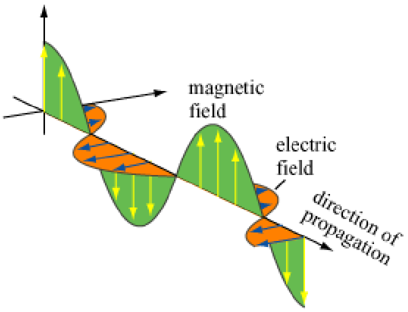

Figure 1. An electro-magnetic wave consists of an electric field and a magnetic field changing together in time and space (https://www.google.rs/search?q=electromagnetic+wave+figure&tbm)

Taken together, all forms of electromagnetic energy are referred to as the electromagnetic spectrum. Radio waves and microwaves emitted by transmitting antennas are one form of electromagnetic energy. Often the term electromagnetic field or radiofrequency (RF) field may be used to indicate the presence of electromagnetic or RF energy(K. Dervić, V. Šinik, Ž. Despotović, M. Bjelica, V. Kerleta).

An RF field has both an electric and a magnetic component (electric field and magnetic field), and it is often convenient to express the intensity of the RF environment at a given location in terms of units specific for each component(V.Šinik , S. Janković, Z. Despotović-2011). For example, the unit "volts per meter" (V/m) is used to measure the strength of the electric field and the unit "amperes per meter" (A/m) is used to express the strength of the magnetic field.

RF waves can be characterized by a wavelength and a frequency. The number of cycles per second is known as the frequency, which is measured in Hertz (Hz).

The effect of mobile phone radiation on human health is the subject of recent interest and study, as a result of the enormous increase in mobile phone usage throughout the world (as of November 2011, there were more than 6 billion subscriptions worldwide)(GSM Association.-2009). Mobile phones use electromagnetic radiation in the microwave range. Other digital wireless systems, such as data communication networks, produce similar radiation.

In 2011, International Agency for Research on Cancer (IARC) has classified mobile phone radiation on the IARC scale into Group 2B - possibly carcinogenic. That means that there "could be some risk" of carcinogenicity, so additional research into the long-term, heavy use of mobile phones needs to be conducted(International Agency for Research on Cancer- 2011).

Many scientific studies have investigated possible health symptoms of mobile phone radiation. These studies are occasionally reviewed by some scientific committees to assess overall risks. A 2007 assessment published by the European Commission Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) concludes that the three lines of evidence, *viz.* animal, *in vitro*, and epidemiological studies, indicate that "exposure to RF fields is unlikely to lead to an increase in cancer in humans"(European Commission Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR)-2008).

SOURCES OF VHF ELECTROMAGNETIC RADIATION

Radiofrequency (or RF) Radiation refers to electromagnetic fields with frequencies between300 kHz and 300 MHz, while “ Microwave (or MW) Radiation ” covers fields from 300 MHz to 300 GHz. Since they have similar characteristics, RF and MW radiation are usually treated together. As well, the lower-frequency boundary of RF radiation is often extended to 10 kHz, or even to 3 kHz, in order to include emissions from commonly used devices.

Radio and TV transmitters

A radio and TV transmitter is usually part of a communication system which uses electromagnetic waves to transport information over a distance.

In electronics and telecommunications a transmitter or radio transmitter is an electronic device which, with the aid of an antenna, produces radio waves.

When antennas are located on tall columns, access by the general population to the base of the columns may be permitted if the exposure is less than the permitted levels. Small antennas of local television and radio stations are frequently located on the tops of tall buildings (skyscrapers), and in such cases thesupervision of roof access is required (K. Dervić, V. Šinik, Ž. Despotović, M. Bjelica, V. Kerleta).

Radar (***RA**dio* ***D**etection **A**nd **R**anging)* is an object detection system which uses radio waves to determine the range, altitude, direction, or speed of objects. It can be used to detect aircraft, ships, spacecraft, guided missiles, motor vehicles, weather formations, and terrain. The radar dish or antenna transmits pulses of radio waves or microwaves which bounce off any object in their path. The object returns a tiny part of the wave's energy to a dish or antenna which is usually located at the same site as the transmitter (http://en.wikipedia.org/wiki/Radar).

The modern uses of radar are highly diverse, including air traffic control, radar astronomy, air-defense systems, antimissile systems; marine radars to locate landmarks and other ships; aircraft anti-collision systems; ocean surveillance systems, outer space surveillance and rendezvous systems; meteorological precipitation monitoring; altimetry and flight control systems; guided missile target locating systems; and ground-penetrating radar for geological observations. High tech radar systems are associated with digital signal processing and are capable of extracting useful information from very high noise levels.
Radars usually operate at radio frequencies (RF) between 300 MHz and 15 GHz. They generate EMFs that are called RF fields. RF fields within this part of the electromagnetic spectrum are known to interact differently with human body.

RF fields below 10 GHz (to 1 MHz) penetrate exposed tissues and produce heating due to energy absorption. The depth of penetration depends on the frequency of the field and is greater for lower frequencies. Absorption of RF fields in tissues is measured as a Specific Absorption Rate (SAR) within a given tissue mass. The unit of SAR is watts per kilogram (W/kg). SAR is the quantity used to measure the "dose" of RF fields between about 1 MHz and 10 GHz. An SAR of at least 4 W/kg is needed to produce known adverse health effects in people exposed to RF fields in this frequency range (http://www.who.int/peh-emf/publications/facts/fs226/en/).

RF fields above 10 GHz are absorbed at the skin surface, with very little of the energy penetrating into the underlying tissues. The basic dosimetric quantity for RF fields above 10 GHz is the intensity of the field measured as power density in watts per square metre (W/m2) or for weak fields in milliwatts per square metre (mW/m2) or microwatts per square metre (µW/m2). Exposure to RF fields above 10 GHz at power densities over 1000 W/m2 are known to produce adverse health effects, such as eye cataracts and skin burns.

HEALTH EFFECTS FROM RADIOFREQUENCY ELECTROMAGNETIC FIELD

At the international level are given guidelines Guidelines for Limiting Exposure to Time-Varying Electric, Magnetic and Electromagnetic Fields (up to 300 GHz) by the International Body for the Protection of Non-Ionizing Radiation Protection (ICNIRP, International Commission on Non-Ionizing Radiation Protection) which are defined limits on the amount of time-varying electric and magnetic fields in open space, especially for general and working population.

The basics of EM interaction with materials were elucidated over a century ago and stated as the well-known Maxwell’s equations. The application of these basics to biological systems, however, is very difficult because of the extreme complexity and multiple levels of organization in living organisms, in addition to the wide range of electrical properties of biological tissues (K. Dervić, V. Šinik, Ž. Despotović, M. Bjelica, V. Kerleta).

There are many factors to be taken in determining how the RF/MT energy absorbed in the body, such as:

- Dielectric compositions
- The size of the body,
- The shape and orientation of the body and polarization fields,
- The complexity (similar to zones) RF / MT field

Interaction of electromagnetic field (EMF) with environment and with tissue of human beings is still under discussion and many research teams are investigating it. Biological tissues are modeled by their permittivity and conductivity. The complex permittivity (ε) of a biological tissue is given by:

$$\underline{\varepsilon} = \varepsilon_r \cdot \varepsilon_0 + j\frac{\sigma}{2\pi f}$$

where, σ (S/m) is the conductivity of tissue in siemens per meter and $\varepsilon_0 = 8{:}854\text{x}10^{-12}$ F/m.

Each object, whether it is a case or a living being, when found in the RF / MW field, can under certain conditions, to enter into resonance with the source of such a field. If the object is a person, its resonant frequency is primarily dependent on the height of the body.

Three different cases:

- when the body is less than the size of the wavelength,
- when they are approximately equal in their size and
- when the body is much larger than the size of the wavelength(K. Dervić, V. Šinik, Ž. Despotović, M. Bjelica, V. Kerleta).

In cases where a body size smaller than the wavelength (Figure 2-a), there is little absorption.

When the wavelength is approximately equal to the size of the body (Figure 2-b), it appears the greatest absorption of the unequal distribution of power. Therefore, it may appear " hot spots" in certain parts of the body.

When the wavelength is smaller than the size of the body (Figure 3-C), the absorption is smaller, while the heating is limited to the irradiated surface.

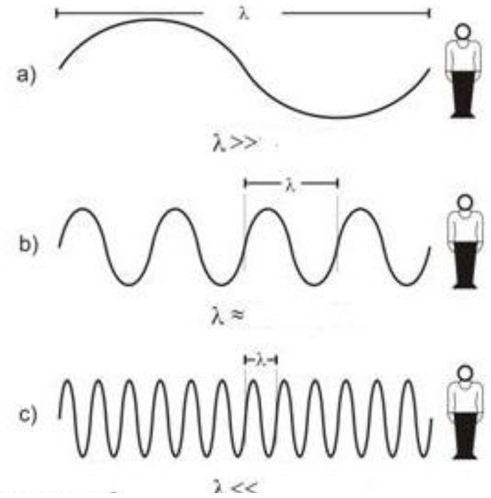

Figure 2. Size of the human body in relation to the wavelength of the electromagnetic wave (K. Dervić, V. Šinik, Ž. Despotović, M. Bjelica, V. Kerleta)

At RF and microwave frequencies, electromagnetic fields penetrate into human body. These fields interact with biological tissue in several ways. The most important interaction can be explained in terms of energy transfer from the electromagnetic field to the tissue material. One measure of this macroscopic effect is the time-averaged absorbed power.

Specific absorption rate (SAR) is a measure of the rate at which energy is absorbed by the human body when exposed to a radio frequency (RF) electromagnetic field; although, it can also refer to absorption of other forms of energy by tissue.

A quantity usually used is known as SAR and has dimension W/kg. SAR can be defined as:

$$SAR = \frac{1}{2} \cdot \frac{\omega \varepsilon_0 \varepsilon_r}{\rho} |E|^2$$

with ω the angular frequency , ε_0 the permittivity of free space, ε_r the imaginary part of the relative complex permittivity, ρ the tissue density in kg/m3 and E is the peak value of the total field inside the tissue material(Savroulacks, P-2003).

We can see that the SAR depends on dielectric parameters therefore the materials of phantoms have to have similar dielectric parameters as human tissues. The human head consists of several tissues, which have different electrical characteristics and form complex-shaped boundaries. The electrical characteristics of human tissues are very different from the normal propagation medium (air), but not so different between each other. For values of SAR are recommended maximum values by committee INCRIP, this value is 2 W/kg in EU(SSI'S Independent Expert Group on Electromagnetic Fields).

INSTRUMENTS FOR THE MEASUREMENT OF ELECTROMAGNETIC FIELDS OF VERY HIGH FREQUENCY

The Selective Radiation Meter (SRM) is a hand-held frequency selective measuring device designed for safety analysis of high frequency electromagnetic fields. Broadcasting equipment operators and radio network providers, measurement services, and authorities can use the SRM to selectively detect individual telecommunications services and evaluate them according to applicable standards(http://www.fra.utn.edu.ar/download/cursos/laboratorio_abierto/narda/Narda_SRM3000_ds_2008.pdf).

The SRM comprises a basic unit plus measuring antenna. The basic unit contains a spectrum analyzer covering the frequency range from 100 kHz up to 3 GHz.

The combination of basic unit plus antenna is portable, robust, battery operated, and provides all the functions needed for evaluating, storing and documenting the results without the need for an external PC. Results can be uploaded to a PC for archiving.

Applications

The SRM was specifically designed as a hand-held measuring device for electromagnetic field safety requirements. It is equipped with tailor made operating modes for the preferred applications, but it can also be used for general field strength measurements, just like an ordinary RF spectrum analyzer. The preferred applications are: comparison measurements in known field environments, survey measurements in unknown field environments , individual telecommunications service measurements. (http://www.fra.utn.edu.ar/download/cursos/laboratorio_abierto/narda/Narda_SRM3000_ds_2008.pdf)

Operation

The SRM basic unit comprises a spectrum analyzer with RF input stage, measurement and operating computer, input panel and display. This means you can set all functions and values directly on the device, using the menus, number keys, softkeys or the rotary control. According to your choice, the SRM also calculates and displays the results directly : as field strengths or as percentages of the permitted limit value, for a single source or an individual channel, as a list of sources or channels, as the proportion due to a telecommunications service, or as the proportions due to all services and their percentage contributions to the overall exposure level.

The SRM automatically uses the following data for this: antenna factors to convert the antenna output voltage into field strength values ,weighting curves specified in current immission safety regulations and standards , telecommunications service frequency range assignments.

Figure 3. Selective Radiation Meter (SRM)

EXAMPLE OF MEASUREMENT AND ASSESSMENT OF EM RADIATION OF A LIVING

Given that our environment is "swamped" the signals of high frequencies of GSM networks, TV signals and a number of radio transmitters, it would be pointless to record all existing signals, large and small forces. For this reason, in this estimation filtered signals are low power and made the measure most dominant signal. As you could see, and all the rooms is the most dominant radiation GSM 900 mobile telephony base stations that are closest in comparison to the observed flat. Positions in the direction of the GSM base stations as expected, measured by the increased radiation of electromagnetic fields GSM frequencies (936 and 952 MHz). During the measurement emitted power is varied and observed only maximum values. The difference between the maximum and minimum power density is variable on average 150-400 $\mu W / m^2$. This means that these high values are not constant but can occur in intervals. To be able to determine the frequency interval, it would be necessary to measure the long-term (at least a week). During the measurements it was found that the maximum intensity of the EM field of GSM base stations appear on the 30% period. Example analysis of high frequency electromagnetic fields in the flat shown in figure 4.

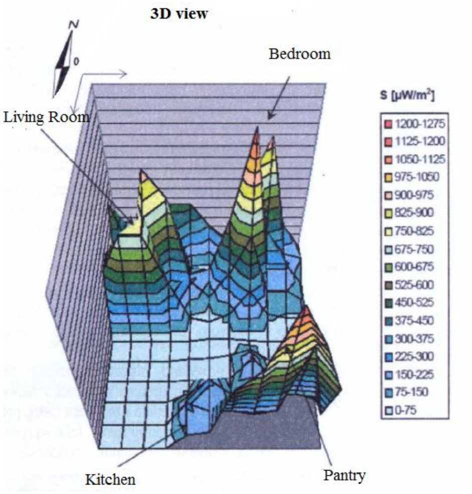

Figure 4. Example analysis of high frequency electromagnetic fields in the flat

CONCLUSION

High-frequency electromagnetic radiation (EMR) is used in mobile and wireless communication (mobile telephony according to the GSM and UMTS standard, cordless phones, wireless local area networks, Bluetooth), many decades also in radio and television technology. The remarkable growth of wireless communication technology over the last decade years has raised public concerns about possible associations between RF fields and adverse health outcomes. At high frequencies, the only mechanism of interaction established to date with living tissues is the transformation ormation of electromagnetic energy in thermal energy in tissues. Current guidelines, limits and regulations prevent any such effect. Moreover, no study has shown adverse health effects at exposure levels below international guideline limits

However, the data of the currently available literature still do not allow to exclude with certainty the possibility of biological effects, and possibly health effects, for exposure intensities lover wer than the levels likely to cause thermal effects. On the other hand, the public continues to be cautious about the effects of the EMR and by large mistrusts the assurance of the authorities with regard to the observance of the safety standards.

With metering methods can be performed checks of electromagnetic radiation and comparison with the reference levels, in order to achieve the approved value, and the limitation set out in the adopted standards and recommendations.

REFERENCES

K. Dervić, V. Šinik, Ž. Despotović, M. Bjelica, V. Kerleta, Radiation of electromagnetic fields at radio frequencies, III International Conference„ECOLOGY OF URBAN AREAS“ 2013, Zrenjanin

http://www.fra.utn.edu.ar/download/cursos/laboratorio_abierto/narda/Narda_SRM3000_ds_2008.p

https://www.google.rs/search?q=electromagnetic+wave+figure&tbm

International Commision on Non-Ionising Radiation Protection (ICNIRP) Guidelines: Guidelines for Limiting Exposure to Time Varying Electric, Magnetic and Electromagnetic Fields (up to 300 GHz), Health Physics, Vol. 74,4 (1998) 494-522

Directive 2004/40/EC of the European Parliament and of the Council of 29 April 2004 on the minimum health and safety requirements regarding the exposure of workers to the risks arising from physical agents (electromagnetic fields),Official Journal of the European Union L 159 of 30 April 2004

Council Directive *98/34/EC of 22 June 1998, laying down a procedure for the provision of information in the field of technical standards and regulations (Official Journal L 204 of 21.07.98) (former Directive 83/189/EEC).*

Savroulacks, P.: *Biological Effect of Electromagnetic Fields.* Springer-Verlag Berlin Heidelberg 2003, ISBN 3-540-429891

SSI’S Independent Expert Group on Electromagnetic Fields: *Health Council of the Netherlands, Mobile Phones; an Evaluation of Health Effects.* 2002, No. 2002/01E, ISBN: 90- 554-9411-9

http://www.123rf.com/photo_10872365_big-television-and-radio-tower-with-several-parabolic-antenna-

https://www.google.rs/search?q=Radio+and+TV+transmitters+fig&sa=N&tbm=isch&tbo=u&source=univ

http://en.wikipedia.org/wiki/Radar

http://www.mmust.elimu.net/BSC%28ELEC_COMM%29/Year_5/ELC-544E

http://www.who.int/peh-emf/publications/facts/fs226/en/

http://en.wikipedia.org/wiki/Transmitter

http://www.mikroe.com/old/books/rrbook/chapter2/chapter2.htm

http://www.radartutorial.eu/01.basics/rb04.en.html

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ENVIRONMENTAL SECURITY IN URBAN AREAS FROM THE ASPECT OF INTELLIGENCE SERVICES

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ABSTRACT

Globalization among many other issues caused rapid urbanization. In such circumstances, urban population is mostly exposed to different kind of risks. Providing security in urban areas in generally is a hard task for policy makers, and all other stakeholders. The concept of sustainable cities is accepted all over the world and, within this framework, environmental issues are also surfacing at the top of the global agenda. Therefore, this is the main point of this paper, providing adequate environmental security in urban areas. In this paper, authors present how urgent it is to understand that intelligence services could be of enormous help in this process. The paper especially points out the importance of positive practice of the most famous intelligence agencies all over the world. Conclusion remarks confirmed that despite the fact that Serbia faces obvious misunderstanding of some of the activities of the intelligence community, as a society we have to establish new approach which would allow them, among other activities defined by the law, to be helpful in the improved response of the institutions to all types of events in which environmental and general security are jeopardized in urban areas. Serbia has to follow the practice of developed countries and leave behind the inheritance from the past.

Key words: *urban areas, intelligence services, prevention, terrorism, actions.*

INTRODUCTION

Urbanization is a continual process in global community, and at the current rate over 65 million people are leaving the countryside each year, moving to the cities; which provides the basis for the prediction that nearly 70% of the population will live in urban areas by 2035 (United Nation, 2014). Almot all cities are expanding without any plan and its population is exposed to the different risks (Radović at all, 2013). The document of the Asian Development Bank’s Urbanisation Strategy 2020 states that “liveable cities” in future will be fostered through support for infrastructure, with programs that focus on water supply, sanitation, waste management, and urban transport; and urban shelter programs of slum upgrading, land development, housing, and housing finance (Weiser and Beswick, 2008). Getting sufficient amounts of clean water to residents will be a priority for every major mega city, as well as providing uninterrupted functioning of other urban infrastructure systems like electricity, waste management, transportation, telecommunication, health facilities, education, and other public services. Among all of these social needs, security is something which is most needed in urban areas. Decreased crime level, antisocial behaviours, prevention of terrorist attacks against critical infrastructure systems, and protection of population and environment are priority tasks for national security services.

In that protection process the work of intelligence services is of paramount importance. Intelligence community all over the world today has to function in a radically changed environment as an important part of the national security system. Threats to national security in any country are more diverse, interconnected, and more complex than at any time in history. Hence, the intelligence community is involved in every aspect of safeguard national interest. Intelligence community has many new tasks: now monitors shifts in human geography, climate, disease, and competition for natural resources because they fuel tensions and conflicts (United States Intelligence Community, 2013).

Intelligence services in the dynamic society today have to deal with new challenges in its work. Professor Mark M. Lowenthal, said that intelligence is information that has already been systematized, processed and evaluated, and that satisfies the expressed needs of decision or policy maker (Lowenthal, 2006). Although attempts to explain the concepts of intelligence are endless, certain fundamental observation are obvious There are so many definition of intelligence in security theory, but for the purpose of this paper authors chose to explain that intelligence is »information not publicly available or analysis based at least in part on such information, that has been prepared for policy makers or other actors inside the government« (Council on Foreign Relations, 1996).

Most scientist consider intelligence from two points of view:

1. As evaluative information which targeted at external targets, and
2. As the information so gathered and evaluated usually for the purpose of national or regional security by the state or the government of a country.

Therefore, authors from a view of activities needed in the area of decreasing environmental risks in urban areas address in the paper the second issue mentioned above: improving the role of intelligence community for better national environmental security.

Based on the above-mentioned facts, there is a specific need that, for those not so familiar with security issues and national security organization in the Republic of Serbia the authors present briefly at the beginning of this paper the established organization of intelligence community. Environmental risks in urban areas permanently increased due to numerous reasons, and policy makers have to have reliable and timely information in future activities. Environmental terrorism as well as eco terrorism are two of those risks recognized by the international community (United Nation, 1987; The USA Environmental Protection Agency-EPA, 1996; Floyd, 2010).

Authors organized this paper in the following way. The introductory chapter is devoted to the presentation of linkage among current activities in the area of environmental protection in urban areas, a brief explanation of intelligence services in the urban risk reduction area, as well as activities of other subjects of national security. The second chapter discusses how Serbia has to move forward regarding the adequate level of environmental security in urban area. Therefore, the intelligence community and counter terrorism measures needed to protect environmental components (air, soil, water, and biodiversity) have to be a part of the intelligence activities in every country. In the second chapter, there are few presentations of current environmental threats interesting for intelligence services in foreign countries, as well as conclusion remarks and reference used in the process of paper preparation in following two chapters of the paper. The main goals of this paper are to attract greater attention of intelligence community to this important area need for the society development in general. The conclusion remarks show that Serbia has to pass the gap between citizen trust and the belief that intelligence community is »a super power which deals only with specific issues«. Serbia has to increase the role of the intelligence community in the process of achieving accepted sustainable development strategy in the society. There is also a discussion about the future plan which would improve environmental security in urban areas as a part of national security strategy.

The methodology used in this article is standard for social researchers: historical analysis, comparative analysis and data analysis. It allows authors to use various documents from electronic databases, books, scientific journals, official documents and positive practice from developed countries like Canada, the United States of America, Israel etc. After a careful analysis of the data, all facts confirm that the activities of those agencies in the area of providing environmental security are rare and insufficient, but some recent news is pretty encouraging. Authors collected all data from open sources and deny intention to encourage anyone to jeopardise fragile environment in the Republic of Serbia. Having in mind all the presented facts, it is clear that intelligence services in Serbia have to be more engaged in the actions helpful to national security stakeholders in the process of providing adequate level of environmental security in urban areas.

WHAT KIND OF ROLE INTELLIGENCE SERVICES SERBIAN SOCIETY COULD EXPECT IN URBAN AREAS

At the beginning of this chapter, authors consider the need to explain briefly the organisation of the established intelligence services. There are three agencies which are a part of a unique security-intelligence system of the Republic of Serbia: Security-Information Agency (SIA), Military Security Agency (MSA), and Military Intelligence Agency (MIA) (Law on the Bases of Security Services Organisation in the Republic of Serbia, 2007). Security-Information Agency is civil, security and intelligence department of the Republic of Serbia (Law on Security-Information Agency, 2009). It is an independent, specialized organization in the system of government organizations, having the status of a legal entity. In accordance with the law, the Agency is in charge of the protection of security of the Republic of Serbia, and, consequently, also environmental security. Article 2 of the Law on Military Security Agency and Military Intelligence Agency defines MSA and MIA as administration bodies within the Ministry of Defence which perform security and intelligence activities significant for defence (Law on Military Security Agency and Military Intelligence Agency, 2009). From current National Security Strategy of the Republic of Serbia adopted in 2009, the role of national security entities are also obliged to help in the emergencies where civil capacities are exhausted.

In accordance with the main goal of the paper, the authors’ intention is also to present briefly why the environmental security has to be more recognized in the work of intelligence services based on the current legislation in the area of environmental protection. The healthy environment is guaranteed under Article 74 of the Constitution of the Republic of Serbia (Constitution of the Republic of Serbia, 2006). In line with this Article, everyone has the right to healthy environment and timely and thorough information about its state. Environmental protection is also provided through criminal law protection. Environmental crime is explicitly laid down by the Criminal Code, which includes a special chapter “Criminal Offences against the Environment” containing 18 offences against the environment, (Articles 260-277) (Criminal Law of the Republic of Serbia, 2014). Therefore, the linkage between intelligence and environmental security in theory and practice is obvious, because some of the intelligence activities are closely linked to the adequate level of national environmental security. In Serbian public, this was for the first time clearly stated by Prime Minister Aleksandar Vučić, who claimed that during the floods in spring 2014, the town of Šabac »had to be defended at any cost, because it represented an enormous environmental threat to a great part of Serbia«, referring to the special report prepared by SIA. The reason for that report lies in the fact that after an unsuccessful process of privatisation, a large number of chemical factory in Šabac was recognized as enormous an environmental threat (Radović and Domazet, 2010).

During the floods in spring of 2014, it was obvious that thelocal government all over Serbiaas well as the Republic of Croatia, and Bosnia and Herzegovina were not adequately prepared for such an extensive disaster. Policy makers faced numerous challenges as to how to conduct the urban risk management; without adequate knowledge and skills in emergency management; without sufficient administrative-capacities; shortage in local budgets; lack of coordination between different hierarchical levels (local, regional and national-central); weak law-enforcement mechanisms. Sometimes even humanitarian relief was a source of corruption instead of response on human basic need. Serbia despite a great public attention and long-term consequences from the past emergencies missed significant actions in the field of promoting a culture of prevention at all levels.However, this did not lead to the improvement of emergency management practices in urban areas. Policy makers in Serbia, as well as a great part of the science community speak loudly about the urgent goals regarding the protection of critical infrastructure, cyber terrorism, and terrorism in general as a great threat to our society, but they remain silent when numerous cities lack drinking water for months, even years. They are speechless about the inadequate management of hazardous waste, inappropriate water management, insufficient surveillance in many fields relaed to environmental health issues. Furthermore, all over the country, there are obvious abuses of enterprises regarding the established environmental laws, and social responsibility strategy (Socially Responsibility Strategy, 2010). Hence, it is a well-known fact that the final goal of environmental terrorism has is possible terrorist action, which will cause smaller or greater damage to one or more environmental components: atmosphere, hydrosphere, biosphere or lithosphere. However this was not enough for our policy makers to recognize it as a domestic environmental threat (Radovic, 2014).

Serbian intelligence services have to become more involved in the area of environmental protection, knowing that some of the environmental risk could bring enormous damage and impact to national security. They have to become more visible as a part of the solution to the problem in two directions. First, it should include efforts to prevent possible attacks and sabotage; as well as the abuse of enterprises due to different reason: social dissatisfaction, neglection of management obligations arising from environmental protection legal framework, in search of a greater profit; corruption in the local community, which hides the actual state of environmental component - contaminated soil, polluted air, or even polluted water or food etc. The second task for intelligence services is to work jointly in the process of public and media education about actual environmental risks and consequences from the possible environmental terrorist threat in Serbia, and the wider region. It is important to understand that terrorist attacks that fail to kill or injure people, or cause environmental degradation could have an important political repercussions by affecting public perception, reducing confidence in institutions and forcing inappropriate political responses (Radovic and Trivan, 2014).

Serbian intelligence community does not work for itself. Depending on the results of intelligence, other institutions could make the necessary decisions and initiate appropriate actions regarding the adequate level of national, regional, and international environmental security. Serbian intelligence community has to follow the positive practise achieved in the work of the Federal Investigation Bureau in the USA (FBI). The FBI has developed a strong response to domestic terrorism threats and together with partners, it endeavours to detect, disrupt and dismantle the environmental extremist movements. Those actions are headed by a headquarters-based team of national intelligence analysts, program managers, and seasonal field agents. Since this paper serves as an initiative for future scientific work regarding similar issues, the authors decided to only mention (without detailed explanation) the need for legal surveillance of citizen communication as a preventive measure. As Serbian intelligence agencies already have been accused of illegal surveillance of private communication, which is against the Constitution, this part of intelligence activities have later been performed in legal way (Europen Court of Human Rights, 2013). Surveillance is needed as help in the process of increasing the level of environmental security, but not to be used for violation of human rights and personal freedom. The experiences during the great flood when some citizens were accused of spreading panic via social networks, has pointed to the urgent need for an improved legal framework in this area, and strict respect of the adopted European framework regarding personal privacy. Scientific and wider community was not so friendly regarding the intelligence work, which had not been based on legal framework even despite the changes recently adopted by the Serbian Parliament. The government changed the current law of intelligence in order to avoid discordance between its work and constitutional definition. Numerous statements could be found in media and this also changes all governmental efforts that have been considered »cosmetics and insufficient’« (Law on Security-Information Agency, 2014).

Serbian society and especially the intelligence community need to have access to the most accurate and timely information available to help them respond to these emergencies in the urban area. Furthermore, it would be unreasonable to deny its purpose, but intelligence community has to work according to the legal framework avoiding any action that can be described as illegal and directed against the fundamental human rights, freedom of speech and the right to privacy. Only this way, the intelligence community will avoid the consequences of possible environmental risks in urban areas.

BE ON THE SAME SIDE: MOVING TOWARDS BETTER ENVIRONMENTAL SECURITY IN URBAN AREAS

Intelligence community all over the world conducts counter-terrorism activities regarding general and environmental security in urban areas. These activities became more intense after the 9/11 attack in New York, which changed the attitude of security services towards the urban security. Numerous agencies performed activities regarding environmental security like Australian Secret Intelligence Service (ASIS), Canadian Security Intelligence Services (CSIS), and Secret Service of Great Britain - MI5 and Military Secret Service MI6, and other European intelligence agencies. Investigation and prevention of environmental terrorism has to be put on the agenda in the same way it has been done with other kinds of terrorist threats. In the region of the Western Balkans, collaboration in the area of environmental security is very important for several reasons. Due to the geopolitical position of the Balkan Peninsula, there are numerous interconnections among countries, like waterways, lakes etc. Hence, intelligence services have to be aware that waterways could jeopardise the security of many towns downstream, because many of our biggest cities are situated on and near the rivers such as Danube, Tisa, Sava, Drina, Morava etc.

In the security theory in general, it is a well-known fact that intelligence operations in urban areas may have more restrictive operational limitation than operations elsewhere. Members of the intelligence community have to collect information about urban areas with sufficient knowledge about cultural, political, social, economic, ethnical and religious factors which impact security issues. This action is crucial for the results, which can only be reached through constant monitoring, assessment and analyses. Cities are heterogeneous and the challenges and solutions in one area of a city many differ greatly from those in other areas of the city. Environmental risks and consequences from those risks will vary based on the unique urban environments of a particular city for example: geographic position, climate conditions, density, sanitation, etc. The population’s exposure to different pollutants, like toxic industrial material (TIMs), and/or attacks with actual weapons of mass destruction (WMD) could also differ in scope and consequences.

Considering numerous experiences from the international community, the authors decided to dedicate substantial importance to the U.S. Urban Area Security Initiative (UASI), (Federal Emergency Management Agency-FEMA, 2013). It is designed to set a strategic direction for the enhancement of regional response capability and capacity in USA. This initiative has goals to:

1. Ensure group decision-making process;
2. Maintain an “all hazards” approach, meaning looking toward and planning for all possible natural (hurricanes, flooding, etc.) and man-made disasters (chemical, biological, nuclear, radiological and explosive terrorist attacks);
3. Emphasize incident command and unified command structure;
4. Enhance capabilities through planning, equipment, training and exercises that include all disciplines;
5. Create a higher level of response capability for emergency response teams;
6. Develop a financing and re-sourcing strategy, and
7. Enhance response capabilities of detection and decontamination, mass casualty, and Urban and Rescue teams.

The recommendation is that maybe it is a time for Serbian policy maker to think about establishing some form of joint task force with government and non government stakeholders in the field of providing better environmental security for Serbian population. Intelligence community has to work closely together to ensure that our cities remain as safe and prepared for any and all emergencies as possible. They have to reduce urban area vulnerability by strengthening the cycle of response and by ensuring that potential targets are identified, assessed and protected.

CONCLUSION

The most influential international organisation today addressed links between environmental sustainability on the one hand, and peace and security on the other. Despite numerous obstacles in providing adequate level of overall and environmental security, all stakeholders are devoted to this action. First of all, the United Nations Organisation with its Peacebuilding Commission, and the United Nations Environmental Program (UNEP), as well as other institutions is starting to highlight these links. The region of Western Balkans has been recognized as one of the vulnerable environmental regions, including Serbia. Despite the numerous obstacles inherited from the past, Serbia has improved its relations with the neighbouring countries. Currently, as a country which started negotiations for a full membership in the European Union, Serbia “promotes cooperation, achieves visible progress on the path to the European Union and strives to improve the lives of the people.” Serbia showed willingness to be a “factor for peace, security, and stability in the Balkans” and beyond. It has also done a lot in the field of environmental security. However, in the provision of environmental security, it could assign a more visible role to intelligence services, just as it devotes much importance to the improvement of the current state of security at national, regional and international levels within fight against terrorism and organized crime. In the future, it would be wise for Serbian intelligence services to adopt new approaches and methods used by most influential intelligence organizations. If they want to be well-prepared to detect, deter, mitigate, respond to, and recover environmental threats to urban areas, they have to be permanently involved in actions.

REFERENCES

Constitution of the Republic of Serbia. (2006). Official Gazette of the Republic of Serbia, No. 98/2006.

Council on Foreign Relations. (1996). Making Intelligence Smarter: Report of an Independent Task Force, New York, USA.

Criminal Law of the Republic of Serbia. (2011). Official Gazette of the Republic of Serbia, br.72/2011, 101/2011, 121/2012, 32/2013, 45/2013 i 55/2014.

European Court of Human Rights. (2013). Case no 48135/06 Youth Initiative for Human Rights, Serbia. 25 June 2013, p. 6.

Floyd, R. (2010). Securitization theory and US environmental security policy. Cambridge: Cambridge University Press.

Law on Military Security Agency and Military Intelligence Agency. (2009). Official Gazette of the Republic of Serbia, No 88/2009.

Law on Security-Information Agency. (2014). Official Gazette of Republic of Serbia, No. 42/02 and 111/09-amendment and the newest 65/2014).

Law on Security-Information Agency. (2002). Official Gazette of the Republic of Serbia, No. 42/02 and 111/09-amendment.

Law on the Basics of Security Services Organisation in the Republic of Serbia (2007). Official Gazette of the Republic of Serbia, No. 116/2007.

Lowenthal, M. M. (2006). Intelligence: from Secrets to Policy, third edition, Washington D.C. CQ Press.

Radović V., & Domazet, S. (2010). Uloga privatizacionog procesa u Republici Srbiji u funkciji ugrožavanja bezbednosti građana i životne sredine - drastični primeri. Poslovna ekonomija. No. 2, pp. 151-169.

Radovic, V., & Andrejevic, A. (2014). Environmental Terrorism as a Threat to Serbian Water Infrastructure Sector-through the Lens of Regional Perspective. NATO Advaced Research Workshop Managing Terrorism Threats to Critical Infrastructure - Challenges for SE Europe, Belgrade 12-15 maj. Serbia.

Radović, V., & Trivan, D. (2014). Do we really understand why environment became an important task for the Intelligence Community in the global world. In Intelligence and Combating Terrorism-New Paradigm and Future Challenges, pp. 53-67. Eds. Denis Čaleta & Paul Shamela, Institute for Corporative Studies and Center for Civil Military Relations, Navall Post Graduate School, Ljubljana, Slovenia.

Radović, V., Vujić, B., & Lečić, D. (2013). Application of ICT as a necessary tool of emergency response in urban areas. 3. International Conference "Ecology of Urban Areas", Zrenjanin: University of Novi Sad, Faculty of Technical Sciences "Mihajlo Pupin", 11 Oktobar, 2013, pp. 518-524, ISBN 978-86-7672-210-5.

Serbian Government. (2010). Serbian National CSR Strategy. Retrieved January 24, 2012 from http://www.minrzs.gov.rs/folder_1/Strategija_konacno.doc, 18. 8. 2014.

Strategija nacionalne bezbednosti Republike Srbije. (2009). Beograd, http://www.vba.mod.gov.rs/strategija_-20nacionalne_bezbednosti_lat.pdf, 15. 08. 2014.

U.S. Environmental Protection Agency-EPA. (1999). Environmental Security: Strengthening National Security through Environmental Protection. Washington, D.C.

United Nation. (2014). Facts about urbanisation. Available at: http://esa.un.org/unup/walcharts/urban-rural-areas.pdf, 2. 9. 2014.

United Nations. (1987). International Ecological Security. UN. Doc A/C.2/42/L. 34 (1987).

Urban Area Security Initiative (UASI). (2013). USA Federal Emergency Management Agency-FEMA. http://www.fema.gov/fy-2013-homeland-security-grant-program-hsgp-0#2, 12. 8. 2014.

US Intelligence Community. (2013). House Permanent Select Committee on Intelligence. James R. Clapper Director of National Intelligence Statement for the Record: Worldwide Threat Assessment of the US Intelligence Community.

Weiser, I., & Beswick, J. (2008). The Asian Development Bank’s Urbanisation Strategy 2020 -A Review of Strategy Changes and An Assessment of New Opportunities for Collaboration. Available at: http://sihp.brandeis.edu/ighd/PDFs/ADB-2020-StrategyChanges-Opportunities-09-08.pdf, 28. 8. 2014.

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FORENSIC ANALYSIS OF MICRO TRACES OF THE EVENTS IN URBAN AREAS

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ABSTRACT

The objective of forensic analysis of micro traces is twofold: to determine the type and the extent of damage after the accident situation in urban areas and to prevent certain actions in order to protect the assets of citizens. It is necessary to determine the type and extent of damage in order to find the offender, no matter if accident is intentional or random event. Timely and justified sanctioning of the offenders in urban areas act in order to prevent individuals with criminal backgrounds to perform criminial acts. Fire on buildings or motor vehicles, as well as usage of explosives on them, are events that are part of lives of citizens in both urban and provincional areas. Timely and professional detection of micro traces, their treatment in the forensic laboratory and the proper interpretation in the legal framework, aim at the effective sanctioning and prevention of the perpetrator of crime, in order to preserve citizen assets.

Key words: *Forensics, micro traces, accidents, urban areas, fires and explosions.*

INTRODUCTION

In real cases, after fire on objects or motor vehicles and after detonations of explosive devices which have been placed within motor vehicles (car bombs), during the investigation micro traces are taken from expected locations. For the situation in which object was on fire, material that hasn't been completely burned and for which is believed that was part of the fire or was buried by burned material, is being sampled (parts of the floor or carpets, parts of electric cables). If the fire occurred on the motor vehicle or if the explosive device was placed underneath, the following material is being sampled: smear from the parts of the vehicle that hasn't been overtaken by fire, earth under the vehicle (from crater or nearby area), nearby objects, etc. Since micro traces are invisible, their fixation and exclusion is being done by collecting of smears (with the certain organic solution: n-pentane or n-hexane, diethyl ether or acetone) from characteristic locations and nearby objects. Broken parts and debris where micro traces are expected to be found are also collected. Type and cause of fire is determined through laboratory analysis of collected material, by procession according to standardized procedure.

In this paper some examples of fire on objects are presented. Paper encompasses accident cases in both urban area (fire on building of "Radnicki Univerzitet", "Putnik" hotel) and distant resort ("Lisine" motel in the upper basin of river Resava).

FIRE ON OBJECTS

Maybe the best definition of fire is that it is an uncontrolled burning of matter which threatens the human lives and causes material damage. It is known that three conditions have to be fulfilled for fire to be caused: existence of fuel material, source of heat and presence of oxygen. The goal of this paper

is not to present the theory of fire, its occurrence, spreading and stopping, but rather to present the forensic approach to accident locations and ways of processing of collected samples [1-3]
According to the following three case studies, types of fire, ways of material sampling and results of laboratory analysis will be presented [7].

The building of “Radnicki Univerzitet” in Novi Sad was destroyed by fire which was the consequence of short circuit on old and damaged electric installations, as shown by conducted analysis. In Figures 1- 5, the moment of fire spread-out on the object is presented.

Figure 1. “Radnicki Univerzitet” burning

Figure 2. Fast expansion of fire to other floors

After fire extinguishing, material from debris was sampled, from locations which were the least under the influence of heat. The results of obtained analysis were without doubts: the cause of fire was old and damaged electric installation. The air pollution after the fire was significant, strongly affecting, due to the wind, flora and fauna down the Danube River.

One part of the hotel “Putnik” was destroyed since fire caught the entrance part and lower levels, Figures 3 and 4. After localization and extinguishing of fire, materials not influenced by the fire were sampled. Since there were indications that the fire was set up, the first author of this paper personally sampled the plastic parts underneath the debris on staircase, and carpet as well.

Figure 3. Hotel „Putnik“ burning

Figure 4. Fire spreading

In the part containing physical and chemical analysis, chromatograms of detected organic solvents and their interpretation, according to which is concluded that fire was set up, are provided.

Catering object – “Lisine” motel was burned completely, Figure 5. Sampled material showed that the cause of fire wasn’t due to the old electric installation, nor the traces of flammable carbohydrates were detected, which would indicate intentional set up. In the end, investigation showed that it was an accident, caused by inattention.

Figure 5. Fire in motel „Lisine“ on the river Resava

FIRES ON MOTOR VEHICLES

Determination of the cause of fire on motor vehicles is based on the material traces and analysis at the scene of accident [7]. The example that will be presented is a fire on the bus of public transportation company “GSP Novi Sad”, which occurred while the vehicle was parked in the company’s parking area, Figures 6 and 7. After conducted analysis of possible causes of fire, based on the damage and deformation of certain parts of bus, there was a doubt that the possible cause of fire is malfunction of electric installation. Thus, the parts of cables are sampled and analyzed in laboratory. Results indicated that the primary short circuit of the conductor of power relay is cause of fire. Details of laboratory analysis are presented in chapter dealing with physical and chemical analysis.

Figure 6. Completely burned bus of “GSP Novi Sad”

Figure 7. Location of the primary fire

Accident caused by the explosive device didn’t cause significant material damage on the nearby objects, while the owner of the vehicle died at the place of accident. Material damage of the vehicle is non-proportional to the estimated amount of explosive, due to the usage of controlled and directed detonation, Figures 8-11.

Figure 8. Vehicle after activation of explosive device

Figure 9. Closer look of the damaged left side

Figure 10. Front part of the vehicle

Figure 11. Damaged vehicle from another angle

Results of the laboratory analysis are provided in chapter dealing with physical and chemical analysis.

Physical and chemical analysis

For the physical and chemical analysis the following methods are used [6]:

- gas chromatography method with mass spectrometer (GC/MS), instrument produced by Agilent.
- Fourier transformation infrared spectrophotometry method (FTIR), Thermo Nicolet Corporation, model Nexus 6700, ATR technique.

By analysis of recorded chromatograms it can be concluded that the retention time of the sample from hotel “Putnik”, after adequate extraction, corresponds to the retention time of the standard of flammable liquid – petrol (Figure 12).

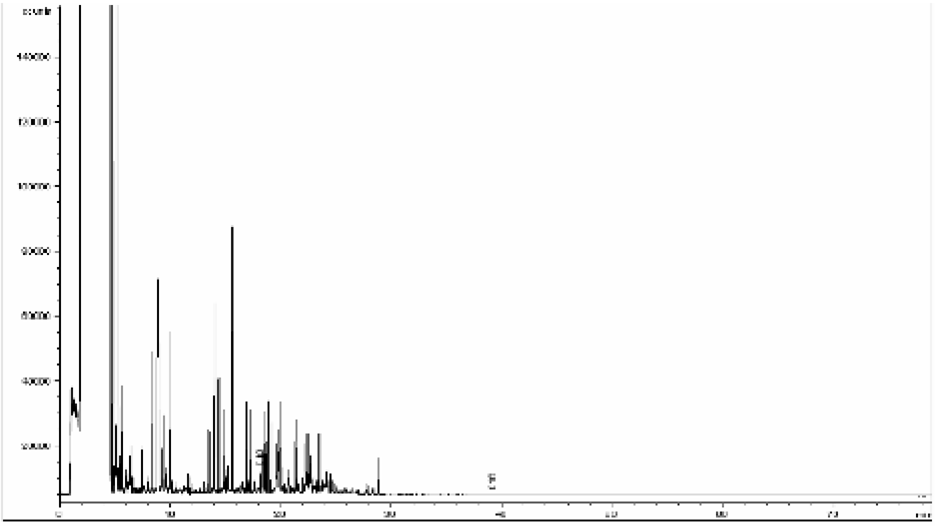

Figure 12. Chromatogram of the petrol sample

By analysis of GC chromatogram it can be concluded that the retention time of the analyzed sample, after adequate extraction, corresponds to the retention time of the standard of 2-methyl-1,3,5-trinitrotoluene.

In the case of the aforementioned fire on the bus of “GSP Novi Sad”, during the analysis the several factors have been taken into account. Since the electric installation can be found in each part of the vehicle, almost all consumers of power were installed through the fusers that were checked. According to Ohms and Joule-Lenz law, fire can be caused in several ways:

1. through heating of electric current conductor, due to the thermic resistance,
2. through short circuit,
3. through high transition resistance (electro-corrosion, back current),
4. through formation of Volt’s arc and
5. through overload of electro-thermic device.

For the analysis of the condition of electric conductors in the moment of fire, the following samples were taken:

1. Electric line above air cleaner, sample number 1.
2. Melted grey piece of metal and its corresponding part that looks as cable, sample number 2
3. Water pump with all remaining cables, sample number 3
4. Hood of the “Webasto” preheater, with the cable and programing panel rests, sample number 4,
5. Electro-hydraulic ventilator valve with cables, sample number 5

Figure 13. Collected samples for laboratory analysis

Through observation with stereomicroscope, melted endings of the conductors due to the volt arc were observed, Figures 14 and 15.

Figure 14. Melted ending of the cable

Figure 15. Closer look of the melted cable

Based on the suspicion that the formed short circuit is the primary cause of fire, not secondary, microstructure of the sample was analyzed by Debye-Scherrer method (X-ray analysis). Using Debye-Scherrer diagram it was concluded that the location of interruption of conductor is rich with oxygen, indicating the primary short circuit causing the fire [4,5].

By analysis of the obtained FTIR spectrogram of the layers of green color it is found that functional groups of investigated sample are corresponding to functional groups of the standard of cuprum oxide, as a consequence of contact between cuprum conductors with oxygen from air and water.

According to the collected evidences it can be concluded that the cause of fire on the “GSP Novi Sad” bus was short circuit on the power conductor of the program panel shielding relay.

For the examples of explosion on vehicles, the following material is sampled for the necessity of forensic investigation: smear of n-pentane and acetone, smear from the chassis of the vehicles in the closer and distant area around the location where it was assumed that the explosive device was placed, different parts of vehicle and parts of the crater under vehicle.

Through laboratory analysis of the collected samples and comparison of the obtained spectra it was concluded that functional groups of samples correspond to the cyclotrimethylenetrinitramine, which was confirmed by laboratory analysis of the obtained GC chromatogram. It is also concluded that the retention time of the analyzed sample corresponds to the retention time of the standard of cyclotrimethylenetrinitramine, which is also known as RDX or hexogen, Figure 16.

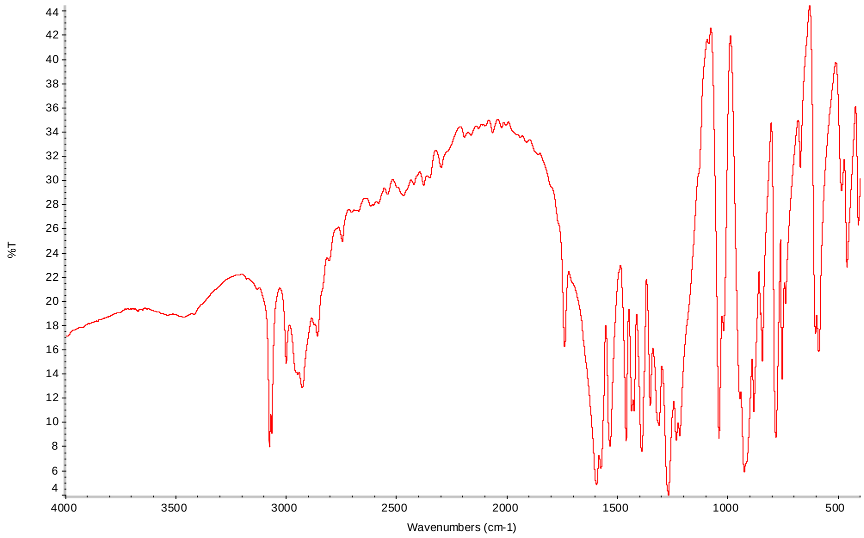

Figure 16. FTIR spectrogram of the military explosive Hexogen (RDX)

CONCLUSION

Accident situations in urban areas lead to the higher or lower pollution of environment, depending on the type of flammable material caught by fire. Presented examples of accident situations and presented methodology of their procession, enables closer understanding of the type of fire and ways of its confirmation, as well as confirmation of fire location and cause of its formation.

REFERENCES

Maksimović R., Todorić U.: Criminalistic Technique, Academy of Police studies, Belgrade, 1997.
Maksimović R., Todorić U., Bošković M.: Method of Physics, Chemistry and Physical Chemistry in Criminalistics, Academy of Police studies, Belgrade, 1996.
Busarčević M., et all: Basic of Crime Experts, Ministry of Interior of Serbia, Belgrade, 2001.
M. Prutton: Introduction to Surface Physics, Clarendon, Oxford 1995.
Kiely, Terrence F.: Forensic evidence: Science and the Criminal law, CRC Press LLC, 2001.
Zorić, V.M.: Analysis of mechanical oscillations in the colored coating and method of application of results in forensic research, Dr. thesis, TF M. Pupin, Zrenjanin, University of Novi Sad, 2009.
Zorić, V.M.: Reports of the completed Trassological and Physical-Chemical expert's National Crime Technical Center Ministry of Interior of Serbia, in the period 2000 - 2012, Belgrade.

PUBLIC HEALTH AND THE ECOLOGY OF URBAN AREAS

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ECONOMIC ASSESSMENT OF DAMAGE FROM THE RADIATION EMERGENCY SITUATION

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ABSTRACT

In work methodological positions, techniques and the recommendations providing the fullest account of factors of the general economic damage at a radiating emergency situation are generalized. The offered conceptual approaches to an economic estimation of a damage give the chance to solve problems of applied character, in particular, to form ecological, economic-economic, investment and social policy at regional level.

Key words: *radiation, the population, health, economic damage.*

INTRODUCTION

Among the environmental problems of the present including a large number of the natural and technogenic emergency situations, the most adverse and dangerous radiation emergencies as they have the long-lived character are considered, and social, ecological and economic consequences of a radiocontamination affect many generations of the people living in polluted territories. The quantitative definition of the factors forming economic damage from a radiation emergency defines paths of further social, ecological and economic development of the region. Otherwise it is fraught with low level of the life raised by incidence and mortality, initiation of the migratory processes leading to stagnation, destruction of a social and economic structure. Definition of the caused economic damage to affected areas allows to carry out necessary decontamination measures, to carry out sufficient social protection of the population living in conditions of radiation influence. Optimization of measures for improvement of a surrounding medium and to providing conditions of activity of the population objective causes an assessment of the economic damage caused by a radiocontamination. Theoretical justification and development of methodological and methodical recommendations about definition of economic damage from a radiation emergency, establishment of relationships of cause and effect between radiation influence and changes in habitat are necessary for determination of optimum volume of held protective events and the directions of ecological and social and economic rehabilitation of the region.

Social and economic problems of the polluted territories demand differentiated approaches to the solution of questions of elimination of the negative consequences of the economic degradation caused by radiation influence, ensuring efficient functioning of an economic complex and transition to steady development on the basis of state programs of rehabilitation of territories.

It should be noted that absence or a failure of rehabilitation actions during the long period causes and predetermines the corresponding sotsio-ekologo-economic effects. Now there is a problem of an economic assessment of the damage, not having the standard decision despite a number of the large radiation emergencies which have occurred in the territory of the former Soviet Union (Sverdlovsk and Chelyabinsk areas, Semipalatinsk, Chernobyl). Therefore scientific definition of economic damage from a radiation emergency has not only informative character, but also allows to use it as the economic tool for an actual assessment of the directions and volumes of rehabilitation measures.

METHODS

The methodology of an assessment of damage from a radiation emergency has to consider social, ecological and economic consequences. It is thus important to define both direct losses, and indirect because the social, ecological and economic damage is bound to influence of radiation and possible nonspecific consequences which can be shown through the long time. Highly appreciating a contribution of a number of scientists and the results received by them, it should be noted that level of a readiness of a problem of definition of economic damage from environmental is represented poor, demands specification in aspect of an assessment of damage in the conditions of a radiation emergency. Definition of losses which are sustained by social, ecological and economic system from restriction of environmental management, activity, need of maintaining and improvement of conditions of the long-lived accommodation of the population on is radioactive the polluted territories demand padding studying, as predetermined the common orientation of this research.

Due to explained above, the purpose of work development of theoretical, methodological and methodical bases of definition of economic damage from a radiation emergency, scientific justification and the offer of approaches and methods, a specification of indexes defining it, justification of techniques of their assessment at creation of conditions for the long-lived accommodation of the population in territories where rehabilitation is carried out is.

FINDINGS AND DISCUSSION

Multilevel character of a problem of an assessment of economic damage and formation of conditions of the long-lived accommodation of the population in a zone of radioactive influence caused need of use of set of scientific approaches, including ecosystem and social and economic which have to be bound to prospects of regional development, the rational environmental management, a sustainable development of the region. Use of opportunities of the specified approaches and methods allows to reach the necessary depth of research, to provide reliability and validity of provisions, to increase objectivity of the analysis, conclusions and recommendations.

As informational base of researches the operating official normative and legal documents of Republic of Belarus regulating development of territories, got to a zone of radiation influence, normative and help and statistical data of the State statistical committee are used, data of managements on economy of regional executive committees, regional committees on natural resources about an ecological, economic, social, demographic state is radioactive the polluted territories of the republic, the theoretical and actual materials containing in published works of scientists-ecologists, economists, experts in environmental management economy, results of characteristic researches of the author, executed RNIUP Mogilyov branch "Radiology institute", Management on problems of consequences of accident on the Chernobyl NPP of the Mogilyov regional executive committee according to plans of researches according to State programs of minimization of consequences of accident on the Chernobyl NPP.

During performance of work the scheme of carrying out an assessment of straight lines and the mediated consequences of a radiation emergency by means of establishment of relationships of cause and effect between radiation influence and the changes caused by it in environment and habitat of the person that allowed to present structure of the factors defining damage, caused to social, ecological and economic systems is defined. Direct consequences of a radiation emergency is the radiocontamination of ecosystems that leads to steady irreversible ecological violations. And, even partial improvement of an ecological situation requires continuous carrying out protective measures on improvement of quality of the environment (figure 1) to which it is possible to refer, for example, deactivation of objects of infrastructure, burial of radioactive materials, actions for decrease in receipt of radionuclides in a surrounding medium. In addition, refer losses of objects of social and production infrastructure to direct consequences of a radiation emergency, radiative effects on the person and the losses of health corresponding to it. To protect the population from radiation influence or, at least, to reduce this influence, it is necessary to solve a number of organizational, economic and technical tasks, i.e. to carry out protective measures.

Refer environmental to the indirect (mediated) consequences of a radiation emergency radionuclides and radiative effects on the population and the territory leading to deterioration of social and economic conditions of accommodation. The ecological component of radiative effects on the territory, in relation to the polluted regions of Republic of Belarus, carries long-term "chronic" character. The radiation emergency led to accumulation of radionuclides on farmlands, in a flood plain and ground deposits of the basin of the Dnieper River, to deduction from water use of some lakes, deduction of arable lands, haymakings, pastures, woods from economic circulation. All this led to essential damage to environment, restriction of environmental management and activity in the region, having had the considerable impact on the developed infrastructure of territories that caused the negative social effects.

Using systems approach in an assessment and identification of problems of social and economic development it is radioactive the polluted territories, the structure of hierarchical set of the factors characterizing social and economic system, their internal and external relations with each other (figure 2) is made. Owing to a radiocontamination there is a decrease in level of the production and agricultural production that leads to the economic consequences having essential impact on development of the polluted territories. Important negative social consequences are specific losses of health which are shown in body height of oncological and genetic diseases, increase of mortality of the population and as a corollary, in the decrease in life expectancy caused by a chronic exposure at continuous accommodation in the territory polluted by radionuclides. At the same time deterioration and a standard of living, bound to economic losses in production, can cause increase of nonspecific incidence of the population. For clearer idea of a picture of social and economic consequences of a radiocontamination of territories, it is necessary to estimate quality and a standard of living of the population living in such territories and to compare the level of nonspecific diseases with control areas.

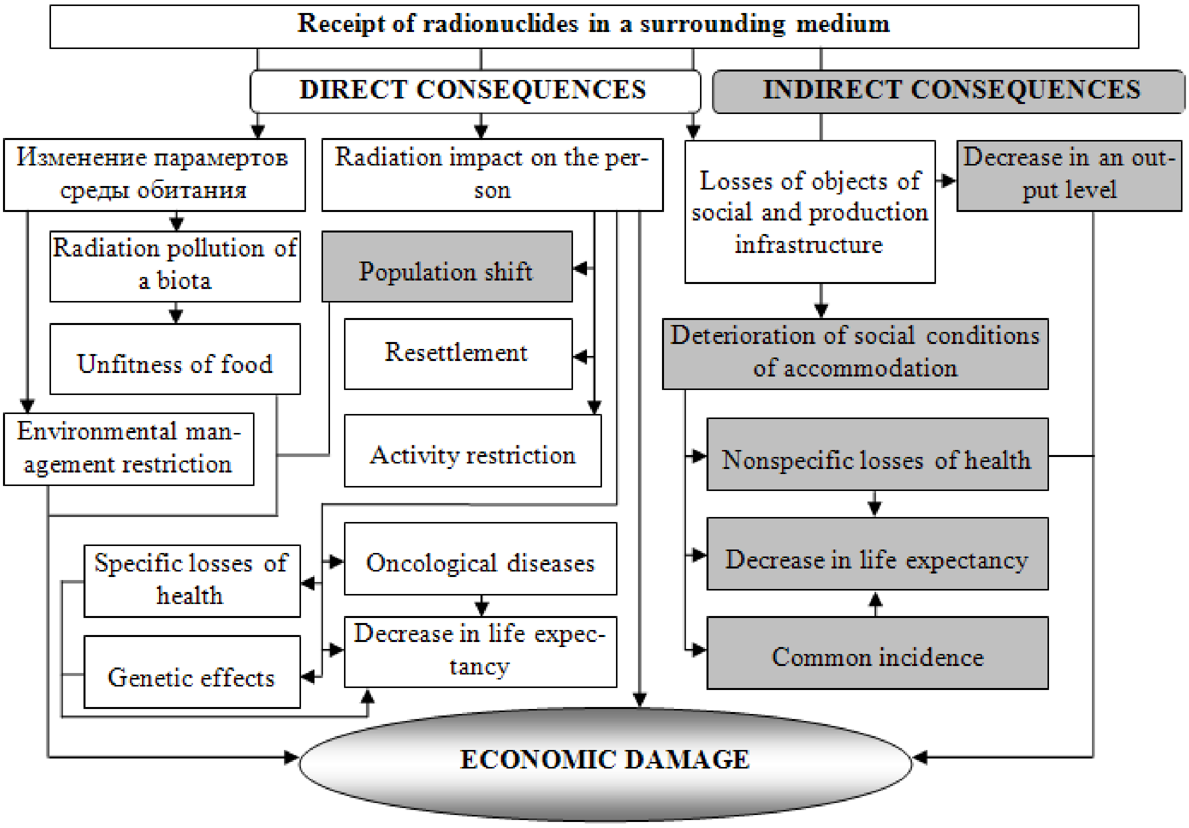

Figure 1. Structure of the straight lines and the mediated consequences forming economic damage at a radiocontamination of territories

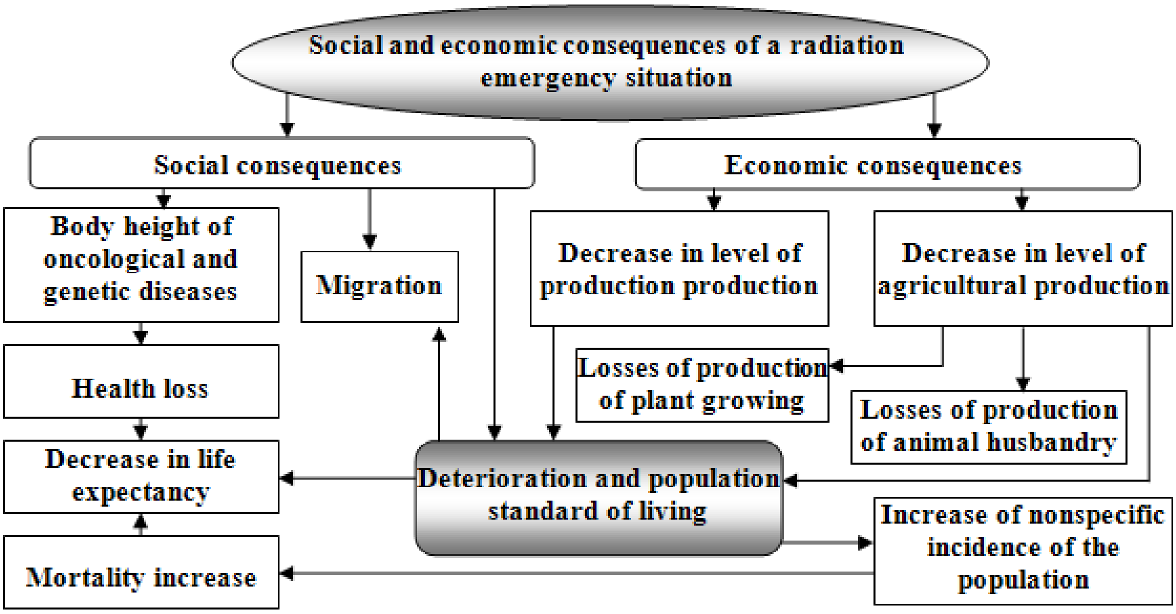

Figure 2. The negative factors influencing socioeconomic system of the region owing to radiation influence

The assessment of economic damage at a radiation emergency has distinctive signs from damage calculation at the routine technogenic environmental, consisting in need of the accounting of a number of features:

- action of radionuclides changes qualitative parameters of an ecosystem, forming for very short period of change of elements of the biosphere which depending on level of radiation influence lead to the stochastic and determined consequences of a state of health;
- because of impossibility of scale rehabilitation of a zone of influence of a radiation emergency rehabilitation of ecosystems can extend only on local sites;
- the radiocontamination has the long-lived character;
- at radiation influence essential distinctions in resistance of elements of an ecosystem to this influence are observed, ecosystems possess low ability of a self-cleaning that leads to accumulation of radionuclides in biosphere components;
- carrying out emergency measures on decrease and the prevention of possible consequences of radiation impact on an ecosystem and the population that leads to withdrawal from using of part of production, inventory, constructions, etc. is required.

Therefore when determining economic damage at a radiatsinny emergency besides traditional stages of its assessment (acquisition about structure and number of pollution, impact of pollution on recipients, definition of area of distribution of pollution, definition of natural indexes of damage, a financial assessment of natural indexes of damage and its compensation), the reference for technogenic pollution of a surrounding medium, it is necessary to include and specific stages (definition of straight lines and the mediated consequences of a radiation emergency, development of the concept of protective and rehabilitation measures, creation of conditions for the long-lived accommodation of the population). Here the financial assessment of consequences represents economic damage, or a monetary assessment of negative changes of a state of health and the living conditions of the person caused by restrictions of environmental management and activity on is radioactive the polluted territories.

All direct costss and share of the mediated expenses go for compensation of a direct loss A (1), bound to immediate radiation influence. To prime, or emergency expenses of D (2) should carry the material inputs on clarification of a radiation situation of d_1, the organization of radiation monitoring and monitoring of d_2, a measure for decrease in receipts of radionuclides in a surrounding medium of d_3, deactivation of objects of activity of d_4, utilization and burial of radioactive materials and d_5 wastage, the organization of the alternate sources of environmental management and d_6 consumption, capital expenditure for resettlement of inhabitants from the polluted territories of d_7, compensation by settled-out d_8.

$$A = \sum_{n=1}^{7} a_n + D, \qquad (1)$$

where a_1 – of expense for compensation of loss of health from radiation influence;
a_2 – losses from restriction of consumption of local food;
a_3 – losses from restriction of consumption of food products of the woods and reservoirs;
a_4 – losses from a housebreaking, production and social infrastructure at resettlement;
a_5 – losses from deduction from a turn of agricultural grounds;
a_6 – losses from destruction of agricultural raw materials and fodder, delivery products.
a_7 – losses of expense for construction of new housing and creation of workplaces.

$$D = \sum_{n=1}^{8} d_n . \qquad (2)$$

Contemporary records allow to carry out an assessment prime, and direct costss as on each area separately, and as a whole on the republic.

To mediated, or to indirect expenses C (3) costs of formation of conditions of the long-lived accommodation of the population can be carried on is radioactive the polluted territories (figure 3). The indirect damage is defined with the following categories a shortage of agricultural production of plant growing and animal husbandry, restriction of consumption of local food (agriculture, a reservoir, the wood), costs of compensation of losses of production, population shift, padding costs of preservation of houses and objects of the social and production infrastructure, caused by activization of migratory processes.

$$C = \sum_{n=1}^{7} c_n , \qquad (3)$$

where c_1 – losses due to population shift;
c_2 – losses at the expense of the nonspecific reasons of deterioration of health;
c_3 – production losses;
c_4 – losses from short-reception of agricultural production of plant growing and animal husbandry;
c_5 – losses from decrease in quality and a standard of living;
c_6 – losses from restriction of consumption of local food (rural economy, a reservoir, the wood);
c_7 – padding costs of preservation of houses and objects of the social and production infrastructure, caused by activization of migratory processes.

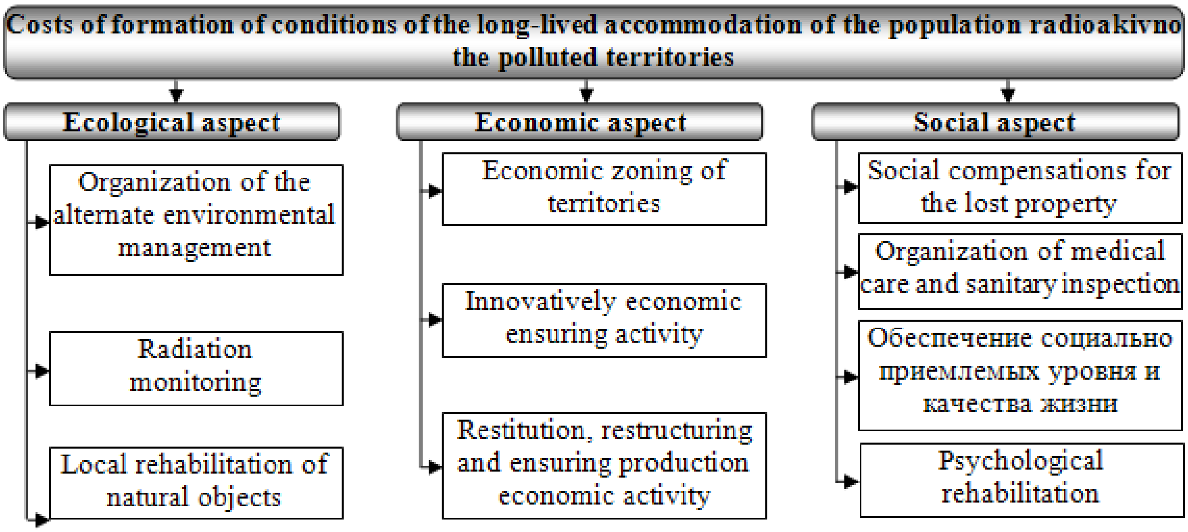

Figure 3. Structure of expenses for ensuring the long-lived accommodation of the population in the territory of radiation influence

It should be noted that by optimization of actions of rehabilitation policy the size of the common economic damage will be depending on duration of radiation impact on the population, i.e. a time frame. Long-term restriction of activity demands costs of formation of acceptable conditions of accommodation on is radioactive the polluted territories that demands development of a padding package of measures on ecological, social and economic rehabilitation of the population and territories, formation of conditions of the long-lived accommodation of the population in the polluted territories with providing particular level of safety. Therefore the common economic damage of Q caused to territories and the population at a radiation emergency, can be defined from the following expression:

$$Q = A + B + C + G + q(r,t), \tag{4}$$

where B – uncompensated part of a direct loss;
G – uncompensated part of indirect damage;
$q\ (r,\ t)$ – padding compensation expenses to the population for accommodation and work in the conditions of a radiocontamination the territories which are defined in the form of funktsiionalny dependence on degree of risk and a time frame.

As appears from (4), the common economic damage in process of performance of rehabilitation actions will increase in time taking into account quality and increase of cost of carried-out actions. Its calculation allows to estimate effectiveness of the expenses directed on elimination of a radiation emergency and its consequences, to optimize the directions of rehabilitation policy as despite the undertaken measures directed on decrease in radiation impact on the population, and subsequently on carrying out rehabilitation actions, the situation in regions of a radiocontamination remains to the composite. And, absence or a failure of target compensations of the mediated economic losses during the long-lived time term conducts to accumulation of social problems in the territories which have undergone radiation influence.

In definition of the common economic damage behavioural parameters of social and psychological rehabilitation of the population have important value, is long living in the radioactive polluted territories which can act as object of operated influence in the course of adaptation to the changed conditions of habitat. Negative experiences of the population, alarming state, gradually collecting, are transformed to social tension of particular degree. Social tension acts as the self-contained subjective factor, capable to affect on all aspects of life. In this regard diagnostics of a social psychological state of the population and measurement of level of social tension – the most important element of system of the public and local administration. Studying of mood of inhabitants of affected territories, the analysis of public reaction to decisions made by the authorities and actions in the course of realization of rehabilitation actions are urged to promote optimization of conditions of the long-lived accommodation of the population on is radioactive the polluted territories (figure 4). At a significance of all factors of a social psychological state of the population the special place belongs to the basic – level and quality of life of people.

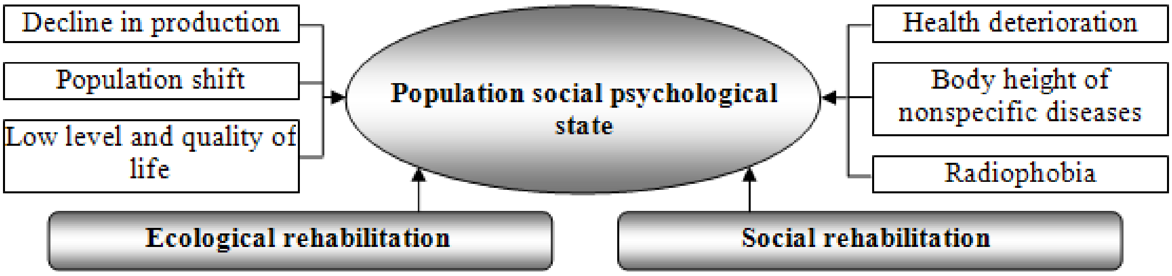

Figure 4. The factors defining a social psychological state of the population it is radioactive the polluted territories

The natural alarm for the future of children "competes" in affected territories to concern about a condition of characteristic health. Thus the majority of young people a problem of characteristic illness see in an adverse radio-ecological situation, state alarm for future family life and desire to go to other place of residence.

The rehabilitation policy on elimination of consequences of a radiation emergency can be presented as follows (figure 5). Formation of conditions of the long-lived accommodation of the population at the raised radiation level has to be defined by interrelation natural and resource, production, agricultural, labor, financial and other potentials, i.e. a comprehensive approach to public reproduction. Assessment of potential of development it is radioactive the polluted territories promotes a choice of efficient administrative decisions in questions of the fissile involvement in economic circulation of human resources that will allow to define characteristic sources of development, to occupy the niche in regional development and, thus, to join in market economic conditions of the common development of the state. In ecological aspect carrying out actions for ensuring radiation safety will improve environmental management conditions, will lower dose load of the population that will lead to decrease of restriction of activity of the population.

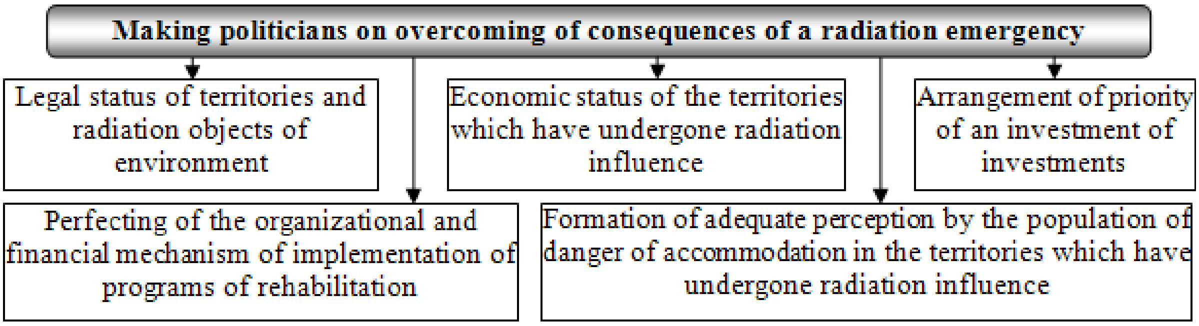

Figure 5. The directions of rehabilitation policy on overcoming of consequences of a radiation emergency

Main goal of economic development it is radioactive the polluted territories creation of the multisector socially focused market economy which is based on scientific and technical providing and informational and industrial technologies with transition to the new quality standards of life and habitat that will affect the solution of social problems of the polluted regions is. The choice of reference points of social and economic policy on prospect has to be based first of all on an objective assessment of human potential, consider demographic processes, the quantitative and qualitative condition of a manpower. Tendencies of development of migratory processes of the last years predetermine further reduction of population of the polluted territories of the republic. In these conditions development of effective demographic policy, definition of its main priorities and tasks for a conclusion from demographic crisis is necessary.

CONCLUSIONS

For development of the material resources of the social sphere by the priority directions there have to be a construction of new housing of the increased comfort, implementation of the program of elimination of a shabby and hazardous dwelling, development of mortgage lending, development of individual housing construction and use, as the main form of financing of housing construction, personal means of citizens with the state support or support of the enterprises. In the field of health care preservation and promotion of health, orientation of health system to its prophylaxis, strengthening of the material resources and introduction of progressive medical technologies with use of the latest medical inventory are priority. Local operating controls has to pay attention to maintaining of worthy level and quality of life of the population, eliminating the crisis phenomena on is radioactive the polluted territories by means of social programs of development of regions.

In work methodological provisions, techniques and the recommendations providing the fullest accounting of factors of the common economic damage at a radiation emergency are generalized, and used for justification of measures for ensuring the long-lived accommodation of the population on is radioactive the polluted territories. The offered conceptual approaches to an economic assessment of damage give the chance to solve problems of applied character, in particular, to form ecological, economic and economic, agricultural, investment and social policy at regional level; to develop and prove the statutiry and normative and administrative documents regulating social and economic rehabilitation and development of territories, undergone to a radiation emergency.

REFERENCES

Научное обоснование Рекомендаций для долгосрочного национального регулирования в отношении населения территорий, подвергшихся радиоактивному загрязнению вследствие аварии на Чернобыльской АЭС в 1986 г. – Вена : Департамент технического сотрудничества (Европейский отдел), 2010. – 111 с.

20 лет после Чернобыльской катастрофы: последствия в Республике Беларусь и их преодоление. Национальный доклад // Под ред. В. Е. Шевчука, В. Л. Гурачесвского. – Минск : Комитет по проблемам последствий катастрофы на Чернобыльской АЭС при СМ РБ, 2006. – 112 с.

Мирончик, А.Ф. Динамика медико-демографических показателей населения экологически-неблагоприятных регионов Белоруссии как составляющая общего мониторинга состояния эко- и биосистем / А.Ф. Мирончик / И.И. Орловский и современные проблемы краеведения : Матер. Всероссийской науч.-практ. конф. - Смоленск: НОУ ВПО «СГУ», 2009. – С. 74-83.

Мирончик, А.Ф. Формирование и расчет дозы внутреннего облучения населения, проживающего в зоне радиоактивного загрязнения / А.Ф. Мирончик, Д.А. Липская / Вестник Могилевского государственного университета продовольствия. – № 2, 2010. – С. 65-73.

Мирончик, А.Ф. Техногенное воздействие и организация комплексного экологического мониторинга территории Могилевской области / А.Ф. Мирончик / Энерго- и материалосберегающие экологически чистые технологии / Матер. VII Междунар. науч.-техн. конф. – Минск: Геопринт, 2007. – С. 253-258.

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METHODS AND SOLUTIONS OF THE PROBLEM OF ELIMINATION OF IODIC DEFICIENCY IN BELARUS

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ABSTRACT

The data characterising a problem of iodic deficiency in territory of Belarus that is the reason of a pathology of a thyroid gland are cited. Ways of the possible decision of the given problem, including the actions directed on preventive maintenance of iodic deficiency are specified.

Key words: *food, iodine, deficiency, prophylaxis, population health.*

INTRODUCTION

Full value of a delivery is determined not only its power value, balance of a diet by proteins, fats and carbohydrates, but also security vitamins and microcells (ME). Deficiency even one of them is capable to start the cascade of metabolic disorders. The iodic deficiency, existing in the millennia in territories of the modern Belarus, was the reason of formation of a zobny endemia, treatment and which prophylaxis were actively begun in Belarus from 20th years of last century.

THEORY

In exchange processes and a metabolism taken ME, and the ME complex and their balance since in an organism between them there is an interrelation [1, 2] matters not separately. ME fall into to irreplaceable substances of food. They are necessary for the person at any age, but children, women are most sensitive to development of a microelement failure a fruit, during pregnancy and feeding by a breast. Especially the population of many countries of the world faced this problem in connection with environmental by production, transport emissions, agricultural poisons (pesticides, nitrites and nitrates, salts of heavy metals) and the radionuclides which have extended as a result of radiation accidents. Failure ME is dangerous that long time is not shown clinically. It is so-called "the hidden hunger" [3]. In food allowances of the population are the reasons of a lack of ME: decrease of the maintenance of ME in the soil; environmental the toksikant, blocking availability of ME to root system of plants; the technological processing of raw materials leading to loss of part of ME; decrease of requirement for energy, and therefore in food; lack of a variety of a diet, transition to a narrow reference set of basic groups of products and ready food; increase in consumption refined, high energy, but poor on vitamins and mineral substances of food (white loaf, pasta, sugar, alcoholic drinks); decrease in a diet of meat and lactic products, loss of a national habit to the regular use of a large number of vegetables, fruit, garden greens; poor use in a food allowance of seafood (fish, mollusks, algas); essential increase of needs of the person in the ME as an important protective factor in the conditions of the scientific and technical progress, the raised neuroemotional pressure, action of harmful factors of production and environment.

FINDINGS AND DISCUSSION

Regions of Belarus, the most affected by accident on the Chernobyl Nuclear Power Station, even before accident were known for poverty of soils on accessible to root system macro - and ME therefore in food of local production (a basis of food allowances of the population) the shortcoming was noted them [1, 4]. In these territories the increase in pathology of a thyroid gland, especially among the children's population, iron deficiency anemias and other diseases is noted [5]. An iodine is ME necessary for a biosynthesis of thyroid hormones (a thyroxine and a triyodtironin). It comes to a human body with food, water, air. 90% of daily need for an iodine are provided at the expense of food, 4-5% of water, about 4-5% enter with air. An iodine contains in fish, meat, sea cabbage, shrimps seafood, milk and lactic products, water, the iodated sodium chloride, buckwheat and oat grain, haricot, salad, beet, eggs, potatoes.

For studying of security of the population of these regions with an iodine we from inhabitants of settlements of the Mogilev, Gomel and Brest areas took away tests of daily diets and test of vegetables (potatoes, cabbage, table beet and carrots). For example, official statistical data of Ministry of Health of Republic of Belarus, reporting materials of policlinic of the Shklov region of the Mogilyov area on number of cases of diseases of thyroid gland registered at the population served by this treatment-and-prophylactic establishment (form No. 12) were object of research the Shklov region of the Mogilev area. In work dynamics of intensive and extensive indexes of incidence of the population of diseases of thyroid gland was studied.

After preliminary sample preparation by methods of a mass spectrometry, nuclear absorption in them the content of iodine is defined. Besides security of the population with an iodine before iodic prophylaxis which was carried out for particular part of the population after accident on the Chernobyl NPP is studied.

When studying mineral structure of vegetables which most are used hour by country people, low concentration (in comparison with tables of chemical composition of foodstuff [6]) an iodine and some other macro - and ME attracts attention. Especially low content of iodine is noted at carrots and in potatoes (table 1).

Table 1: Content of Iodine in the vegetables consumed by inhabitants of the Mogilev, Gomel and Brest areas

Vegetables	Actual contents	Data of tables of chemical structure	Vegetables	Actual contents	Data of tables of chemical structure
Cabbage	3,0	10,7	Potatoes	0,3	5,0
Carrots	0,4	5,0	Beet	0,5	3,4

The content of iodine in average daily diets of inhabitants instead of the recommended 140 mkg made only 50 mkg. Approximately same results are received also by other researchers [3]. It should be noted the lowest receipt of ME chrome, a cobalt, copper, a selenium which participate in processes of a krovoobrazovaniye and a metabolism of hormones of thyroid gland. In 81% of tests the content of iodine is lower than admissible level (in 25% very low, heavy deficiency; in 43% an average, in 13% mild deficiency) and only in 19% its contents answers the recommended. The considerable fluctuations of the values received by us that is probably bound to identity of a delivery of separate families in day of sample drawing are revealed. The fact of higher maintenance of iodine in the diet consumed in families of teachers, medics which have the larger income better is noted are informed on need of the use of products with the high content of iodine (sea fish, seafood). Low level of security is an iodine the main reason of distribution of the diseases caused by deficiency of an iodine in an organism (DDI) [3]. According to screening inspection by endocrinologists thyroid pathology is revealed at 59% of residents of these villages.

Considering the obtained data on intake of iodine with delivery products in an organism and also given screening inspection of the population it is possible to draw a conclusion on poor security of the population of these villages with such important ME, as an iodine that conducts to development of DDI. The factors contributing to development of DDI are: the heredity burdened on DDI (genetic defects of a biosynthesis of thyroid hormones); impurity of water nitrates; the high content in it of calcium, humin substances that complicates an iodine absorption; deficiency in a surrounding medium and food of Zincum, manganese, a selenium, a molybdenum, a cobalt, copper and excess of calcium (the imbalance of ME promotes violation of a biosynthesis of thyroid hormones); application of the medicinal preparations blocking Iodidum transport in thyroid gland cages (periodate, potassium perchlorate); application of the preparations breaking the organization of an iodine in thyroid gland (derivativ thioureas, tiouratsila, some Sulfanilamidums, paraben, aminosalicylic acid); existence of goitrogenic factors in products (the thiocyanides and isocyanates containing mainly in cabbage white, color, broccoli, Bruxelles; turnip, turnip, horse-radish, salad); impact of infectious and inflammatory processes, especially chronic, helminthic invasions, unsatisfactory sanitary and hygienic and social conditions. In these situations compensatory opportunities of thyroid gland to support an optimum level of thyroid hormones in blood sharply decrease.

There are theories which allowed to develop a number of well approved methods of prophylaxis and DDI treatment. However in recent years there were new data which force to look at this pathology in a new way. All these factors can be divided into three groups conditionally: data on influence macro - and ME on the thyroid gland function; ecological risk factors; new technologies in diagnostics. Despite the considerable efforts directed on elimination of iodic deficiency, a disease, to them the caused, most widespread noninfectious illnesses of mankind: 141 million people have a risk of development of DDI, at 97 million the craw is revealed and at 0,9 million various violations of intellectual development, neurologic and separate neurophysiological anomalies [3] are observed. DDI meet almost in all regions of Ukraine. Belarus and Russia [6]. Thus, a lack of ME, in particular, a selenium, a cobalt, copper, chrome, gland leads to development of yoddefitsitny pathology, even at iodine enough in a delivery. DDI body height against providing the population with the iodated salt is explained recently by it. At the considerable proportion of the population the lack of an iodine is combined with deficiency of a selenium and iron that once again confirms need of correction of food allowances of the population of such regions with a number necessary biogenic elements [2, 3, 5].

In the world different methods and means of mass, group and individual prophylaxis are tested. As the major etiological factor of these diseases is considered poor intake of iodine in an organism, the majority of measures of mass, group and individual prophylaxis is aimed at providing an organism with iodine enough. The basic, universal and most economic method of mass prophylaxis of DDI is considered the use of the iodated salt [5]. It considerably improves providing with a population iodine, but the quantity of DDI considerably does not decrease [7]. Preventive measures for the prevention of development of a craw have to be carried out taking into account severity an iodine deficiency of the particular region and a complex assessment of an ecological situation as a whole [2, 8]. At the same time, it is necessary to notice that preventive and medical actions of DDI have to lean on a complex of detailed medico-ecological researches and be carried out taking into account level of a microelement imbalance of an organism of the patient.

Targeted researches and events for prophylaxis of the endemic craw, held in the 1950-1970th years, allowed to reduce considerably in the republic abundance and weight of clinical manifestations of DDI. However the developed strategy of prophylaxis yodode-fitsita was unefficient, and in the eighties last century after the termination of target distribution of an antistrumin body height of incidence by a craw began. Biological effects of influence of a Chernobyl ^{131}I and deficiency of a stable iodine caused body height of incidence of thyroid gland, including and nodal pathology that demanded immediate actions for detailed studying of iodic security and abundance of DDI in the republic. In 1996-1999 Ministry of Health of Belarus with support of the European regional bureau of the World organization of health care conducted the first national research on studying of abundance of a craw and an iodic failure among the children's and teenage population. It was as a result established that abundance of iodic deficiency in the republic made 62-92%, and abundance of a craw reached 28%. The iodated salt the main source of receipt of iodine in an organism, periodically was used in food only by 30% of the surveyed children, individual and group prophylaxis by iodine preparations practically was not carried out.

CONCLUSIONS

On the basis of the conducted researches and taking into account the developed negative factors (geochemical deficiency of an iodine in the soil and water; deficiency of an iodine in food of local production; termination of group prophylaxis by an antistrumin; use of unstable Iodidum of a potassium; the poor awareness of the population on advantage of the iodated salt and its infrequent use by the population) in Belarus was developed the State strategy of elimination of DDI. This strategy was based on large-scale and ubiquitous use of the iodated salt and included the following actions: change of legislative and regulatory base; change of quality of the iodated salt made in Belarus; wide knowledge of the population of importance of a microcell of an iodine for organism and health development; hygienic and medical monitoring of iodic providing the population, defining effectiveness of held events.

For realization of this strategy in Belarus the Resolution of the Chief state health officer No. 11 of 21.03.2000 was accepted. "About carrying out prophylaxis the iodine-deficiency of diseases" and the Resolution of Council of ministers No. 484 of 06.04. 2001. "About the prevention of diseases, bound to deficiency of an iodine". Standards according to the content of iodine in salt to 40±15 mg/kg of salt were changed, and as a source of an iodine began to use stabler iodite of a potassium. Were changed technical specifications in which at manufacture of finished food products (bread, sausage products, canned food) routine salt was replaced with the iodated. In all establishments of public catering when cooking obliged to use only the iodated salt. In mass media broad informational work about need of use of the iodated salt for prophylaxis deficiency of an iodine was developed. The system of hygienic and medical monitoring was developed for monitoring of effectiveness of carried-out researches.

Monitoring of effectiveness of realization of the State strategy of elimination of DDI showed that abundance of iodic deficiency across Belarus was reduced with 80,9 to 14,0%. The use of the iodated salt increased from 30,0% in 1996 to 96,6% in 2010. Seafood uses 85,2%, and individual antigoitrogenic prophylaxis is carried out by 20,7% of the surveyed school students. Organism saturation by an iodine led to reliable reduction of abundance of a craw as a whole on the republic over the last ten years with 17,2 to 12,8%. As a whole the received results testify to effectiveness of realization of the State strategy of elimination of DDI based on recommended UNICEF ubiquitous preventive use of iodated salt as the universal remedy of prophylaxis deficiency of an iodine.

REFERENCES

Бабенко, Г.А. Микроэлементозы человека: патогенез, профилактика, лечение / Г.А.. Бабенко / Микроэлементы в медицине, 2001. - Т. 2. - № 1. - С. 2-5.

Мирончик, А.Ф. Динамика медико-демографических показателей населения экологически-неблагоприятных регионов Белоруссии как составляющая общего мониторинга состояния эко- и биосистем / А.Ф. Мирончик / Орловский и современные проблемы краеведения : матер. Всеросс. науч.-практ. конф. – Смоленск : НОУ ВПО «СГУ», 2009. – С. 69-76.

Дисбаланс микроэлементов в организме детей с экологозависимой патологией / В.В. Утенина / Гигиена и санитария, 2002. - № 5. - С. 57-59.

Мирончик, А.Ф. Особенности питания населения, проживающего в экологически неблагоприятных регионах Беларуси / А.Ф. Мирончик, Е.А. Мирончик / Экологические проблемы природно-технических комплексов : Тез. докл. I Междунар. экологич. симпозиума. В 2-х томах. Т. 2. – Полоцк : УО «ПГУ»,2004.–С.205-209.

Перевозников, О.Н. Итоги многолетнего мониторинга содержания 137Cs в организме у населения, проживающего на территориях, радиоактивно загрязненных вследствие Чернобыльской аварии / О.Н. Перевозников. С.Ю. Нечаев, Н.Ф. Рубель / Межд. ж. радиац. медиц., 2002. - Т. 4. - № 1-4. – С. 120-127.

Химический состав пищевых продуктов: справочник; под ред. И.М. Скурихина, М.Н. Волгорева. - М. : Агропромиздат, 1987. - 310 с.

Орзун, В.Н. Проблема мікроелементів у харчуванні населения Украіні та шляхи іі вирішення / В.Н. Корзун, О.П. Козярин, А.М. Парац / Пробл. Харчування, 2007. - № 1. - С.5-11.

Результаты внедрения стратегии ликвидации йодной недостаточности в республике Беларусь / Т.В. Мохорт [и др.] / Эндокринол. ж., 2007. - № 2(8). - С.39-43.

NANOTECHNOLOGY IN ENVIRONMENTAL PROTECTION

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NANOTECHNOLOGY IN WASTE WATER TREATMENT: A REVIEW

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ABSTRACT

A Demand of clean and affordable water supply is significantly increasing with the fast growing population growth, global climate change, and water quality deterioration. 97.5% of all water on Earth is salt water, leaving only 2.5% as fresh water of which less than 1% is accessible for direct human uses. Achievement of proper treatment and disinfection without the formation of harmful byproducts calls for new technologies. Technological innovation to enable integrated water management including waste water treatment is the need of the day. Nanotechnology is one of the potential technologies in advancing wastewater treatment to improve treatment efficiency. It has a unique characteristic of high surface area to volume ratio which can be efficiently used for removing toxic metal ions, disease causing microbes, organic and inorganic solutes from water. Due to this characteristic nanoparticles can easily disperse in water and help in disinfection. They do not generate byproducts that are harmful for environment. Different types of nanomaterials have proved to be efficient for this purpose – metal containing nanoparticles, carbon nanotubes (CNT), zeolites, nanofiltration membranes etc. This paper presents a review of the recent development of nanotechnology in waste water treatment. 125 research papers have been studied covering nanomaterials, their characterization, and synthesis mechanism, potential applications of nanotechnology in wastewater treatment, their limitations and hazards. Two analysis has been carried out using the analytical hierarchy process (AHP), first analysis were carried out to compare the potential of applications of nanotechnology in wastewater treatment with other existing technology and second analysis were carried to prioritize the drawbacks for implementing the nanotechnology for waste water treatment. It has been observed from the study that application of nanotechnology has a wide range of benefit over traditional technologies. This review will definitely help researchers and other stakeholders in the field of application of wastewater treatment.

Key words: *Nanotechnology, Waste water treatment, AHP, CNT.*

INTRODUCTION

The current water supply system faces enormous challenges worldwide. Nearly 780 million people throughout the world still lack access to improved drinking water sources (WHO, 2012). The world is facing formidable challenges in meeting rising demands of clean water as the available supplies of freshwater are depleting due to (i) extended droughts, (ii) population growth, (iii) more stringent health based regulations and (iv) competing demands from a variety of users (U.S. Bureau report 2003; EPA 1998, WHO 1996).It is urgent to implement basic water treatment in the affected areas (mainly in developing countries) where water and waste water infrastructure are often non-existent. The increasingly stringent water quality standards, compounded by emerging contaminants, have brought new scrutiny to the existing water treatment and distribution systems widely established in developed countries. The global climate change accentuates the already uneven distribution of fresh water, destabilizing the supply.

Today a number of techniques are used for treatment of water i.e. treating with chemical and physical agent such as chlorine and its derivatives, Ultraviolet light (Droste 1997), Boiling, Low frequency ultrasonic irradiation (Gupta et al 2006), Distillation, Reverse Osmosis, Water sediment filters (fiber and ceramic) Activated carbon, Solid block, Pitcher and faucet-mount filters, Ion exchange water Softener, Ozonisation etc (Tiwari et. al. 2008).

Existing waste water treatment technologies are efficient but are not free of problems. Pressure-driven membrane processes are the most widely used membrane technologies in water treatment applications (Ulbricht 2006, Hoek et al 2011). Although, the use of gas separation, pervaporation, and electrochemical membrane processes for industrial and environmental separations have also increased dramatically in the past few decades (Bernardo at al 2009). Membrane fouling is the biggest disadvantage and irreversible fouling often leads to discard of membrane which is not economical. Pressure driven processes require huge energy to operate and back-flushing requires water or vacuum. Activated Sludge Processes require long time and huge land area for their operation. Sludge handling is also a problem. Constructed wetlands and aerated lagoons are open hence attracts a lot of flies and spreads foul smell which is not healthy for the associated flora and fauna. Most of all sometimes their efficiency is questionable.

Research is underway to use advanced technologies such as nanotechnology in water purification for safe drinking. Nanotechnology, the deliberate manipulation of matter at size scales of less than 100 nm, holds the promise of creating new materials and devices which take advantage of unique phenomena realized at those length scales, because of their high reactivity due to the large surface to volume ratio (Ichinose et al 1992). Nanoparticles are expected to play a crucial role in water purification (Stoimenov et al 2002; Tiwari et al 2008).

The rapid growth in nanotechnology has spurred significant interest in the environmental applications of nanomaterials. In particular, its potential to revolutionize century-old conventional water treatment processes has been enunciated recently (USEPA, 2007; Shannon et al., 2008).Nanomaterials are excellent adsorbents, catalysts, and sensors due to their large specific surface area and high reactivity. It can even be mixed with aqueous suspensions and thus can behave as colloid. Nanoparticles can achieve energy conservation due to its small size which can ultimately lead to cost savings. Unlike conventional chemical disinfectants, these anti microbial nanomaterials are not strong oxidants and are relatively inert in water. Therefore, they are not expected to produce harmful disinfection by products. Nanoparticles have great advantage of treating water in depths and any location which is generally left out by other conventional technologies (Prachi et al 2013). If properly incorporated into treatment processes, they have the potential to replace or enhance conventional disinfection methods (Alvarez et al 2008).

Nearly 125 Research papers have been reviewed covering nanomaterials, their characterization and synthesis mechanism, potential applications of nanotechnology in wastewater treatment, their limitations and hazards. While reviewing the papers, it was found that a lot of work has been done on the preparation, characterization, application in waste water treatment and their efficiency mostly in laboratory scale and pilot scale. But works on retention and reuse of nanomaterials are scant. The research questions that arise are how effective is nanotechnology with respect to other existing technology? Why nanotechnology is not being implemented though it has the aspects? This paper aims to review the recent development of nanotechnology in waste water treatment. The analytical hierarchy process (AHP) analysis will be done to compare the potential of applications of nanotechnology in wastewater treatment with other existing technology.

METHODOLOGY

This paper adopts both primary and secondary research techniques. The next section covers the literature review that addresses the presence of nanotechnology as an emerging technology in waste water treatment. It also gives idea about the synthesis mechanism of different nanomaterials and their characterisation technique, their potential application in waste water treatment, their limitations and potential hazards. Section 4 is the AHP analysis. A questionnaire is developed based on four major of waste water treatment – Environmental, Operational, Economical and Social. These criteria were further sub divided into many sub criteria which were identified from the primary research and literature survey. The alternative technologies for waste water treatment were also identified from the literature survey. Then a questionnaire was developed based on T. L .Satty scale. The importance of each and every criteria, sub criteria and alternatives were collected through a questionnaire survey from various stake holders and experts in these fields. The rating thus obtained was converted to a crisp value by using standard statistical tools. The crisp value obtained was used to analyse through Super Decision software.

LITERATURE REVIEW

Nanotechnology in Waste Water Treatment

Significant research on the application of nanotechnology has been found in literature. Recently, several natural and engineered nanomaterials have also been shown to have strong antimicrobial properties, including chitosan (Qi et al., 2004), silver nanoparticles (Morones et al., 2005), photocatalytic TiO2(Cho et al., 2005; Wei et al., 1994), fullerol (Badireddy et al.,2007), aqueous fullerene nanoparticles (nC60) (Lyon et al.,2006), and carbon nanotubes (CNT) (Kang et al., 2007). High surface to volume ratio helps them to easily disperse in water and help in disinfection. Potential applications of different nanoparticles have been shown in Table 1.

Table 1: Literature Review

Name of nanomaterials	Preparation Technique	Characterisation Method	Findings	Potential hazard	Limitations / Research gap	References
Carbon nanotubes (CNT)	a) Electric Arc Discharge. b) Chemical Vapour Deposition c) Laser Ablation.	SEM, TEM, UV-vis spectra, Raman Spectroscopy, XRD etc	Can be used as adsorbent. Removes Heavy Metal ions, Trihalo methanes (THMs), Chlorophenol.	N/A	Retention, Regeneration and reuse are not found.	Chiu et al 2006; Zhang et al 2006; Lu et al (2005, 2006);
Graphene	a) Chemical Vapour Deposition. b) Mechanical Exfoliation.	SEM, TEM, Ultraviolet–visible spectroscopy, Fourier transform infrared spectroscopy	Used as adsorbent Removes Dyes and Heavy Metals, organics.	N/A	Regeneration and reuse are not found.	Pradeep et al 2011
Nano-crystalline Zeolites	Traditional Hydrothermal method.	SEM, TEM, HREM, Powder X-ray Diffraction, Nitrogen Adsorption Isotherms, Dynamic Light Scattering, Electron Microscopy, FTIR and solid-state NMR.	Removes Ammonia, Organic pollutants like (HCFC's) and Heavy Metals.	N/A	---	Sanhez et al 2003; Larsen [2007] Sharma et al 2013; Qiu et al 1998

Nanoscale Zerovalent Iron	Reduction of ferric ion by sodium borohydride	Particle size distribution, SEM, TEM images, XRD analysis.	Removes Inorganic ions, Heavy Metal ions & Chlorinated organic compounds.	N/A	Reusability and regenaration.	Zhang et al (2005, 2006); Wang et al 2007.
Silver Nanoparticles	a) Chemical Method – reduction of Ag+ions. b) Solid State Thermal decomposition. c) Biosynthesis.	UV-vis spectroscopy, TEM images, FTIR and XRD analysis.	Antibacterial property is used to kill bacteria.	If it enters the urban water cycle it will be a problem.	Removal after treatment is a problem.	Kar et al 2012.
TiO2 Nanoparticles	a) Sol-gel method. b) Biosynthesis.	UV spectroscopy, XRD, FTIR, AFM, TEM and SEM analysis.	Removes heavy metal ions, phenol, toluene etc.	N/A	Separation from solution.	Pena et al 2005; Hasegawa et al 2006; Crittenden et al 2005.
Bimetallic Nanoparticles	a) Chemical method. b) Biochemical method	High resolution TEM images, Electrochemical measurement, energy-dispersive X-ray, XRD.	Removes Brominated organic compounds, Chloromethane, Trichloroethane.	Intrusion in water cycle may be harmful.	Retention, Regeneration and reuse are not found.	Lim et al 2007; Zhang et al 2001.
Dendrimers	Chemical Synthesis.	UV spectroscopy, DSC, TEM images	Removes metal ions and Bacteria	N/A	Reusability	Rau et al 2003
Nano membranes	a) Film Deposition. b) Chemical method.	Pore size, TEM, FESEM.	Removes bacteria, ions.	N/A	---	Tang et al 2007

Lee et.al 2013 demonstrated that the nano-platelets of Graphene oxide prepared membrane which suppresses the fouling hence reducing cleaning time. Varma et al (2013) successfully removed Nickel (II) from waste water using Graphene nano-composites (Graphene –MnO2 composite) as adsorbent. Graphene nanosheets have the ability of extraction of dye from aqueous solution. Graphene –CdS composite was used as adsorbent to remove organic dye Rhodamine B from wastewater. The composite reveals a high photo degradation rate under visible light irradiation which is very promising for removing organic dyes from waste water (Lü et.al 2014). CNTs are very powerful absorbents for a wide variety of organic compounds. Many water pollutants have very high affinity for carbon nanotubes and pollutants can be removed from wastewater using CNTs instead of Activated Charcoal.

It has been observed that CNT's are capable of removing Zinc from waste water. Trihalomethane and Chlorophenol were reported to be absorbed by MWCNTs from solution (Lu et al 2006). Zeolites are used in a wide range of environmental applications, including water purification. Zhijianet.al. (2012) worked on synthesis of nano-zeolite from coal fly ash, described its potential for nutrient sequestration from anaerobically digested swine wastewater (ADSW). Nanoscale zero-valent iron (NZVI) having a large surface area and high surface reactivity is a newly developed nanotechnology for water purification, providing enormous flexibility for in situ applications (Zhang 2003). Chen et. al. (2011) used Bentonite supported NZVI to remediate electroplating waste water with removal efficiencies for Cr, Pb and Cu > 90%. Chen et. al. (2010) used kaolin supported NZVI as a remediation which was efficient in removing Pb(II) (98.8%) and total Cr (99.8%) from an electroplating wastewater. Fan et. al. (2009) tried to remove Azo dye from waste solution using NZVI but the result obtained had several parameters that hinders the efficiency. Yoon et. al. (2009) studied the bactericidal effects of NZVI under de-areated conditions. It was found that NZVI in aqueous solution rapidly inactivated Escherichia coli (E. coli).

Bimetallic nanoparticles have been proven to be effective in removal of organic contaminants from wastewater (Mallouk 2002). Fe nanoparticles and Fe/Pd, Fe/Pt, Fe/Ag, Fe/Ni and Fe/Co have been found to reduce a variety of organic pollutants to less toxic by products (Jhang et. al. 2003). Ni/Fe and Pd/Fe nanoparticles are used for hydro halogenation of chlorinated aliphatics (Hao 2005), chlorinated aromatics (Feng 2006) and polychlorinated biphenyls (Wang 2006) but Ni has better corrosion stability and lower cost than Pd and this makes Ni more efficient for wastewater treatment (Zhao 2005). Kaegi et. al. (2011) investigated the behaviour of silver nanoparticles in a pilot wastewater treatment plant fed with municipal wastewater. It was found silver nanoparticles were absorbed into the biosolid and they bound with sulphur to produce Ag2S. However, the main application of silver nanoparticles is as an antibacterial agent and it is now well accepted that the antimicrobial activity of nano-silver largely stems from the release of silver ions (Xiu et al., 2011, 2012, Li et al 2013). TiO2 is suitable for applications in water treatment because it is stable in water, non-toxic by ingestion and low-cost. The high surface area of TiO2 nanoparticles creates a larger catalytic surface for the production of hydroxyl radicals that are strong oxidizing agents (Morimoto et al 2010). When UV light is used to activate the nanoparticles, efficient removal of aromatic organic compounds can be achieved. The removal of heavy metals can also be done by the use of TiO2. TiO2 nanoparticles when used as a packing material can effectively pre-concentrate and extract heavy metals from river water and seawater. This has been effectively accomplished in batch and column experiments at the natural pH of coastal waters (Quetel et al 2010). TiO2 have shown arsenic adsorption performance superior to activated carbon (Deliyanni et al.,2003; Mayo et al., 2007).

Dendrimers represent a novel class of three-dimensional, highly branched, globular macromolecules which include hyper-branched polymers, dendrigraft polymers and dendrons. Recently, poly (amidoamine) (PAMAM) dendrimers have been developed which was used in the remediation of wastewater with a variety of transition metal ions such as Copper(II) (Mamadou et al 2004). The high concentration of nitrogen ligands within the interior branches makes PAMAM dendrimers useful as chelating agents for copper ions. Similarly, for the remediation of other metals from water, researchers have also employed an ethylene diamine core (Yinhui et al 2005).A dendrimers – ultrafiltration system was designed to recover metal ions from aqueous solutions (Diallo et al 2005). Tang et al. 2007 systematically investigated the fouling of reverse osmosis (RO) and nanofiltration (NF) membranes by humic acid, a recalcitrant natural organic matter (NOM). Kim et al. 2010 reviewed the role of engineered nanomaterials in (pressure driven) membrane technology for water treatment, to be applied in drinking water production and wastewater recycling.

AHP ANALYSIS

The AHP analysis was done according to the discussed methodology. In this study two the AHP analysis has been carried out. The first analysis was carried out to obtain the best suitable technology according to the four sustainable pillars. The second analysis was carried out to identify the drawbacks in implementing nanotechnology as an alternative waste water treatment technology. The first AHP analysis carried out in this study was a four level hierarchy structure (figure.1). It consists of a single goal node that is the effective technology and at the criteria level there were four nodes. The last level in the hierarchy structure that is the alternatives cluster consists of eight nodes that are the available technologies for waste water treatment given in the table.2. The second AHP analysis is a two level structure consisting of goal level and alternative level with seven nodes consisting of the drawbacks hindering the application of the nanotechnology.

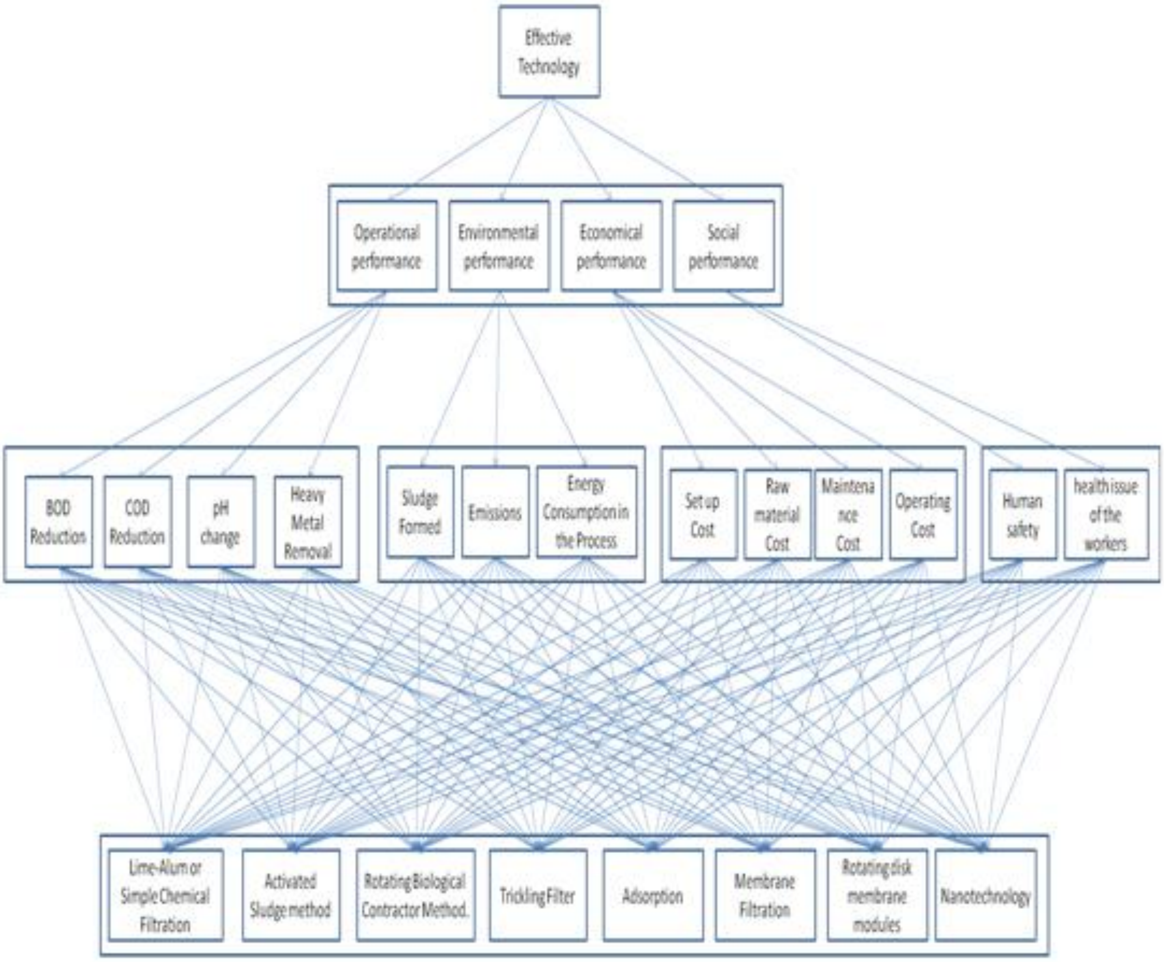

Figure 1. The AHP structure

Table 2: Criteria for AHP analysis

Constructs	References	Sub-Criteria	References /Field Study	Technologies	References /Field Study
Operational Performance	Schneider et al (2014)	BOD Reduction	Devi et al (2008), Gustavsson et al (2012)	Coagulation and Flocculation	Ismail et al (2012)
		COD Reduction	Devi et al (2008).	Activated Sludge Method	Mowla et al (2014)
		pH change	Lijklema (1972)	Rotating Biological Contractor Method	Sirianuntapiboon et al (2007), Hassard et al (2014)
		Heavy Metal Removal	Rudnicki et al (2014)	Trickling Filter	Wang et al (2007)
Environmental Performance	Govindan et al (2014)	Sludge Formed	Zhao et al (2014), Zhang et al (2014)	Adsorption	Meier at al (2002), Bhatnagar et al (2010)
		Emission	El-Fadel et al (2001), Pereira et al (2014)	Membrane Filtration	Huotari et al (1999)
		Energy Consumption of the Process	Pereira et al (2014)	Rotating Disk Membrane Modules	Bhattacharjee et al (2006), Luo et al (2010).
Economical Performance	Mata et al (2013),	Setup Cost	Cools et al (2011)	Nanotechnology	Qu et al (2013)
		Raw Material Cost	Ammari (2014)		
		Maintenance Cost	Field Study		
		Operating Cost	Cassano et al (2011)		
Social Performance	Mata et al (2013), Govindan et al (2014)	Human Safety	Werschkun et al (2014)		
		Health Issue of the Workers	Werschkun et al (2014), Field Study		

AHP analysis to find the best suitable technology

The AHP analysis through the Super Decision software revealed that environmental performance was the most important with Eigen vector value of 0.549493639 followed by social performance 0.24760687. The analysis of the sub criteria level with respect to the four criteria revealed that in term of operational performance COD reduction(0.45352) is the most important followed by heavy metal removal (0.24202), in term of the environmental performance criteria emission (0.44343) is the most important followed by the energy consumption in the process (0.38737), in term of the economical performance set up cost (0.37880) is the most important followed by the operating cost (0.24284) and in term of the social performance health issues of the worker (0.83333) is the most important followed by human safety (0.16667). The analysis of the AHP considering the goal nodes and the available technologies at the alternative level of the hierarchy structure revealed that the adsorption with over all Eigen vector value of 0.234393, is the best followed by the activated sludge method with Eigen vector of 0.220636 and the least important is the rotating disk membrane modules with value of 0.081115 as given in the table.3. The analysis revealed that nanotechnology is one of the three best technologies for waste water treatment and then also it has been found that nanotechnology was limited to pilot project and research application. The analysis revealed that it could be the best alternative and could become one of the most sustainable technologies for waste water treatment if the drawbacks are addressed effectively as listed by the second AHP analysis. The detail ranking of each of the technology has been given in the table.3.

Table 3: Rank of the technology based on AHP analysis

Technology	Eigen vector from over all analysis	Rank
Lime-Alum Simple Chemical Filtration	0.090323	5
Activated Sludge Method	0.220636	2
Rotating Biological Contractor Method	0.081115	6
Trickling Filter	0.075	7
Adsorption	0.234393	1
Membrane Filtration	0.115089	4
Rotating Disk Membrane Modules	0.061081	8
Nanotechnology	0.122364	3

AHP analysis to find the drawbacks of nanotechnology

The second AHP analysis revealed that the viability of nanotech in real condition is the most important drawback with Eigen vector value of 0.294756 followed by the reuse issue of nanomaterials (0.185734) and cost (0.162758). The list important issue is regeneration of the material (0.047385) as given in the table.3. The analysis yielded a priority list of the drawbacks which are effecting the application of nanotechnology.

Table 4:

Criteria	Eigen Vector	Rank	References
Separation of Nanomaterials After Treatment	0.111514	4	Bhattacharya et al (2013)
Regeneration of Materials	0.047385	7	Li et al (2013)
Reuse Issue of Nanomaterials	0.185734	2	Bhattacharya et al (2013)
Immobilization of Nanomaterials In Water	0.086662	6	Alvarez et al (2008)
Fabrication of Nanomaterials Embedded in Solid Matrix	0.11119	5	Alvarez et al (2008)
Viability of Nanotech in Real Condition	0.294756	1	Alvarez et al (2008)
Cost	0.162758	3	Li et al (2013

DISCUSSION AND CONCLUSION

Various on-going researches and environmental application of nanoparticles cause the emanation of nanoparticles into the environment. These nanoparticles may possess potential risk for aquatic and terrestrial life (Bhattacharya et. al. 2013). Moreover, the detection of nanomaterials release in urban water cycle and its separation is a foremost obstacle for risk assessment. Several researchers made an effort for separation of nanoparticles via sedimentation and flocculation protocol. Moreover, till date the most effectual technique is membrane separation (e.g. nanofiltration and reverse osmosis) which has already been employed for the removal of pathogens from water. Chin et al (2006) established ceramic membranes to be more proficient than polymeric membranes in photo catalytic or catalytic

Ozonation applications due to its resistance towards UV and chemical oxidants. However, highly dispersed nanoparticles consisting of smaller range of particles when applied in waste water treatment may escape from the downstream treatment system (membrane filter) and enter the product water that finally results in premature material loss thus rendering potential human health and environmental hazards. To overcome these limitations effective methods are required to anchor the nanoparticles to reactor surfaces or the selective layer of filtration membranes. Hence, present condition demand development superior surface coating techniques viz, nanoparticles surface functionalization, membrane fouling minimization by the nanomaterials suspension, nanoparticles impregnation onto filter packing materials, e.g. granular activated carbon, or ion exchange resins and amalgamation of antimicrobial nanomaterials with existing water treatment systems.

Nanotechnology is a very promising area that can show the waste water treatment a new dimension. At the same time, they have some limitations and retention and reuse of the materials is a challenging issue. Nanomembranes and graphene based Nanomembranes are better solution which doesn’t pose any environmental hazard. Metal nanoparticles pose environmental hazard as they disperse very easily and their introduction in the urban water cycle will not be good. Carbonaceous nanomaterials on the other hand are easy to synthesize and mostly used as adsorbents. Regeneration and reuse of these are challenging. Much research work in this area is required as the amount of work is scant. Also, possible effects of the nanomaterials should be found in order to ensure their application. Addressing all these will certainly make nanotechnology a promising era in the field of waste water treatment.

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REFERENCES

Qilin Li, Shaily Mahendra, Delina Y. Lyon, Lena Brunet, Michael V. Liga, Dong Li, Pedro J.J. Alvarez; Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications; Water Research 42 (2008) 4591 – 4602.

Xiaolei Qu, Pedro J.J. Alvarez, Qilin Li; Applications of nanotechnology in water and wastewater treatment; Water Research 42 (2008) 3931 – 3946.

Sayan Bhattacharya, Indranil Saha, Aniruddha Mukhopadhyay, Dhrubajyoti Chattopadhyay, Uday Chand Ghosh and Debashis Chatterjee; Role of nanotechnology in water treatment and purification: Potential applications and implications; Int. Journal of Chemical Science and Technology; 2013; 3(3): 59-64.

Dhermendra K. Tiwari, J. Behari and Prasenjit Sen; Application of Nanoparticles in Waste Water Treatment; World Applied Sciences Journal 3 (3): 417-433, 2008.

US Bureau of Reclamation and Sandia National Laboratories, 2003; Desalination and water purification technology roadmap a report of the executive committee Water Purification.

World Health Organization, 1996. Guidelines for drinking-water quality; Geneva: WHO, Vol: 2.

US Environmental Protection Agency, 1998b; Microbial and disinfection by-product rules. Federal Register, 63: 69389-69476.

Droste, R.L., 1997; Theory and practice of water and wastewater treatment. New York: Wiley (Book).

Gupta, S., J. Behari and K. Kesari, 2006; Low frequency ultrasonic treatment of sludge. Asian J. Wat, Envi and Pollu., 3-2: 101-105.

Ichinose, N., Y. Ozaki and S. Kashu, 1992; Superfine particle technology. Springer, London,(Book).

Stoimenov, P.K., R.L. Klinger, G.L. Marchin and K.J. Klabunde, 2002. Metal oxide nanoparticles as bactericidal agents. Langmuir, 18: 6679-6686.

USEPA, 2007. In: Science Policy Council (Ed.), US Environmental Protection Agency nanotechnology white paper. EPA 100/B-07/001 Washington, DC.

Shannon, M., Bohn, P.W., Elimelech, M., Georgiadis, J.G., Marinas, B.J., Mayes, A.M., 008. Science and technology for water purification in the coming decades. Nature 452, 301–310.

Prachi, Pranjali Gautam, Deepa Madathil, A. N. Brijesh Nair; Nanotechnology in Waste Water Treatment: A Review; International Journal of Chem Tech Research; Vol.5, No.5, pp 2303-2308, July-Sept 2013

Wei, C., Lin, W.Y., Zainal, Z., Williams, N.E., Zhu, K., Kruzic, A.P.,Smith, R.L., Rajeshwar, K., 1994. Bactericidal activity of TiO2 photocatalyst in aqueous media: toward a solar-assisted water disinfection system. Environ. Sci. Technol. 28 (5), 934–938.

Lyon, D.Y., Adams, L.K., Falkner, J.C., Alvarez, P.J.J., 2006. Antibacterial activity of fullerene water suspensions: effects of preparation method and particle size. Environ. Sci. Technol. 40 (14), 4360–4366.

Kang, S., Pinault, M., Pfefferle, L.D., Elimelech, M., 2007. Singlewalled carbon nanotubes exhibit strong antimicrobial activity. Langmuir 23, 8670–8673.

Cho, M., Chung, H., Choi, W., Yoon, J., 2005. Different inactivation behavior of MS-2 phage and Escherichia coli in TiO2 photocatalytic disinfection. Appl. Environ. Microbiol. 71 (1), 270–275.

Badireddy, A.R., Hotze, E.M., Chellam, S., Alvarez, P.J.J., Wiesner, M.R., 2007. Inactivation of bacteriophages via photosensitization of fullerol nanoparticles. Environ. Sci. Technol. 41, 6627–6632.

Morones, J.R., Elechiguerra, J.L., Camacho, A., Holt, K., Kouri, J. B., Ramirez, J.T., acaman, M.J., 2005. The bactericidal effect of silver nanoparticles. Nanotechnology 16 (10),2346–2353.

Qi, L., Xu, Z., Jiang, X., Hu, C., Zou, X., 2004. Preparation and antibacterial activity of hitosan nanoparticles. Carbohydr. Res. 339 (16), 2693–2700.

Sangit Varma, Dhanashree Sarode, Sagar Wakale, B. A. Bhanvase, M. P. Deosarkar; Removal of Nickel from Waste Water Using Graphene nanocomposite; International Journal of Chemical and Physical Sciences IJCPS Vol. 2, Special Issue - March 2013.

Wei Lü, Jie Chen, Yao Wu, Lianfeng Duan, Yue Yang and Xin Ge; Graphene-enhanced visible-light photocatalysis of large-sized CdS particles for wastewater treatment; Nano. Research Letters 2014, 9:148.

MaryTheresa M. Pendergast, Eric M.V. Hoek; A Review of Water Treatment Membrane Nanotechnologies; Energy and Environmental Science; January 28, 2011 (Review only file).

M. Ulbricht, Advanced functional polymer membranes, Polymer, 2006, 47, 2217-2262.

P. Bernardo, E. Drioli and G. Golemme, Membrane gas separation: A review/state of the art, Ind. Eng. Chem. Res., 2009, 48, 4638-4663.

Jaewoo Lee, Hee-Ro Chae, Young June Won, Kibaek Lee, Chung-Hak Lee, Hong H. Lee, In-Chul Kim, Jong-min Lee; Graphene oxide nanoplatelets composite membrane with hydrophilic and antifouling properties for wastewater treatment; Journal of Membrane Science Volume 448, 2013, Pages 223–230.

George Z. Kyzas, Eleni A. Deliyanni and Kostas A. Matis; Graphene oxide and its application as an adsorbent for wastewater treatment; Journal of Chemical Technology and Biotechnology Volume 89, Issue 2, pages 196–205, February 2014.

Chungsying Lu, Yao-Lei Chung, Kuan-Foo Chang; Adsorption thermodynamic and kinetic studies of trihalomethanes on multiwalled carbon nanotubes; Journal of Hazardous Materials B138 (2006) 304–310.

Chen XiaoYan a, Khunjar Wendell b, Jun Zhu c, Li JiangLi a, Yu Xianxian a, Zhang Zhijian; Synthesis of nano-zeolite from coal fly ash and its potential for nutrient sequestration from anaerobically digested swine wastewater; Bioresource Technology 110 (2012) 79–85.

Wei-xian Zhang; Nanoscale iron particles for environmental remediation: An overview; Journal of Nanoparticle Research 5: 323–332, 2003.

Li-na Shi, Xin Zhang, Zu-liang Chen; Removal of Chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron; Water Research 42 (2008) 886 – 892.

Xin Zhang, Shen Lin, Xiao-Qiao Lu, Zu-liang Chen; Removal of Pb(II) from water using synthesized kaolin supported nanoscale zero-valent iron; Chemical Engineering Journal 163 (2010) 243–248.

Jing Fana, Yanhui Guoa, Jianji Wang, Maohong Fan; Removal of Pb(II) from water using synthesized kaolin supported nanoscale zero-valent iron; Chemical Engineering Journal 163 (2010) 243–248.

Changha Lee, Jee Yeon Kim, Won II Lee, Kara L. Nelson, Jeyong Yoon, and David L. Sedlak; Bactericidal Effect of Zero-Valent Iron Nanoparticles on Escherichia coli; Environ Sci Technol. 2008 July 1; 42(13): 4927–4933.

Xu, X.; Zhou. M.; Hao, P.; Hao, Z. (2005) Catalytic Reduction of Chlorinated and recalcitrant Compounds in Contaminated Water. J. Hazard. Mater., B123, 89-93.

Bettina Schrick, Jennifer L. Blough, A. Daniel Jones, and Thomas E. Mallouk; Hydrodechlorination of Trichloroethylene to Hydrocarbons Using Bimetallic Nickel-Iron Nanoparticles; Chem. Mater. 2002, 14, 5140-5147.

SUN YP, LI XQ, CAO J, ZHANG WX, WANG HP; CHARACTERIZATION OF ZERO-VALENT IRON ANOPARTICLES; ADV COLLOID INTERFACE SCI. 2006 JUN 30;120(1-3):47-56. EPUB 2006 MAY 12.

FENG HE AND DONGYE ZHAO; PREPARATION AND CHARACTERIZATION OF A NEW CLASS OF STARCH-STABILIZED BIMETALLIC NANOPARTICLES FOR DEGRADATION OF CHLORINATED HYDROCARBONS IN WATER; *ENVIRON. SCI. TECHNOL.*, 2005, 39 (9), PP 3314–3320.

Teik-Thye Lim, Jing Feng, Bao-Wei Zhu; Kinetic and mechanistic examinations of reductive transformation pathways of brominated methanes with nano-scale Fe and Ni/Fe particles; Water Research 41 (2007) 875 – 883.

Ralf Kaegi, Andreas Voegelin, Brian Sinnet, Steffen Zuleeg, Harald Hagendorfer, Michael Burkhardt and Hansruedi Siegrist; Behavior of Metallic Silver Nanoparticles in a Pilot Wastewater Treatment Plant; Environ. Sci. Technol. 2011, 45, 3902–3908.

Xiu, Z.M., Ma, J., Alvarez, P.J.J., 2011; Differential effect of common ligands and molecular oxygen on antimicrobial activity of silver nanoparticles versus silver ions; Environmental Science and Technology 45 (20), 9003-9008.

Xiu, Z.M., Zhang, Q.B., Puppala, H.L., Colvin, V.L., Alvarez, J.J.P., 2012; Negligible article-specific antibacterial activity of silver nanoparticles; Nano Letters 12 (8), 4271-4275.

Mayo, J.T., Yavuz, C., Yean, S., Cong, L., Shipley, H., Yu, W., Falkner, J., Kan, A., Tomson, M., Colvin, V.L., 2007. The effect of nanocrystalline magnetite size on arsenic removal. Science and Technology of Advanced Materials 8 (1-2), 71-75.

Deliyanni, E.A., Bakoyannakis, D.N., Zouboulis, A.I., Matis, K.A., 2003. Sorption of As(V) ions by akaganeite-type nanocrystals. Chemosphere 50 (1), 155-163.

Morimoto Y, Kobayashi N, Shinohara N, Myojo T, Tanaka I, Nakanishi J.; Hazard Assessments Of Manufactured Nanomaterials; J Occup Health. 2010 Oct 20.

C. R. QUETEL, E. VASSILEVA, I. PETROV, K. CHAKAROVA AND K. I. HADJIIVANOV; FIRST RESULTS ON FE SOLID-PHASE EXTRACTION FROM COASTAL SEAWATER USING ANATASE TIO2 NANO-PARTICLES; ANAL BIOANAL CHEM. 2010 MAR; 396(6):2349-61.

XU Y, ZHAO D; REMOVAL OF COPPER FROM CONTAMINATED SOIL BY USE OF POLY(AMIDOAMINE) DENDRIMERS; ENVIRON SCI TECHNOL. 2005 APR 1;39(7):2369-75.

Mamadou S. Diallo, Simone Christie, Pirabalini Swaminathan, James H. Johnson, Jr., William A. Goddard III; Dendrimer Enhanced Ultrafiltration.1. Recovery of Cu(II) from Aqueous Solutions Using PAMAM Dendrimers with Ethylene Diamine Core and Terminal NH_2 Groups; Env. Sci. Tech. 2005,39, 1366-1377.

Diallo, M.S., Christie, S., Swaminathan, P., Johnson, J.H., Goddard, W.A., 2005. Dendrimer enhanced ultrafiltration. 1. Recovery of Cu (II) from aqueous solutions using PAMAM dendrimers with ethylene diamine core andterminalNH2 groups. Environmental Science and Technology 39 (5), 1366-1377.

Chuyang Y. Tang, Young-Nam Kwon, James O. Leckie, Fouling of reverse osmosis and nanofiltration membranes by humic acid—Effects of solution composition and hydrodynamic conditions, Journal of Membrane Science 290 (2007) 86–94.

Jeonghwan Kim , Bart Van der Bruggen, The use of nanoparticles in polymeric and ceramic membrane structures: Review of manufacturing procedures and performance improvement for water treatment, Environmental Pollution, 158, (2010), 2335-2349.

Naresh N. Mahamuni, Yusuf G. Adewuyi, “Advanced oxidation processes (aops) involving ultrasound for waste water treatment: A review with emphasis on cost estimation” Ultrasonics Sonochemistry Volume 17, Issue 6, August 2010, Pages 990–1003.

Jianquan Luo[a, b], Luhui Ding[a, ,], Yinhua Wan[b], Patrick Paullier[c], Michel Y. Jaffrin[c]”Application of NF-RDM (nanofiltration rotating disk membrane) module under extreme hydraulic conditions for the treatment of dairy wastewater” Chemical Engineering Journal Volume 163, Issue 3, 1 October 2010, Pages 307–316.

Johannes Meier, Thomas Melin, Ludger H. Eilers“Nanofiltration and adsorption on powdered adsorbent as process combination for the treatment of severely contaminated waste water” Desalination Volume 146, Issues 1–3, 10 September 2002, Pages 361–366.

Xiaolei Qu, Pedro J.J. Alvarez, Qilin Li “Applications of nanotechnology in water and wastewater treatment “Water Research Volume 47, Issue 12, 1 August 2013, Pages 3931–3946 .

Qun Hui Wang[a, b, ,], Lanhe Zhang[a], Shulei Tian[a], Paul Ta-Chin Sun[b], Weimin Xie[a]‘‘A pilot-study on treatment of a waste gas containing butyl acetate, ***n***-butyl alcohol and phenylacetic acid from pharmaceutical factory by bio-trickling filter”Bioresource Technology Volume 98, Issue 2, January 2007, Pg 266–272.

L. Larbi[a, ,], N. Fertikh[b], A. Toubal[b] “Study of Material Used in Nanotechnology for the Recycling of Industrial Waste Water ” Physics Procedia Volume 55, 2014, Pages 317–323 ,8th International Conference on Material Sciences, CSM8-ISM5.

Amit Bhatnagar[a, b, , ,], Mika Sillanpää ” Utilization of agro-industrial an municipal waste materials as potential adsorbents for water treatment—A review” Chemical Engineering Journal,Volume 157, Issues 2–3, 1 March 2010, Pages 277–296.

Hanna M Huotari[a,], Ingmar H Huisman[b], Gun Trägårdh[b] ”Electrically enhanced crossflow membrane filtration of oily waste water using the membrane as a cathode,Journal of Membrane Science,Volume 156, Issue 1, 24 April 1999, Pages 49–60.

Qun Hui Wang[a, b, ,], Lanhe Zhang[a], Shulei Tian[a], Paul Ta-Chin Sun[b], Weimin Xie[a] “A pilot-study on treatment of a waste gas containing butyl acetate, ***n***-butyl alcohol and phenylacetic acid from pharmaceutical factory by bio-trickling filter” Biochemical Engineering Journal Volume 37, Issue 1, 2007, Pages 42–48.

Suntud Sirianuntapiboon, Chollada Chuamkaew “Packed cage rotating biological contactor system for treatment of cyanide wastewater” Bioresource Technology,Vol. 98, Issue 2, 2007, Pages 266–272.

Francis Hassard[a], Jeremy Biddle[a, b], Elise Cartmell[a], Bruce Jefferson[a], Sean Tyrrel[a], Tom Stephenson[a,] ” Rotating biological contactors for wastewater treatment – A review” Process Safety and Environmental Protection.

Ibrahim M. Ismail[a, ,], Ahmed S. Fawzy[a], Nabil M. Abdel-Monem[a], Mahmoud H. Mahmoud[b], Mohamed A. El-Halwany[b] “Combined coagulation flocculation pre treatment unit for municipal wastewater’’Journal of Advanced Research,Volume 3, Issue 4, October 2012, Pages 331–336.

P. Rudnickia, Z. Hubickib, D. Kołodyńskab, Evaluation of heavy metal ions removal from acidic waste water streams” Chemical Engineering Journal,Volume 252, 15 September 2014, Pages 362–373.

Jianguo Zhao, Xiurong Chen, Fengkai Lin, Na Yang, Hua Huang, Jun Zhao” Mechanism of toxicity formation and spatial distribution in activated sludge treating synthetic effluent containing bisphenol A (BPA)”Chemical Engineering JournalVolume 250, 15 August 2014, Pages 91–98.

Xiaolei Zhang[a], Song Yan[a], Rajeshwar D. Tyagi[a, ,], Rao Y. Surampalli[b], Jose R. Valéro[a] “Lipid production from *Trichosporon oleaginosus* cultivated with pre-treated secondary wastewater sludge” Fuel Volume 134, 15 October 2014, Pages 274–282.

Amir Mowla, Mehrab Mehrvar, Ramdhane Dhib Combination of sonophotolysis and aerobic activated sludge processes for treatment of synthetic pharmaceutical wastewater; Chemical Engineering Journal,Vol. 255, 2014, Pg 411–423.

Rani Devi[a, ,], Vijender Singh[b], Ashok Kumar[c]“COD and BOD reduction from coffee processing wastewater using Avacado peel carbon” Bioresource Technology Volume 99, Issue 6, April 2008, Pages 1853–1860.

L. Gustavsson, M. Engwall“Treatment of sludge containing nitro-aromatic compounds in reed-bed mesocosms – Water, BOD, carbon and nutrient removal” Waste Management, Vol 32, Issue 1, 2012, Pg 104–109.

L. Lijklema “Factors affecting pH change in alkaline waste water treatment—III: A dynamic simulation” Water Research Volume 6, Issue 2, February 1972, Pages 165–182.

M El-Fadel, M Massoud “Methane emissions from wastewater management” Environmental PollutionVolume 114, Issue 2, September 2001, Pages 177–185.

Tarek G. Ammari “Utilization of a natural ecosystem bio-waste; leaves of *Arundo donax*reed, as a raw material of low-cost eco-biosorbent for cadmium removal from aqueous phase” Ecological Engineering,Volume 71, October 2014, Pages 466–473.

Jan Cools[a, ,], Steven Broekx[c], Veronique Vandenberghe[a], Hannes Sels[b], Erika Meynaerts[c], Peter Vercaemst[c], Piet Seuntjens[c, f, g], Stijn Van Hulle[b], Hilde Wustenberghs[e], Willy Bauwens[d], Marc Huygens[a] “ Coupling a hydrological water quality model and an economic optimization model to set up a cost-effective emission reduction scenario for nitrogen” Environmental Modelling & Software,Volume 26, Issue 1, January 2011, Pages 44–51,Thematic Issue on Science to Improve Regional Environmental Investment Decisions.

D. Cassano[a, c], A. Zapata[b], G. Brunetti[c], G. Del Moro[a], C. Di Iaconi[a], I. Oller[b], S. Malato[b, ,], G. Mascolo[a, ,]” Comparison of several combined/integrated biological-AOPs setups for the treatment of municipal landfill leachate: Minimization of operating costs and effluent toxicity,Chemical Engineering Journal,Volume 172, Issue 1, 1 August 2011, Pages 250–257.

C. Matos, S. Pereira, E.V. Amorim, I. Bentes, A. Briga-Sá; “Wastewater and greywater reuse on irrigation in centralized and decentralized systems — An integrated approach on water quality, energy consumption and CO_2 emissions”Science of The Total Environment,Volume 493, 15 September 2014, Pages 463–471.

Maximilian Schneider, , Philo Boras, Hendrik Schaede, Lukas Quurck, Stephan Rinderknecht; Effects of Operational Strategies on Performance and Costs of Electric Energy Storage Systems**;** 8th International Renewable Energy Storage Conference and Exhibition 2013;Energy Procedia,Vol. 46, 2014, Pg 271–280.

Kannan Govindan , Susana G. Azevedo, Helena Carvalho, V. Cruz-Machado; Impact of supply chain management practices on sustainability; Journal of Cleaner Production xxx (2014) 1-14.

Teresa M. Mata, Nídia S. Caetano, Carlos A.V. Costa, Subhas K. Sikdar, António A. Martins; Sustainability analysis of biofuels through the supply chain using Indicators; Sustainable Energy Technologies and Assessments 3 (2013) 53–60.

Chungsying Lu, Huantsung Chiu; Adsorption of zinc (II) fromwater with purified carbon nanotubes; Chemical Engineering Science 61 (2006) 1138 – 1145.

Xiao-qin Li, Daniel W. Elliott, and Wei-xian Zhang; Zero-Valent Iron Nanoparticles for Abatement of Environmental Pollutants: Materials and Engineering Aspects; Critical Reviews in Solid State and Materials Sciences, 31:111–122, 2006.

Ya-qi Cai, Yu-e Cai, Shi-fen Mou, Yi-qiang Lu; Multi-walled carbon nanotubes as a solid-phase extraction adsorbent for the determination of chlorophenols in environmental water samples; Journal of Chromatography A, 1081 (2005) 245–247.

T.S. Sreeprasad, Shihabudheen M. Maliyekkal1, K.P. Lisha, T. Pradeep; Reduced graphene oxide–metal/metal oxide composites: Facile synthesis and application in water purification; Journal of Hazardous Materials 186 (2011) 921–93.

E. Alvarez-Ayuso, A. Garcıa-Sanchez, X. Querol; Purification of metal electroplating waste waters using zeolites; Water Research 37 (2003) 4855–4862.

Jiasheng Cao, Daniel Elliott and Wei-xian Zhang; Perchlorate reduction by nanoscale iron particles; Journal of Nanoparticle Research (2005) 7: 499–506.

Xiao-qin Li and Wei-xian Zhang; Iron Nanoparticles: the Core-Shell Structure and Unique Properties for Ni(II) Sequestration; Langmuir 2006, 22, 4638-4642.

Rong Chenga, Jian-long Wang, Wei-xian Zhang; Comparison of reductive dechlorination of p-chlorophenol using Fe^0 and nanosized Fe^0; Journal of Hazardous Materials 144 (2007) 334–339.

Soumitra Kar, R.C. Bindal, P.K. Tewari; Carbon nanotube membranes for desalination and water purification: Challenges and opportunities; Nano Today (2012) 7, 385—389.

Maria E. Pena, George P. Korfiatis, Manish Patel, Lee Lippincott, Xiaoguang Meng; Adsorption of As(V) and As(III) by nanocrystalline Titaniumdioxide; Water Research 39 (2005) 2327–2337.

Mst. Shamsun Nahar, Kiyoshi Hasegawa , Shigehiro Kagaya; Photocatalytic degradation of phenol by visible light-responsive iron-doped TiO2 and spontaneous sedimentation of the TiO2 particles; Chemosphere 65 (2006) 1976–1982.

Yong Sheng Chen, John C. Crittenden, Stephen Hackney, Larry Sutter, David W Hand; Preparation of a Novel TiO2-Based p-n Junction Nanotube Photocatalyst; Environmental Science & Technology, VOL. 39, NO. 5, 2005, 1201 – 1208.

Hsing-Lung Lien, Wei-xian Zhang; Nanoscale iron particles for complete reduction of chlorinated ethenes; Colloids and Surfaces A: Physicochemical and Engineering Aspects 191 (2001) 97–105.

Eva R. Birnbaum , Karen C. Rau & Nancy N. Sauer (2003) Selective Anion Binding from Water Using Soluble Polymers, Separation Science and Technology, 38:2, 389-404, DOI: 10.1081/SS-120016581.

ENVIRONMENTAL ASPECTS OF TRAFFIC IN URBAN AREA

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THE OXYHYDROGEN AS A SUPPLEMENTARY FUEL FOR COMPRESSION IGNITION ENGINES

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ABSTRACT

The paper presented the experimental research on using the fuel mixture diesel/oxyhydrogen for running the commercial vehicle Dacia Logan equipped with diesel engine 1.5 dci. A dry type electrolyzer is used for generating the HHO and engine parameters like power, torque and specific consumption is obtained with dynamometer MAHA LPS 3000 R100. The flow rates of the HHO were up to 1 l/min. The results revealed that specific consumption was higher for speeds 2000 – 2500 rpm and lower for 2000 – 2500 rpm with negligible differences in engine parameters like power or torque.

Key words: *oxyhydrogen, internal combustion engine, diesel, specific consumption, power, torque.*

INTRODUCTION

Verhelst et al. (2009) reveals that spark ignition engines can be relatively easily converted to hydrogen using port fuel injection (PFI). However, because of the lower volumetric energy density of a hydrogen–air mixture and the occurrence of abnormal combustion phenomena such as backfire, hydrogen-fueled PFI engines suffer from a power deficit in comparison with gasoline engines. They reported measurements on a single-cylinder hydrogen engine equipped with a supercharger and an exhaust gas recirculation (EGR) system. Using EGR combined with supercharging and a three-way catalyst (TWC) shown significant increase of the power output while limiting tailpipe emissions of NOx.

Dieguez et al. (2014) presented a research on commercial 1.4 L four-cylinder Volkswagen spark-ignition engine previously adapted to operate on pure hydrogen that has been fueled with hydrogen/methane mixtures with 5–20 vol.% methane (29.6–66.7 wt.%). A clear positive effect of reducing the spark advance on the specific NOx emissions has been observed. In the case of CO and unburned hydrocarbons (HCs), their specific emissions increase with the methane content of the fuel mixture. However, they also increase as k increases in spite of the lower fuel concentration due to a proportionally higher reduction of the power. The effect of the increase of the engine speed is positive on the CO and HCs emissions but negative on that of NOx due to improved mixing and higher temperature associated to intensified turbulence in the cylinders.

Liu et al. (2008) presented the effect of injection timing on mixture formation in a manifold injection H2ICE for various engine speed and equivalence ratio by CFD simulation. They claimed that in hydrogen internal combustion engine (H2ICE) easily occur inlet manifold backfire and other abnormal combustion phenomena because of the low ignition energy, wide flammability range and rapid combustion speed of hydrogen. It was concluded that H2ICE of manifold injection have a limited injection end timing in order to prevent backfire in the inlet manifold. Also the limit of injection end timing of the H2ICE was proposed and validated by engine experiment.

Yamada and Mohamad (2010) confirmed that hydrogen internal combustion engine (HICE) wastes more heat, and producing nearly three times more water than a conventional engine. It was described the principle behind a novel waste heat recovery sub-system that exploits the water produced by an HICE as the working fluid for an open-cycle power generation system based on the Rankine cycle. A fundamental thermodynamic model shows the contribution of the sub-system to the overall thermal efficiency of the HICE at various engine speeds, with and without a condenser. The results show that the condenser is not cost-effective and that the overall thermal efficiency with the proposed sub-system is 27.2% to 33.6%, representing improvements of 2.9% to 3.7%, at engine speeds of 1500 to 4500 rpm.

Huang et al. (2011) proposed a fuzzy control bio-hydrogen internal combustion engine (ICE) generating system. The ICE technology is composed of thermodynamics, mechanical engineering, hydrodynamics, and electrical engineering. The study establishes a fuzzy control system with an output generator and an ICE with solenoid valve that controls bio-hydrogen injection. They found that experimental system successfully output stable power and carried out parameters of bio-hydrogen flow rate, air/fuel ratio, injection pressure, and ignition timing.

Sun et al. (2012) presented reviews on research and development of hydrogen fuelled engines in China, and reports the most achievements obtained by Chinese researchers in the field of the hydrogen fuelled engines which involve hydrogen-enriched gasoline engine, hydrogen-enriched diesel engine, hydrogen-(compressed) natural gas dual (HNG/HCNG) fuel engine, and pure hydrogen internal combustion engine (H2ICE).

Sun et al. (2013) investigated the cycle variation characteristics of a port fuel injection hydrogen internal combustion engine (PFI-HICE). They found that COVimep decreases as fuel/air ratio increases from 1000 to 5500 rpm, and engine speed minimally affects COVimep. Also the ignition advance angles that correspond to the minimum COVimep of the PFI-HICE decrease as fuel/air ratio increases. The effect of ignition advance angle on COVimep diminishes as fuel/air ratio increases. The COVimep of the PFI-HICE rapidly decreases as throttle increases when the throttle is less than 20%. Injection timing only slightly affects COVimep under high-speed conditions, and COVimep increases when hydrogen is injected in intake periods under low-speed conditions. They claimed that COVimep improves the stability of PFI-HICEs.

Chiriac and Apostolescu (2013) investigated the performance of a conventional tractor diesel engine running alternatively with B20 and petroleum diesel at various speeds and full load and then, with the same fuels enriched with hydrogen, at 60% load and two speeds. It was found that compared with petroleum diesel, the engine fueled with B20 has significantly higher NOx emissions at all speeds and lower smoke and CO emissions, while both fuels combustion closely resembles. The addition of hydrogen to B20 by aspiration into the intake air flow at 60% load led to an increase of NOx emission and to lower smoke and CO emissions. Hydrogen addition to petroleum diesel showed a beneficial effect on NOx and CO emissions, while smoke was sensitive only at 2400 rpm.

Kose and Ciniviz (2013) presented the research on compression ignition engine (CI) with 17/1 compression ratio, four cylinders, four stroke, turbocharger and 3.908 liters engine powered by diesel fuel that was injected directly to combustion chamber and hydrogen was added to inlet manifold at rates of 2.5%, 5% and 7.5% as volume. The obtained results reveals an increase in engine torque, power, thermal efficiency, nitrogen oxides (NOx) and exhaust gasses temperatures were acquired at every hydrogen addition ratio while a decrease in hydrocarbons (HC), carbon monoxide (CO) and oxygen (O2). While engine torque exhibited an increase at a rate of 8.3% comparing with standard diesel operation at 1250 min^{-1} and 7.5% hydrogen addition ratio, engine power increased 17% at 2250 min^{-1} engine speed and 7.5% hydrogen addition ratio. Brake thermal efficiency of 2.5% was obtained as 40.4% comparing with 33% value of SDI at 1750 min^{-1}. The lowest CO, CO2, HC and NOx emission values were obtained at 2250 min^{-1} engine speed and 2.5% hydrogen addition ratio as 0.013; 2500 min^{-1} engine speed and 7.5% hydrogen addition ratio as 7.4%; 1250 min^{-1} engine speed and 2.5% hydrogen addition ratio as 10 ppm and 1000 min^{-1} engine speed and 7.5% hydrogen addition ratio as 1092 ppm respectively comparing with standard diesel operation.

Kosar et al (2011) presented the research on a small gasoline engines running on slightly rich mixture, without catalytic converter. It was found that when the gasoline engines are operated with pure hydrogen, NOx emissions increase and the backfire occurs. Also the specific fuel consumption and NOx emissions were reduced by about 57% and 66%, respectively at hydrogen operation. Moreover, the values near zero for CO, CO2 and HC emissions were obtained. The test results showed that the small gasoline engine can operate with pure hydrogen at a suitable lean mixture without any backfire, and provide important improvements in emissions and fuel consumption without using any exhaust control system, electronic ignition system and fuel injection system which increase cost of engine.

King (2011) presented the review on using the hydrogen obtained by electrolyze. Most investigators believe the energy is from burning hydrogen. A hypothesis is proposed in this work that the dominant energy is not coming from hydrogen, but rather it is coming from charged water gas clusters, which activate and coherently trap zero-point energy.

THE EXPERIMENTAL SETUP

The experimental setup consists of dynamometer MAHA LPS 3000 R100 (Fig. 1), installation for hydrogen generation (Figs. 2 and 3) and commercial vehicle Dacia Logan with 1,5 L diesel engine. Besides classic performance measurements with recording of engine power, torque, engine speed and speed, the dynamometer offers in its load simulation mode comprehensive diagnostic possibilities as the ability to connect external measurement equipment like emission tester or a fuel consumption meter.

The installation for hydrogen generation is composed of recipient for electrolyze with cathode, anode and plates. The electrolyzer with dry cells with the small volume of electrolyte, 11 electrodes, medium voltage (10-14 V) and hydroxide sodium with higher concentration of 28%. The PWM pulse modulator, presented in Fig. 3 is used for stabilization of the electric current used in electrolyzer.

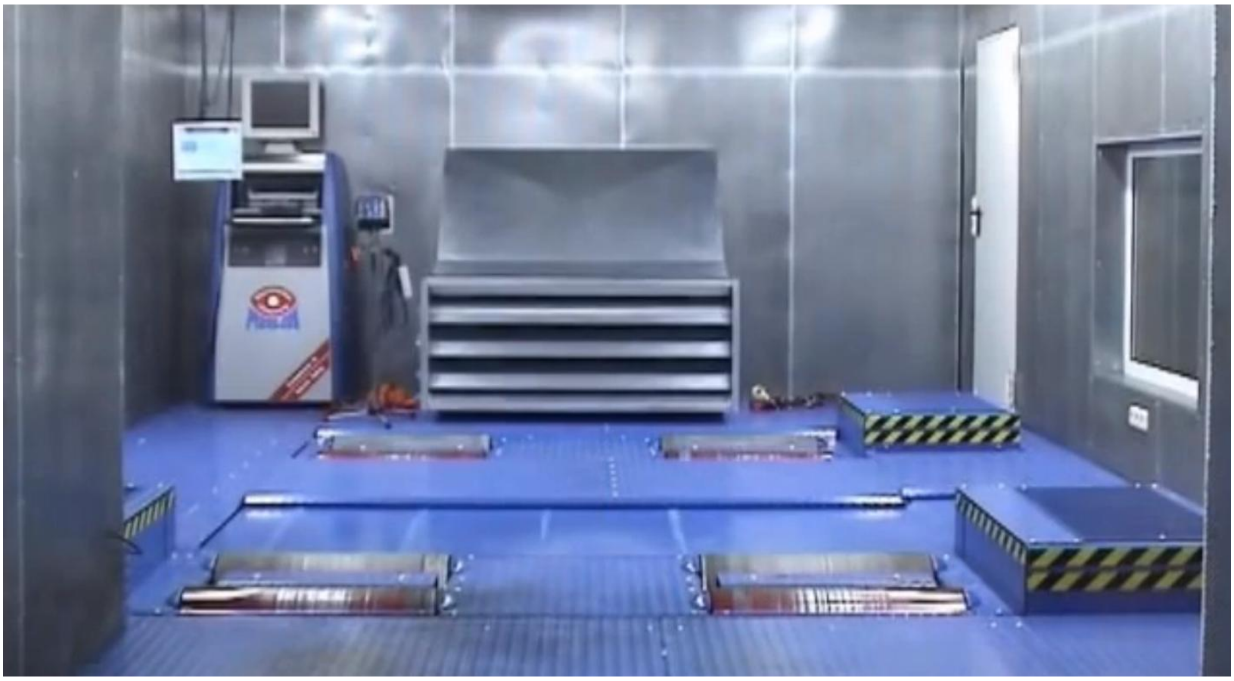
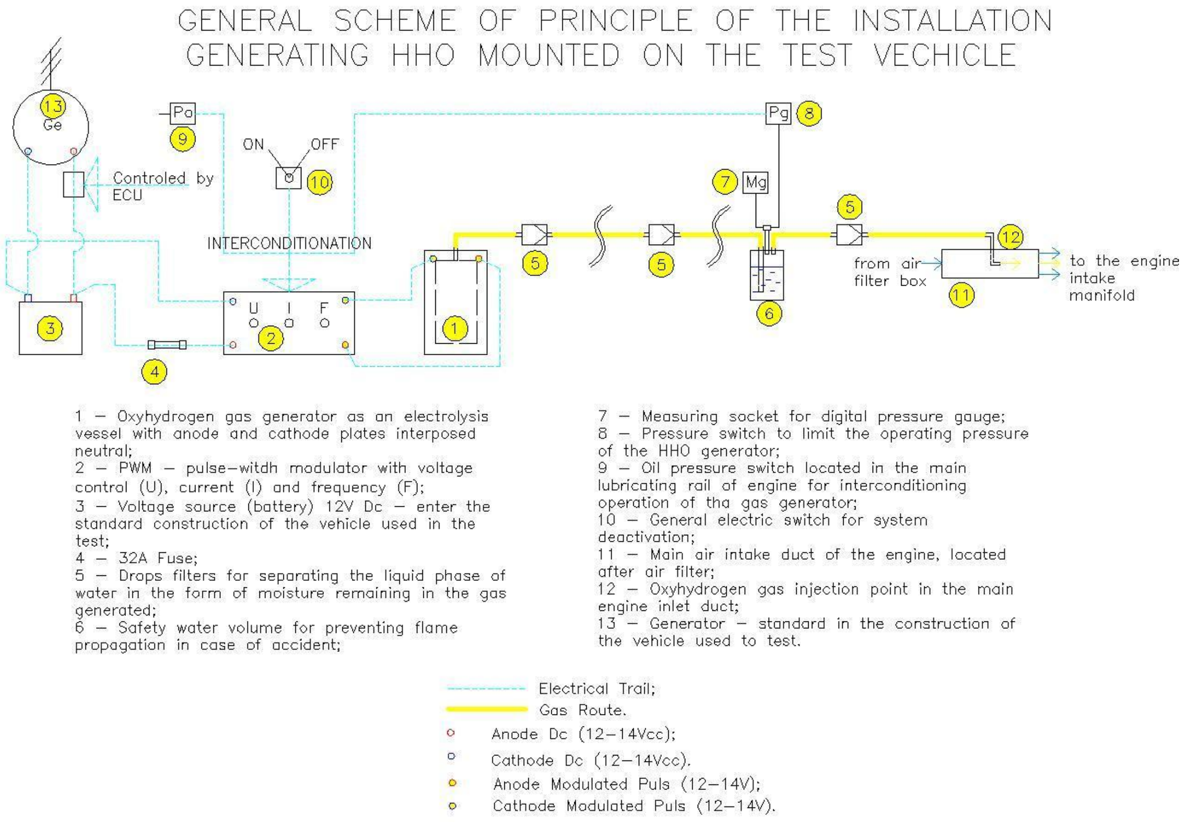


Figure 1. Roller dynamometer MAHA LPS 3000 R100



GENERAL SCHEME OF PRINCIPLE OF THE INSTALLATION GENERATING HHO MOUNTED ON THE TEST VECHICLE

1 – Oxyhydrogen gas generator as an electrolysis vessel with anode and cathode plates interposed neutral;
2 – PWM – pulse-witdh modulator with voltage control (U), current (I) and frequency (F);
3 – Voltage source (battery) 12V Dc – enter the standard construction of the vehicle used in the test;
4 – 32A Fuse;
5 – Drops filters for separating the liquid phase of water in the form of moisture remaining in the gas generated;
6 – Safety water volume for preventing flame propagation in case of accident;
7 – Measuring socket for digital pressure gauge;
8 – Pressure switch to limit the operating pressure of the HHO generator;
9 – Oil pressure switch located in the main lubricating rail of engine for interconditioning operation of tha gas generator;
10 – General electric switch for system deactivation;
11 – Main air intake duct of the engine, located after air filter;
12 – Oxyhydrogen gas injection point in the main engine inlet duct;
13 – Generator – standard in the construction of the vehicle used to test.

Electrical Trail;
Gas Route.
Anode Dc (12–14Vcc);
Cathode Dc (12–14Vcc).
Anode Modulated Puls (12–14V);
Cathode Modulated Puls (12–14V).

Figure 2. General scheme oxyhydrogen generator

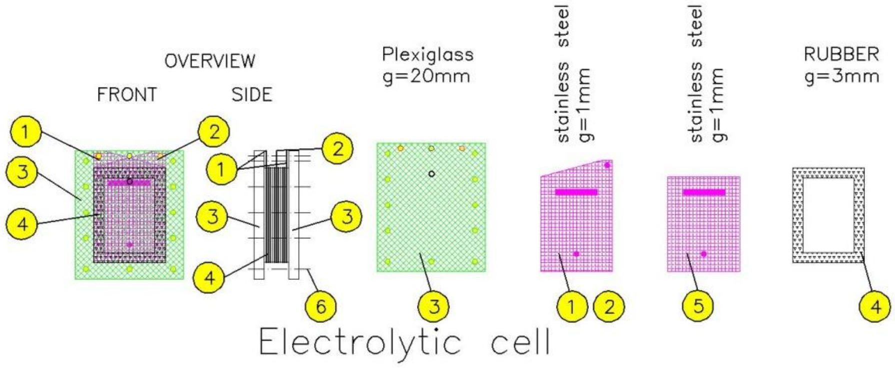


Figure 3. The components of the oxyhydrogen generator

Also the filter for liquid separation is used as well as the pressure switch for limitation of the working pressure in the installation for hydrogen generation at 350 Pa. Besides, the pressure switch is used for oil pressure in order to stop the hydrogen generator if the engine is not working. The working characteristics of the electrolyzer is presented in the table 1. Moreover the technical data of the engine are presented in the table 2. It has to be mentioned that injection point of the HHO is on the engine manifold.

The experiment consists of power, torque and specific consumption measurements. Initially the diesel oil is used as the reference fuel followed by the blend of diesel oil and hydrogen at different ratios (max. hydrogen flow rate 1 l/min). It has to be mentioned that the air pressure and temperature were the same for all the measurements. Moreover the injection map of the engine is not modified.

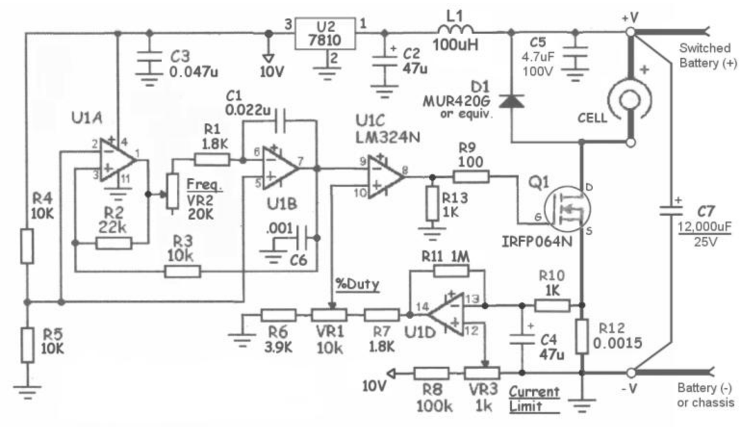


Figure 4. Wiring diagrams of Pulse With Modulator (PWM)

Table 1: The electrolyzer properties

Hydrogen flow rate [*l* / min]	Electric current [A]	Voltage [V]	Area of the plates (electrodes) [mm]	Electrolyte	Configuration of the electrodes
up to 1,5	1.5 < I < 20	8 < U < 14	140 x 185	NaOH, 28 %	3 main and 8 intermediate electrodes

Table 2: The engine properties

Volume [cm^3]	Nr. Cylinders	Nr. valves	Pollution	Max. power [kW]	Max. Torque [Nm]	Max. speed [rot/min]
1461	4	8	Euro 3	48	160	2000
Injection type	Fuel	Consumption (complete cycle)	Consumption (urban cycle) [l/100 km]	Consumption (extra-urban cycle) [l/100 km]	CO2 emissions [g/km]	Vol. ratio
Common rail	Diesel oil	4.8	5.8	4.3	128	18.3:1

RESULTS AND DISCUSSIONS

Measurements are made for various mixtures of diesel fuel and oxyhydrogen that was injected directly in engine intake manifold. The maximum flow rate of the HHO was up to 1 l/min. The blended mixture was labeled with PWM1 to PWM7, considering the absence of the flow meter for the hydrogen. The HHO flow rate was varied with electronic wave modulator with maximum values for voltage U = 13.6 V and electric current I = 20.6 A (PWM7) and minimum values for U = 9.7 V and I = 2.66 A (PWM1). The electrolyte concentration was 28 % Vol.

In Figs. 5.1, 5.2, 7, 9, 11, 13, 15, 17, 19 the engine torque and power versus engine speed was presented. It might be observed higher values for the engine torque (10 %) and power (11 %) compared with original performance of the engine (Fig. 5.2) for both diesel fuel and diesel/HHO mixture. It is explained in the following way: the engine is working with diesel/HHO mixture for three years without modifications of the injection maps. On the other hand the combustion of the mixture is faster (Yilmaz et al. 2010) and at higher temperatures (Kose and Ciniviz, 2013), some kind of cleaning of the engine compared with the precedent situation when it was working only with diesel fuel. Consequently decreasing of the ignition advanced angle was automatically done through the proper injection management. Finally the uniform rotation of the engine crankshaft is observed with lower noise. So these modifications might lead to higher powers and torques through increases of the efficiency of thermodynamic cycle.

Moreover the notable differences between diesel and diesel/HHO mixture are no observed for the engine power and torque. This might be explained through the low flow rates of the HHO that can not influence the maximum values of the engine performance. On the other hand these low flow rates have an impact on specific consumptions (local reduction of 15 – 20 %) at speeds from 1500 to 2000 rpm (Fig. 2.1). Besides at speeds from 2000 to 2500 rpm, local increases of specific consumptions about 15 – 25 % are observed.

The measurements of the engine parameters for speeds lower than 1500 rpm were not possible with this type of dynamometer. On the other hand for engine speeds higher than 3000 rpm, the specific consumptions are approximately the same regardless the fuel type used in this research.

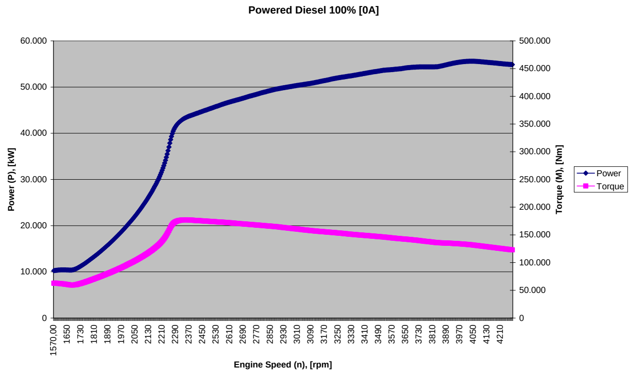


Figure 5.1. Diesel powered 100% - Power and Torque Characteristics Logan 1.5DCI Euro3

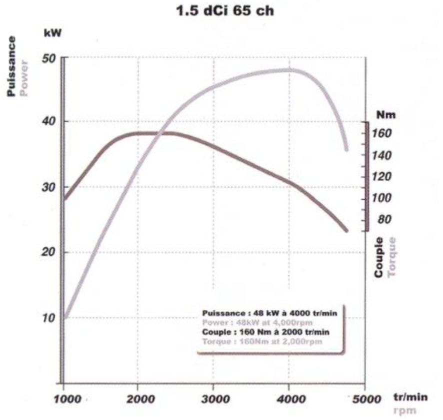


Figure 5.2. Diesel powered 100% -Original features Power and Torque Logan 1.5DCI Euro3

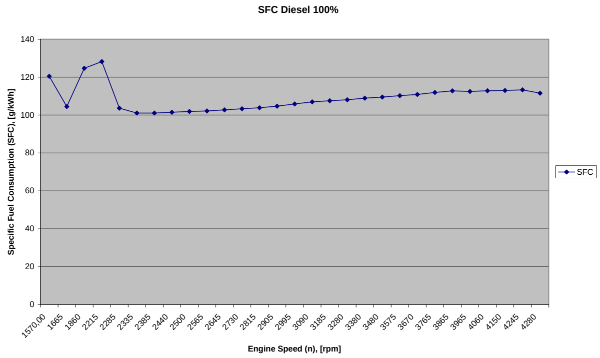


Figure 6. Diesel powered 100% - Specific Fuel Consumption Logan 1.5DCI Euro3

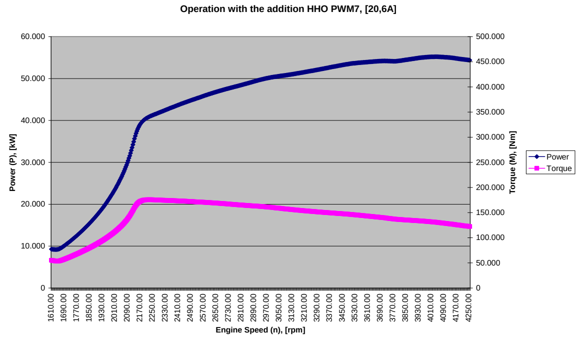


Figure 7 Operation with the addition HHO (PWM7) - Power and Torque Characteristics Logan 1.5DCI Euro3

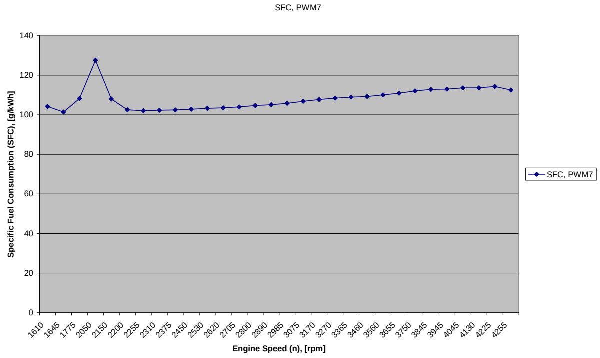


Figure 8. Operation with the addition HHO (PWM7) - Specific Fuel Consumption Logan 1.5DCI Euro3

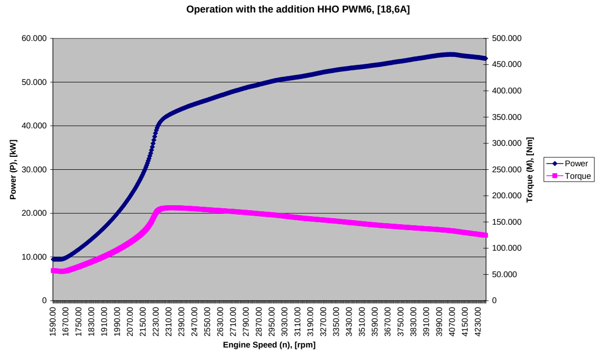


Figure 9. Operation with the addition HHO (PWM6) - Power and Torque Characteristics Logan 1.5DCI Euro3

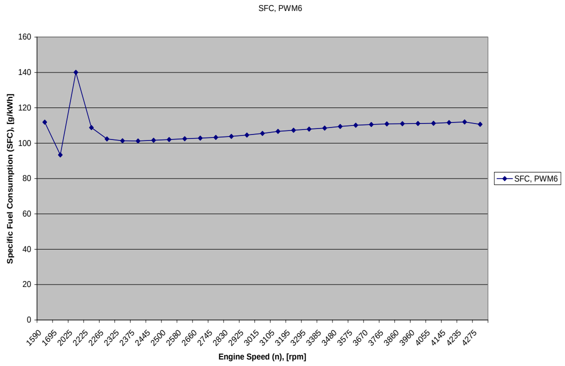


Figure 10. Operation with the addition HHO (PWM6) - Specific Fuel Consumption Logan 1.5DCI Euro3

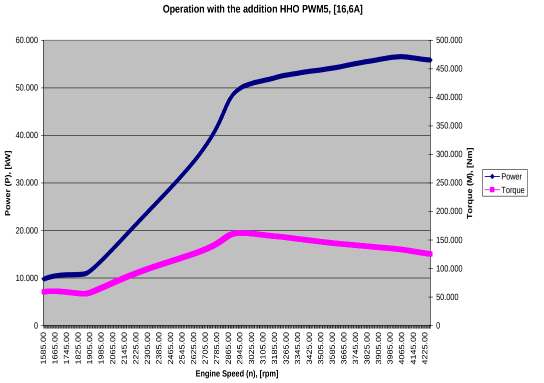


Figure 11. Operation with the addition HHO (PWM5) - Power and Torque Characteristics Logan 1.5DCI Euro3

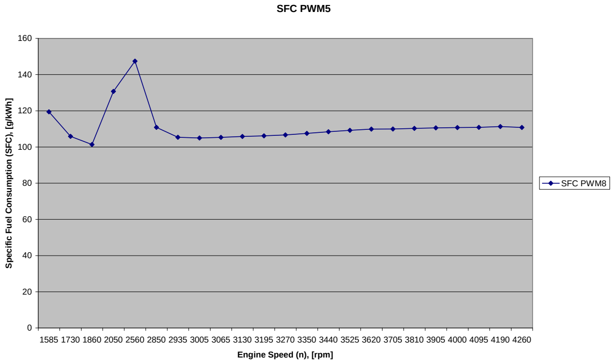


Figure 12. Operation with the addition HHO (PWM5) - Specific Fuel Consumption Logan 1.5DCI Euro3

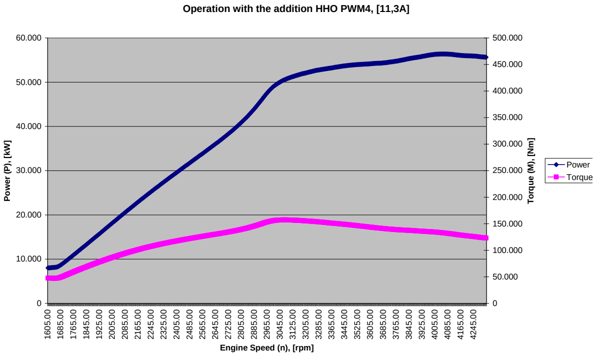


Figure 13. Operation with the addition HHO (PWM4) - Power and Torque Characteristics Logan 1.5DCI Euro3

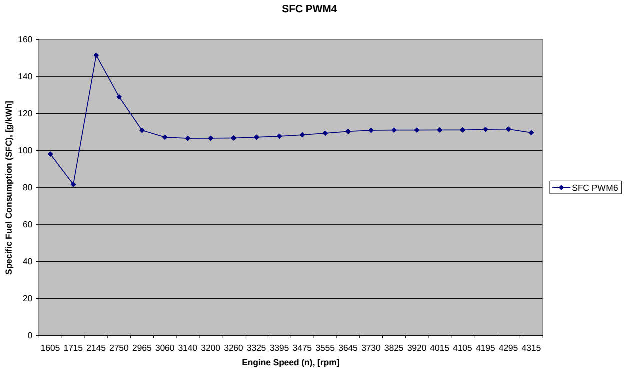


Figure 14. Operation with the addition HHO (PWM4) - Specific Fuel Consumption Logan 1.5DCI Euro3

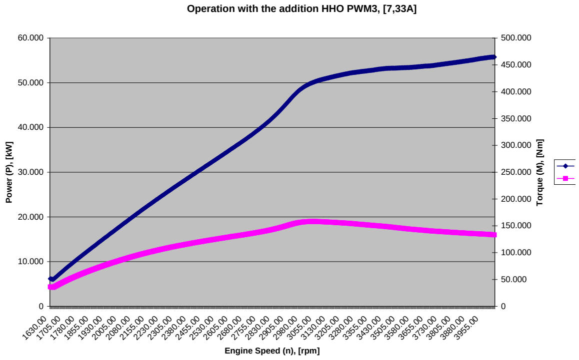


Figure 15. Operation with the addition HHO (PWM3) - Power and Torque Characteristics Logan 1.5DCI Euro3

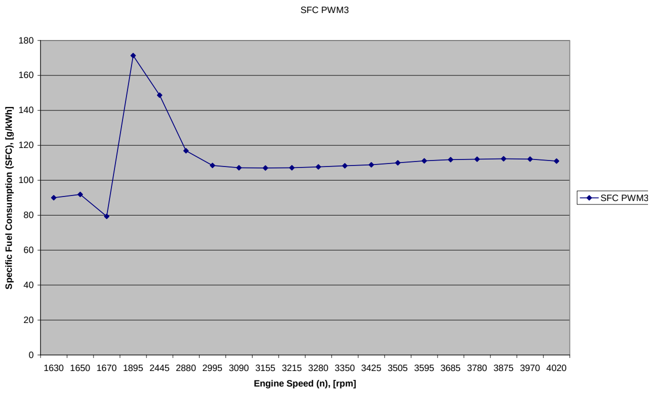


Figure 16. Operation with the addition HHO (PWM3) - Specific Fuel Consumption Logan 1.5DCI Euro3

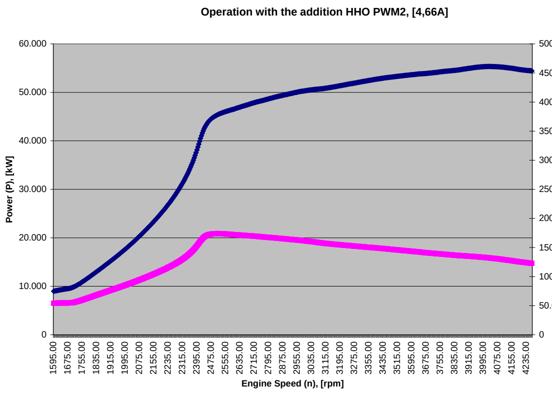


Figure 17. Operation with the addition HHO (PWM2) - Power and Torque Characteristics Logan 1.5DCI Euro3

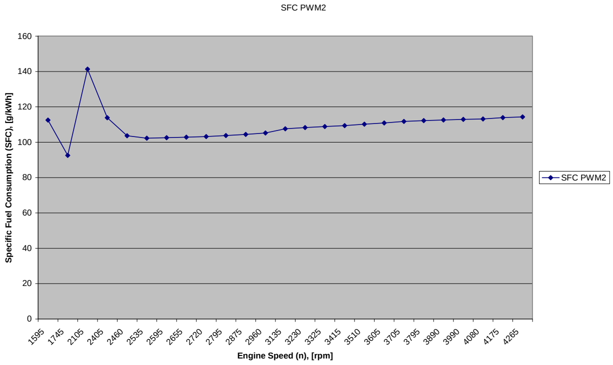


Figure 18. Operation with the addition HHO (PWM2) - Specific Fuel Consumption Logan 1.5DCI Euro3

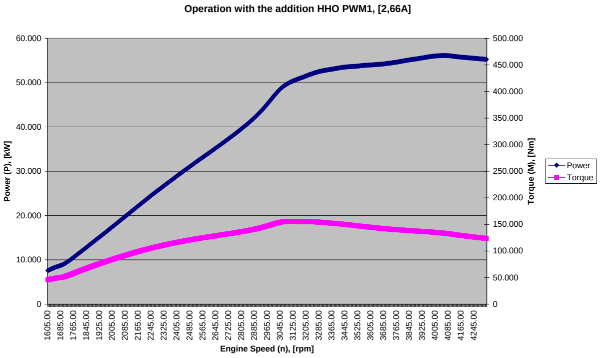


Figure 19. Operation with the addition HHO (PWM1) - Power and Torque Characteristics Logan 1.5DCI Euro3

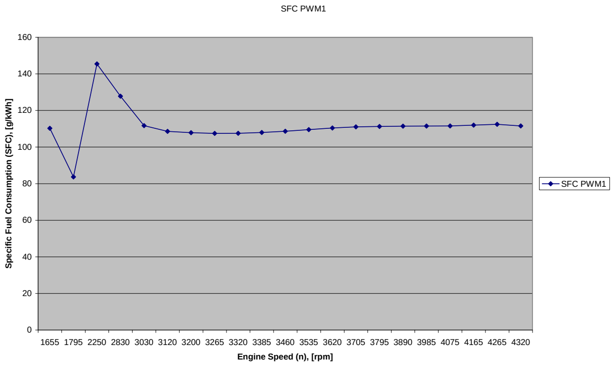


Figure 20. Operation with the addition HHO (PWM1) - Specific Fuel Consumption Logan 1.5DCI Euro3

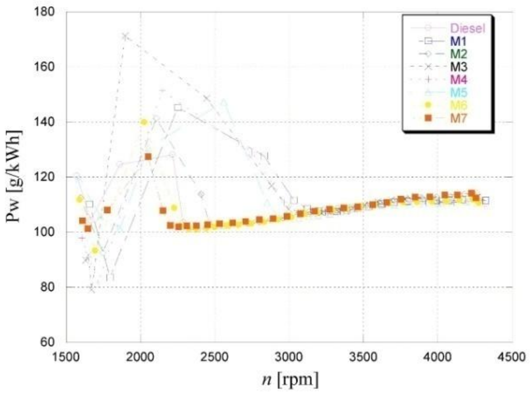


Figure 21. Comparative Overview specific fuel consumption Euro3 Logan 1.5DCI

CONCLUSIONS

Adding the HHO in the intake manifold of the 1.5 l diesel engine, for flow rates up to 1 l/min might influence the following phenomena:

- Uniform rotations of the engine crankshaft for speeds 1500 – 2000 rpm;
- No impact on the engine parameters;
- Higher specific consumption for speeds 2000 – 2500 rpm;
- Lower specific consumptions for speeds 1500 – 2000 rpm;
- Same specific consumptions for speeds higher than 2500 rpm.

On the other hand, considering period of three years on running the engine with diesel/HHO mixture, it might be observed:

- Stable running of the engine;
- Increasing the period of maintaining the initial color of the engine oil;
- Changing the color of the exhaust pipe and muffler.

ACKNOWLEDGMENT

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REFERENCES

S. Verhelst, P. Maesschalck, N. Rombaut, R. Sierens (2009). Increasing the power output of hydrogen internal combustion engines by means of supercharging and exhaust gas recirculation. International Journal of Hydrogen Energy, 34 (10), 4406-4412.

P.M. Dieguez, J.C. Urroz, S. Marcelino-Sadaba, A. Perez-Ezcurdia, M. Benito-Amurrio, D. Sainz, L.M. Gandia (2014). Experimental study of the performance and emission characteristics of an adapted commercial four-cylinder spark ignition engine running on hydrogen–methane mixtures. Applied Energy, 113, 1068–1076.

X. Liu, F. Liu, L. Zhou, B. Sun, H. J. Schock (2008). Backfire prediction in a manifold injection hydrogen internal combustion engine. International Journal of Hydrogen Energy, 33, 3847 – 3855

N. Yamada, M. N. A. Mohamad (2010). Efficiency of hydrogen internal combustion engine combined with open steam Rankine cycle recovering water and waste heat. International Journal of Hydrogen Energy, 35 (3) 1430–1442.

S. Huang, C. Lin, C. Wu, C. Wu, C. Chu, H. Chen, S. Wang (2011). Fuzzy control of a bio-hydrogen internal combustion engine generating system. International Journal of Hydrogen Energy, 36, 8774-8778.

Z. Sun, F. Liu, X. Liu, B. Sun, D. Sun (2012). Research and development of hydrogen fuelled engines in China. International Journal of Hydrogen Energy, 37, 664-681.

B. Sun, D. Zhang, F. Liu (2013). Cycle variations in a hydrogen internal combustion engine. International Journal of Hydrogen Energy, 38, 3778-3783.

R. Chiriac, N. Apostolescu (2013). Emissions of a diesel engine using B20 and effects of hydrogen addition. International Journal of Hydrogen Energy, 38 (30), 13453-13462.

H. Köse, M. Ciniviz, An experimental investigation of effect on diesel engine performance and exhaust emissions of addition at dual fuel mode of hydrogen (2013). Fuel Processing Technology, 114, 26–34.

M. Kosar, B. Ozdalyan, M. B. Celik (2011). The usage of hydrogen for improving emissions and fuel consumption in a small gasoline engine, J. of Thermal Science and Technology, 31 (2), 101-108.

M. B. King (2011). Water Electrolyzers and the Zero-Point Energy. Physics Procedia, 20, 435–445.

A. C. Yilmaz, E. Uludamar, K. Aydin (2010). Effect of hydroxy (HHO) gas addition on performance and exhaust emissions in compression ignition engines. International Journal of Hydrogen Energy, 35 (20), 11366-11372

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THE STUDY OF THE IMPACT OF EMISSIONS FROM ROAD TRAFFIC ON CONTAMINATION BY H.M IN THE KRRABA TUNNEL

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ABSTRACT

For more than three decades mosses are used for assessing the environmental pollution all over the world. Based on the European Moss Survey Program and ICP- Vegetation protocol, the sampling is done at least 300 m far away from the national and rural roads. This study is the first attempt in Albania, where mosses are used for the study of pollution by heavy metals, emitted by traffic inside the tunnel. The experiment was realized in Krraba tunnel, with a length of 2600m, on Tirana –Elbasani highway. This study was carried out by using the active bio-monitoring methods and Hypnum Cupressiforme moss species as bio-monitor. The moss bag samples were prepared by using a moss sample from a rural area that where taken about 3 km far from the highway. The moss is washed with de-ionized water prior exposure at the tunnel. 7 moss bag samples were prepared out of which 6 were exposed in the tunnel while one sample was not exposed and is used as a background. The first sample was placed in the front of the tunnel while the least one on the exit of the tunnel. Four others samples were placed inside the tunnel every 500m. Moss samples were exposed, without irrigation, for two months (15 Nov 2014 to 15 January 2014). Seven metals (Fe, Zn, Ni, Mn, Hg, Pb and Cu) significantly related to traffic emission were determined by using AAS technique in the exposed moss samples and in the background sample. The contents of these metals in six exposed samples are significantly higher than the background sample. The highest content of these elements were found at the centre of the tunnel (station 4 and 5). The results of our study demonstrate the usefulness of mosses for surveying heavy metals emissions and deposition arising from road traffic sources, even under extremely adverse condition of the tunnel environment.

Key words: *mosses, bio-monitor, moss bag, heavy metals, traffic emission*.

INTRODUCTION

The use of native terrestrial mosses as bio-monitor is now a well-recognized technique in studies of atmospheric contamination. (Fernandez and Carballeira 2002)

Mosses are low plant that thrive in a humid climate and posses many properties that make them suitable for monitoring air pollutants. (Oninawa 2001). Nutrient uptake from the atmosphere is promoted by their weakly developed cuticule (so nutrients and water taken directly from the leaves), large surface to weight ratio and their habits of growing in groups. Mosses are good air – quality monitors mainly due to the fact that their water sources are atmospheric moisture and precipitations and their big desiccation tolerance allowing them to survive long time without water supply, still proceeding photosynthesis and thus ability to stay in the study area to long, although exposed to possible pollutants (Hajek and Bockett 2008). Thickness of moss leaves are unicellular, making exhibited in all directions to capture the nutrient. The accumulation of pollutants in mosses occur through a number of different mechanisms: as layers of particles or entrapment on the surface of cells, incorporation into outer walls of cells through ion exchange processes and metabolically controlled passage into the cell (Brown & Bates 1990). The attachment of particles is affected by the size of the particles and surface structure of the mosses. In cell walls occurs the first capturing step of heavy metal cations. (Koedman and Büscher 1983). The chemical composition of deposition has a large effect on the accumulation of pollutants, because the uptake of mosses for individual elements varies considerably (Berg et al 1996). The uptake efficiency of the most common heavy metal follow mostly the order Pb > Co > Cr > Cu > Mo > Ni > V > Zn > As. (Zechmeister et al 2003). Metals occur in air in different phases, as solids, gases or absorbed to particles having aerodynamic sizes ranging from below 0.01 to 100 µm. Fine particulate matter (FPM) include particles with aerodynamic diameters of 2.5µm or less. Several toxic metals including lead, zinc, nickel, iron, cupper, mercury and their compounds are associated with FPM in air.

Air quality bio-monitoring becomes by two methods:
1 - passive method, that uses mosses directly from the study area.
2 - active methods which means transplantation of a moss species from another area, in the study area (this method is used mainly in urban or industrial areas).

In our study we used active bio-monitoring methods for the assessment of air pollution in the Krraba tunnel, mainly from heavy metals. On average 5000 vehicles (low tonnage) pass the tunnel, at 24 hours, which contribute to air pollution.

Air quality measurements in tunnels represent a cumulative contribution from all sources vehicle-generated pollutants under real traffic conditions, including direct emission and resuspension. (Grieshop et al 2006)

Combustion of fuel and oil, frictional wear of tires, brake linings, bearing and road construction materials as well as resuspension of soil and road dust by on-road vehicles, contribute to atmospheric particles. (Pant and Harrison 2013)

Fuel combustion in vehicle engines is the main source of heavy metal pollution in the tunnel environment. As a result of combustion emitted FPM and soot particle, which contain heavy metals, as a minor ingredient in the fuel (Pacyna et al 2009). Pollution also realized as a result of consumption of tires or motor parts. The dust, generated as a result of road traffic, constitute 15% of the amount of dust released into the atmosphere. This shows that the impact of road traffic pollution to the environment is considerable.

Materials and methods

Study area

The study area includes the Krraba tunnel, with a length of 2600 m, which is located along the Tirana-Elbasan highway, about 12 km from Elbasan and 17 km from Tirana. The carpet moss samples (*Hypnum Cupressiforme*) were collected about 3 km from the study area. Extraneous material was first removed from the collected moss, than samples are cleaned from soil particles in laboratory and were prepared for the exposure.

Figure 1. a. moss samples (moss bag) prepared for exposure. b. tunnel entrance. c. tunnel inside

The moss samples were placed in plastic box 7 (10x15 cm), which were covered with plastic mesh spacing 1 cm in order to avoid loss of material. Six of the prepared boxes were placed inside the tunnel at appropriate places at height around 2m from the base, at distances 0m, 450m, 100m, 1500m, 2000m, 2600m. The exposure period (without irrigation) was 15 November 2013 to 15 January 2014.

Chemical treatment of moss samples

Wet digestion of a homogeneous sub-sample was applied. About 0.5 g moss sample was transferred to the half pressure Teflon tubes and 10 ml nitric acid (9:1) was added. The closed tubes were put at room temperature for 48 hours and were digested for 3 hours at 80-90 ºC. The temperature was increased at 200ºC and was kept for an hour for further digestion. The tubes were opened and the acid was evaporated till very small volume. After cooling, the mass was transferred to 25 ml volumetric flasks with Osmoses treated water. Heavy metals such as Cu, Pb, Mn and Ni were determined by AAS technique, equipped with electro thermal system by using novA400, Analytic Jena instrument. Flame AAS was used for Zn and Fe determination; CVAAS was used for mercury determination.

The unexposed moss sample, was used as background one. Determination of heavy metal levels in the background sample was carried out using the same methods as at exposed samples.

3. Results and Discussion

Based on the content of metals in the analyzed moss samples, are presented the distributing graphs of the elements, according to exposure stations see figure 2. On the Y-axis given metal content in samples exposed expressed in µg /g dry weight.

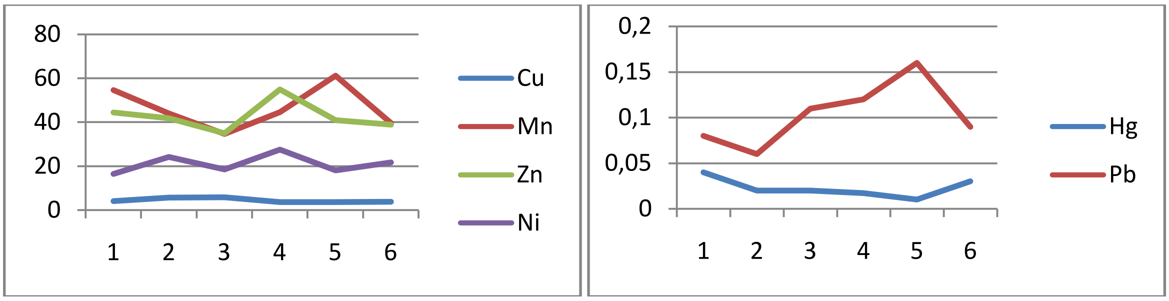

Figure 2. The distribution of elements at sampling sites

As seen from the graph elements such as Fe, Mn, high values represent the 3.4 and 5 stations (stations that are almost in the midst of tunnel) while at stations 1,2 and 6 they present low values (stations at the entrance and exit of the tunnel).

Descriptive statistics was applied to the results obtained. Minimal, maximal and mean values for 12 elements which presented high value of variance are presented at table1

Table 1: Descriptive statistics

Element	**Cu**	**Mn**	**Zn**	**Fe**	**Ni**	**Pb**	**Hg**
Mean	4.382	45.450	42.613	6411	21.008	0.105	0.023
Median	3.848	44.308	41.352	6603	20.014	0.100	0.021
Minim	3.614	34.373	34.973	4713	16.418	0.065	0.013
Maxim	5.733	61.164	54.858	7572	27.514	0.162	0.038

By processing of the experimental data we see that the elements represent different variance. The values of the coefficient of variance (CF), expressed in percentage, are given in table 2 and figure 3

Table 2: The CV values (%)

Element	Cu	Mn	Zn	Fe	Ni	Pb	Pb
CV%	22.90	21.03	15.93	19.00	20.12	33.02	33.02

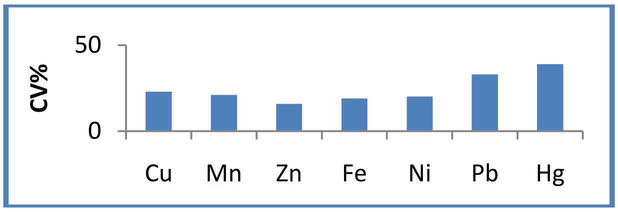

Figure 3. Graphical presentations of the CF values

Correlation and Cluster Analysis

To distinguish the different sources of elements emissions, correlation analysis of elements and their cluster analysis was carried out. The results of correlation analysis are listed in Table 3.

From the above results, note that we have very high correlation between elements. More than 90% of the road traffic emissions of Cu were due to brake wear. For Ni more than 80% is estimated to be due to exhaust emissions and for Zn around 40% of road traffic emissions are estimated to be due to exhaust emissions. Pb is also mainly due to exhaust emissions (90%).(Johansson et al 2009). So, pollution sources from heavy metals Cu, Mn, Zn, Fe, Ni, P and Hg in the tunnel are different. They can come as a result of burning fuel but also as a result of consumption of motorized parts or corrosion.(Handler et al 2008)

Table 3: Results of the correlation analysis

Element	**Cu**	**Mn**	**Zn**	**Fe**	**Ni**	**Pb**
Mn	**0.840**					
Zn	**0.956**	**0.955**				
Fe	0.697	0.335	0.565			
Ni	**0.909**	**0.969**	**0.988**	0.527		
Pb	**0.703**	**0.855**	**0.785**	0.133	**0.770**	
Hg	0.254	0.162	0.270	**0.581**	0.295	-0.252

Cluster Analysis of Variables: Cu, Mn, Zn, Fe, Ni, Pb, Hg

```
Correlation Coefficient Distance, Single Linkage Amalgamation Steps
Final Partition: Cluster 1:Cu  Mn  Zn  Ni  Pb
                 Cluster 2:Fe
                 Cluster 3: Hg
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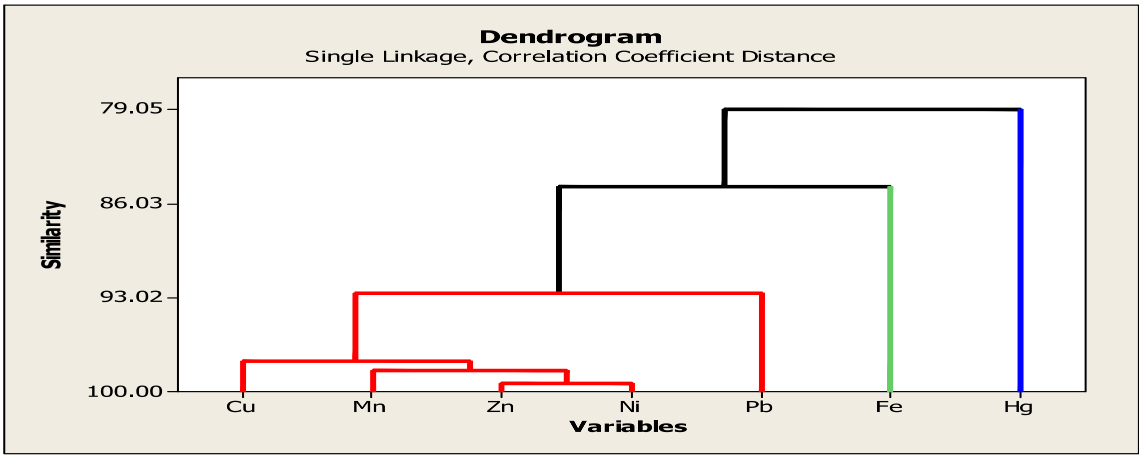

Figure 4. The grouping of elements according to the similarity of distribution at stations

Group 1: which is the largest group of elements (Cu, Mn, Zn, Ni and Pb), most of whom have over 95% similarity. These are typical element emissions from traffic, but also by fuel combustion, lubricant oils, brake and tire dressing (Gustafsson et al 2008). The similarity over 95% between Ni, Zn, Mn and Cu supported by the fact that they are released from corrosion of galvanized parts, lubricating oil, tire wear and brake emission.

Inclusion of Pb in this group, but with lower similarities, supports the fact that the main source of Pb is fuel combustion emissions.

Group 2: contains Fe, which has 84% similarity with the first group. Emission source for Fe are consumption of motor vehicle parts, as result of friction, but also by corrosion of vehicle body parts.

Group 3: contains Hg, which has a 79% similarity with other elements. This shows that the main source of Hg pollution is associated with traffic

Cluster Analysis of Observations: Cu, Mn, Zn, Fe, Ni, Pb, Hg
Euclidean Distance, Single Linkage Amalgamation Steps
Final Partition : Number of clusters: 3
Distances Between Cluster Centroids

```
          Cluster1  Cluster2  Cluster3
Cluster1      0.00   2752.72   1786.14
Cluster2   2752.72      0.00    966.84
Cluster3   1786.14    966.84      0.00
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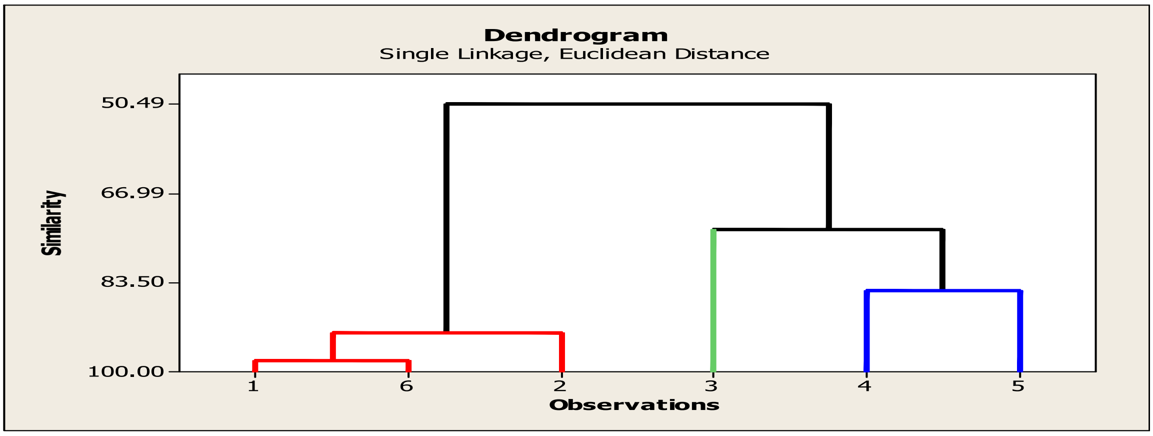

Figure 5. The grouping of stations according to the similarity of the elements distribution

The monitoring stations, according to the similarity of the distribution of elements in them, divided into three groups.

Group1 includes three stations with the similarities between them are over 95%, and respectively are 2 station 1 (at the entrance of the tunnel), station 2 (450 m from the entrance of the tunnel) and station 6, (at the exit of the tunnel). These stations are less polluted, because they are under the influence of external air. The direction moving of vehicles in this tunnel is one direction, from station1 (entrance) to station 6 (exit). The similarity of station 2, with these stations, related to the fact that vehicles during the movement create air displacement, bringing air from outside the tunnel.

Group 2 Includes station 3, which have many similarities to the stations 4 and 5. At this station begin to appear the effects of pollution as the result of traffic. The similarity about 50% with the first group of stations, tells that at this station, as a result of pollution, have different values of elements concentrations.

Group 3 Includes the stations 4 and 5 with similarity of elements distributing in them about 80%. This shows that the level of pollution in them is almost the same. The similarity about 75% with station 3, shows that the station 3 represents pollution, while the similarity about 50% with the first group stations shows that they appear to be unpolluted.

Multivariate analysis

Multivariate statistical analysis (factor analysis) was used to identify and characterize different pollution sources.
The results of principal component factor analysis of the correlation matrix for elements in moss samples are presented below.

Factor Analysis: Cu, Mn, Zn, Fe, Ni, Pb, Hg

```
Principal Component Factor Analysis of the Correlation Matrix
Rotated Factor Loadings and Communalities
Varimax Rotation
Variable   Factor1  Factor2  Communality

Cu           0.879    0.391        0.925
Mn           0.964    0.114        0.942
Zn           0.946    0.313        0.993
Fe           0.348    0.825        0.801
Ni           0.935    0.308        0.969
Pb           0.934   -0.264        0.942
Hg          -0.026    0.915        0.838
Variance    4.4635   1.9457       6.4092
% Var        0.638    0.278        0.916
```

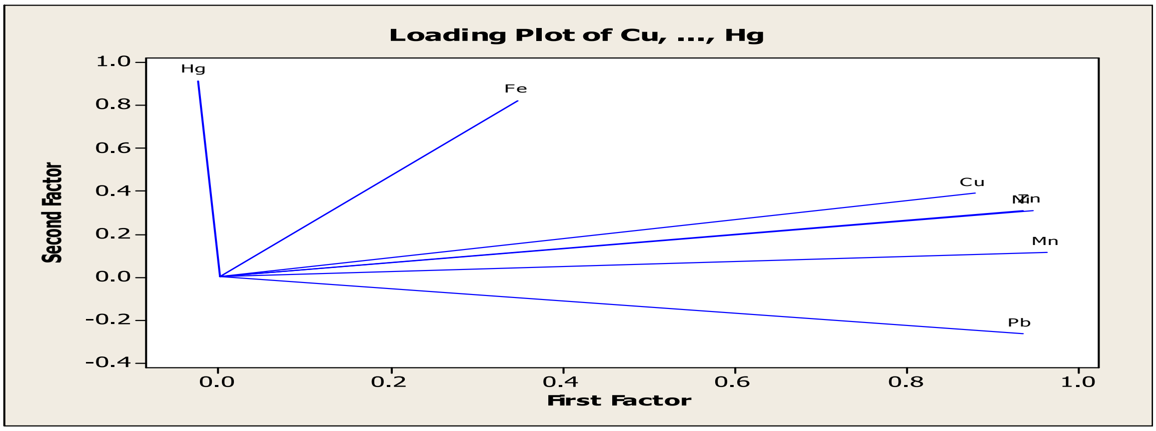

Figure 6. Loading plot of elements

The table present two extracted factors explaining about 92% (91.6%) of total variance for study area.

Factor1: explains 63.8% of the total variance and is associated mainly with the elements Cu, Mn, Zn, Ni and Pb, which have high positive values. These are typical elements that are emitted by vehicle traffic. Their content in moss samples is associated with the road dust, which formed as a result of road material and tire vehicle consumption.

Factor 2: explains 27.8% of the total variance and is associated mainly with the elements Fe and Hg, which have high positive values, which mainly comes from different emissions originate from traffic and lubricating oils, car air conditioners, etc. The addition of these elements in road traffic also increased as a result of circulation of depreciated vehicles.

For a better interpretation of pollution levels in different stations inside the tunnel, was used the rate of contamination factor (CF) used by Fernandez & Carballeira. The CF values are calculated as the ratio of the value of the concentration of each element in monitoring stations to the value of the element concentration in the unexposed sample. The table 4 presents the values of CF for each element in the monitoring station. The degree of contamination is classified into six groups based on the values of CF see table 5.

As seen from the obtained data, the pollution in the central part of the tunnel estimated to be at the C3 degree.

Table 4: The values of contamination factor (CF)

Stac / Ele	**Cu**	**Mn**	**Zn**	**Fe**	**Ni**	**Pb**	**Hg**
S1	**2.45**	**2.83**	**2.29**	**1.52**	**0.63**	**1.61**	**0.55**
S2	**3.46**	**2.28**	**2.16**	**1.47**	**0.93**	**1.30**	**0.29**
S3	**3.54**	**1.80**	**1.81**	**0.95**	**0.71**	**2.15**	**0.31**
S4	**2.26**	**2.31**	**2.84**	**1.10**	**1.06**	**2.47**	**0.24**
S5	**2.23**	**3.16**	**2.11**	**1.19**	**0.69**	**3.25**	**0.18**
S6	**2.30**	**2.05**	**2.00**	**1.51**	**0.84**	**1.84**	**0.37**

Table 5: Classification of environmental conditions by CF given by Fernandez and Carballeira(2002)

CF	> 27	8-27	3.5-8	2-3.5	1-2	<1
Clasification	C6	C5	C4	C3	C2	C1
Contaminate degree	Extreme	Higly	Middle	Lightly	No conta	No conta

CONCLUSION

The use of moss as a bio-monitor is today a well-known method for the assessment of air pollution from dry and wet atmospheric precipitations. Mosses, due to very high ion exchange capacity are today excellent bio-monitors, especially for the assessment of air pollution by heavy metals.

From the above data results that the tunnel is easily polluted, this is because traffic density is low (about 5000 vehicles per 24 hours). Metals such as Cu, Pb, Mn, Zn, which are relates to traffic emissions, are the main polluters. Also note that the tunnel is put into use in May 2013.

REFERENCES

Berg, T., Pedersen, U., & Stennes, E. (1996). Environmental indicators for long-ranga atmospheric transported heavy metals based on national moss survey.Environ Monitoring Assess; 13-18.

Brown, D.H., & Bates, J.W. (1990). Bryophytes and nutrient cycling. Botanical Journal of the Linnean Society. 104: 129-147.

Fernandez, J. A., & Carballeira, A. (2002). Biomonitoring metal deposition in Galicia (NW Spain) with mosses: factors affecting bioconcentration.. Chemosphere. 46: 535-542.

Greishop, P.A., Lipsky, M.E., Pekni, J.N., Setoshi, T., & Robinson, L.A. (2006). Fine particles emission factor from vehicles a highway tunnel: Effect of fleet composition and season. Atmospheric Environment. 40:287-298.

Gustafsson, M., Blomgvist, G., Gudmundsson, A., Swietlicki, E., Bonguard, M., Lindbom, J., & Ljungman, A. (2008). Properties and toxicology effect of particles from the interaction between tyres, road pavement and winter traction material. Science of Total Environment. 393: 226-240.

Hajek T, Beckett PR 2008 Effect of water content components on desiccation and recovery in sphagnum mosses. Annals of Botany 101:165-173.

Handler, M., Puls, Ch., Zbiral, J., Marr, I., Paxbaum, H., & Limbeck, A. (2008). Size and composition of particulate emissions from motor vehicle in the Kaisermühlen- Tunnel Vienna. Atmospheric Environment. 42: 2173

Johansson, Ch., Norman, M., & Burman, L. (2009). Road traffic emission factors for heavy metals Atmospheric Environment. Volume 43, Issue 31, Pages 4681–4688.

Koedman N. and Bűscher P. (1983). Studies on the possible role of cation exchange capacity in the soil preference of mosses. Plant Soil 70: 77-93.

Onianwa, P.C. (2001). Monitoring Atmospheric Metal Pollution:A review of the use of mosses as indicators. Enviromental Monitoring and Assessment. 71:13-45.

Pant, P., & Harrison, M.R. (2013). Estimation of contribution of road traffic emission to particulate matter concentretations from field measurements. Atmospheric Environment. 77: 78-97.

Pacyna, J. M., Pacyna, E. G., & Aas, W. (2009). Changes of emissions and atmospheric deposition of mercury, lead, and cadmium, Fifty Years of Endeavour, Atmospheric Environment. 43: 117–127.

Zechmeister HG, Hoenwallner D, Riss A, Hanus-Illnar A. (2003). Variation in heavy metal concentrations in the moss species abietinella abietina (Hedw) Fleisch according to sampling time,with site variability and increase in biomass. Science of the Total Environment 301: 55-65.

NOISE AND VIBRATIONS IN URBAN AREAS

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LANDSCAPE EFFECTS ON SOUNDSCAPE

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ABSTRACT

Sound is one of the main way to perceive and communicate with the world. Soundscape is a new concept which can be defined as the acoustic reflection of landscape. A quality of soundscape represents an important component among the factors that contribute to creating and preserving the individual and the social well-being of people. Soundscape researches are directed towards urban and rural planning, landscape values, sustainable development, health and quality of life. In this study samples of soundscape researches will be given to understand relationship between landscape and soundscape and the effects of sounds on people's perceptions in urban areas.

Key words: *Sound, landscape ecology, landscape values, soundscape.*

INTRODUCTION TO SOUNDSCAPE

Sound is an important component of the majority of terrestrial, freshwater, and marine ecosystems and becomes an essential context with which organisms daily interact performing their vital functions. Sound is transmitted in air and in water as well, but soil and rock are permeable to vibration to some extent. Thus, the transmission of sounds that occurs in solids, in liquids, and in a gas medium has different and distinct physical modalities (such as speed, impedance, excess of attenuation) (Farina, 2014).

Kariel (1980) examined the effects of sounds on outdoor recreation environments. Some mountaineers and campers of two different groups were selected to evaluate some verbally described sounds. Although some difference was found between the two sample groups, the presence of sounds was more significant than the difference between the two groups. The results suggested that the sounds themselves have an impact that may exceed that of group differences.

The soundscape is defined as the entire sonic energy produced by a landscape and is the result of the overlap of three distinct sonic sources: geophonies, biophonies, and anthrophonies. Geophonies are the result of sonic energy produced by nonbiological natural agents such as winds, volcanoes, sea waves, running water, rain, thunderstorms, lightning, avalanches, earthquakes, and flooding. Biophonies are the results of animal vocalizations (song, contact and alarm calls, voices). Anthrophonies are the result of all the sounds produced by technical devices (engines, blades, wheel revolutions, industries, etc.) (Farina, 2014).

According to Payne et al. (2009) soundscapes are the totality of all sounds within a location with an emphasis in the relationship between individual's or society's perception, understanding and interaction with the sonic environment.

LANDSCAPE EFFECTS ON SOUNDSCAPE

Landscapes can be defined as functional ecological spaces were the observed patterns reflect the interaction between natural processes and human activities (Wiens et al., 1993). The heterogeneous distribution of objects and resources and their potential rearrangement through time, can be perceived by visual cues. These visual attributes are necessary to describe the spatial structure and configuration and to detect changes resulting from the natural processes and human activities (Mazaris et al., 2009).

The appearance of the landscape and its corresponding soundscape, reflect the heterogeneity of the environment and the use of the land in such a way that the uniqueness of the locations are accentuated by the sounds. In this sense, the study of sounds as implicit time dependent processes inherent in any landscape, could provide an additional layer of information for landscape analysis (Botteldooren et al., 2006), aiming towards the comprehension of the cognitive landscapes (Mazaris et al., 2009)

Landscape effects on overall soundscape preference depend more on preferences for individual sounds. The effects of visual landscape on the perception of individual sounds could be more important in natural sounds than in artificial sounds, and more in experienced occurrence of than preference for individual sounds; for functional landscape the effects are reversed (Liu et al., 2013)

A typical passive soundmark, water, in the form of fountains, springs or cascades, is often used as a landscape element in open public spaces. As Kaplan (1987) has stated, in the visual aesthetic field there are ‘primary landscape qualities’, which have a special effect on preference, and water and foliage were two such qualities first identified. Similarly, the sound of water can be defined as a ‘primary soundscape quality’. The sound of water was classified as ‘favourite’ by 79.3% of the interviewees, and the introduction of water elements has dramatically improved the soundscape quality in the urban squares in a research that conducted in Sheffield (Yang and Kang, 2005b)

It has been found that natural landscapes are particularly sensitive to the presence of man-made sounds. Man-made sounds can denote the existence of activities which are not present in the image, and signal a deterioration in the environmental quality of the landscape. Images modify the effects of sounds and also determine environmental quality. Natural sounds, meanwhile, may improve the quality of built-up environments to a certain extent. However, any incongruence between sound and image in a landscape quite clearly diminishes the value assigned it, indicating the need to conserve singular soundscapes. Such cases call for the application of soundscape conservation measures in protected natural spaces, cultural landscapes and parks and green areas (Carles et al., 1999).

In terms of active soundmarks, providing suitable spaces for people to generate activities is very important. Hard spaces and green spaces as well as thoroughfares should be well arranged in a square. A green space may enhance the natural appeal of a square, attract wild animals’ activities such as birdsong and improve the microclimatic conditions and sound level distribution. Hard spaces are useful for generating many activities, especially for young people, such as skateboarding. As well as designing space form and surface materials to generate exciting sound environments for such activities, it is also important to reduce possible disturbance to other users, by introducing sound-absorbent ground and noise barriers, for example (Yang and Kang, 2005b).

For soundscape design, when the background sound level is not excessive, say below 65 dBA (Yang and Kang, 2005a), which can be achieved by designing square forms and boundaries, landscape elements, urban furniture and noise barriers, introducing soundmarks may have dramatic effects. According to the type of sounds, we can classify soundmarks as ‘passive’ and ‘active’. The former are intentionally designed functional and/or aesthetic elements with pleasant sounds, such as fountains and sonic sculptures, whereas the latter are sounds generated by interesting activities (Yang and Kang, 2005b).

REFERENCES

Botteldooren, D., De Coensel, B., & De Muer, T. (2006). The temporal structure of urban soundscapes. *Journal of Sound and Vibration, 292*(1), 105-123.

Carles, J. L., Barrio, I. L., & de Lucio, J. V. (1999). Sound influence on landscape values. *Landscape and urban planning, 43*(4), 191-200.

Farina, A. (2014). *Soundscape Ecology: Principles, Patterns, Methods and Applications*: Springer.

Kaplan, S. (1987). Aesthetics, affect, and cognition environmental preference from an evolutionary perspective. *Environment and behavior, 19*(1), 3-32.

Kariel, H. G. (1980). Mountaineers and the general public: a comparison of their evaluation of sounds in a recreational environment. *Leisure Sciences, 3*(2), 155-167.

Liu, J., Kang, J., Luo, T., & Behm, H. (2013). Landscape effects on soundscape experience in city parks. *Science of the Total Environment, 454*, 474-481.

Mazaris, A. D., Kallimanis, A. S., Chatzigianidis, G., Papadimitriou, K., & Pantis, J. D. (2009). Spatiotemporal analysis of an acoustic environment: interactions between landscape features and sounds. *Landscape ecology*, *24*(6), 817-831.

Payne, S., Davies, W., & Adams, M. (2009). Research into the practical policy applications of soundscapes concepts and techniques in urban areas. DEFRA report NANR200, June 2009.

Wiens, J. A., Chr, N., Van Horne, B., & Ims, R. A. (1993). Ecological mechanisms and landscape ecology. *Oikos*, 369-380.

Yang, W., & Kang, J. (2005a). Acoustic comfort evaluation in urban open public spaces. *Applied Acoustics*, *66*(2), 211-229.

Yang, W., & Kang, J. (2005b). Soundscape and sound preferences in urban squares: a case study in Sheffield. *Journal of Urban Design, 10*(1), 61-80.

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IMPORTANCE OF MONITORING OF TRAFFIC NOISE FOR THE HEALTH OF INHABITANTS OF ZRENJANIN

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ABSTRACT

In this paper is present monitoring of noise as a product of traffic in Zrenjanin. The purpose of this research is to point out the problems caused by the traffic noise based on the given results and to present the health hazard of noise pollution to the institutions and organisations. Measurements of sound levels were performed at several locations in Zrenjanin, along the main road: Milutin Milankovic Boulevard next to the Special hospital for pulmonary diseases „Dr Vasa Savic“ and the corner of Nikola Pasic street near the shopping centre „Mala Varos“. We chose the locations to show the levels of noise in the near vicinity of the hospital, and residential and business zones. The reason for this choice is the fact that the most damaging effect of the traffic noise is sleep disturbance, and the ones who are most affected by the noise are the people with extreme sensitivity to noise (10% population). The results of these measurements, in accordance with legal regulations, can serve as basis for future measurements, with effect to improve the quality of life of inhabitants globally.

Key words: *Environmental noise, traffic noise, monitoring, sound levels, human health impact.*

INTRODUCTION

Noise is every sound which can have unpleasant, disturbing and harmful efect. That sound can be pleasant or non-disturbing under different circumstances. Every day noise or noise pollution to which we are exposed is one of the biggest problems of the human environment, especially in city areas.

SOURCES AND DISTRIBUTION OF NOISE IN THE ENVIROMENT

Environmental noise, or as it is often called noise pollution, is defined as the noise created by all sources of noise that occur in the human environment, except the noise in the work environment created by the industrial machines. Noise in the environment has very complex origin and stochastic appearance. There are various sources of noise and they can be divided as:

a) Outdoor noise,
b) Indoor noise.

Traffic noise

Numerous studies show that sleep disorders are the most common disorders which are caused by the traffic noise. It is estimated that 40% of population in Europe are exposed to the traffic noise equivalent to the sound pressure level above 55 dB during daytime, and 20% population is exposed to the noise pollution of above 65 dB.

There is not enough accurate data on number of city inhabitants who are directly affected by noise poll in Serbia.

Impact of noise on human health

Noise is one of the health hazard physical agents whose detrimental effects were known long ago. Noise levels present in the environment are not high enough to cause hearing loss but they can cause all kinds of non-auditive effects. The most sensitive to noise are children younger than 6 years and people older than 65 years. Women in middle age are more sensitive than men of that age. Noise is a stressogenic factor and it affects psychosomatic health because it causes specific and non-specific effects, as well as permanent and temporary body reactions. We can discern: Psychophysiological effects of noise, psychological symptoms and behaviour change.

Table 1: Environmental noises and their respective levels of noise in decibels (dB)
(Source: Institute of Public Health, Subotica)

Sound	**intensity of sound (dB)**
Threshold of hearing	0
Whisper	20
Normal conversation	50
Apartment in the busy street	60
Busy street	70
Car	70
Truck	90
Plane	120
Threshold of pain	130

In Table 2 are given appropriate sound levels.

Table 2: From Protocol on highest appropriate levels of noise in working and living environment (Source: Law on Environmental Protection)

Zones of noise	Purpose	The highest approved levels of noise (dB) Outdoor / indoor Day/night day/night
 1. 2. 3. 4. 5.	Recreational Residential Predominantly residential Predominantly business Industrial	 50 40 30 25 55 40 35 25 55 45 35 25 65 50 40 30 limit≤ 80 40 30

In Table 3 are given levels of traffic noise.

Table 3: Levels of traffic noise (Source: Regulations of noise)

Main city roads (high traffic)	75 dB
Crossroads in the city centre (high traffic)	75 dB
Local roads (65% truck traffic)	70 dB
Local main roads	55 dB
Residential area streets	55 dB

LOCATIONS OF MEASUREMENT

Location 1 is situated next to the business building „Mala Varoš“ where several city owned companies are situated and 50 meters from the building is a residential building which has several businesses in the ground floor. Picture in Figure 1 is taken during measurement.

Figure 1. The corner of Nikola Pašić street, Žitni square - view from the other corner (Lakatus, 2014.)

Location 2 is situated on part of the main city road next to a wall approximately 50 meters from the building of the hospital for pulmonary diseases „Dr Vasa Savić“. Picture in Figure 1 is taken during measurement.

Figure 2. Part of the city main road near the hospital for pulmonary diseases (Lakatus, 2014.)

Data on the time frame for the measurement of the levels of noise for both locations

Measurement of the levels of noise for the purposes of this thesis was held on March 31st, 2014, under weather conditions that were earlier described.

Location 1

Žitni square, near the shopping centre „Mala Varoš“, on Nikola Pašić street, next to the building and approximately 50 m from the residential building.

Instrument was 5m from the road
Altitude on which the instrument was: 1,5 m.
Time frame for each measument (day, evening and night): 30 minutes
Day: 09:39 h – 10:09 h
Evening: 18:33 h – 19:03 h
Night: 22:19 h – 22:49 h

Location 2

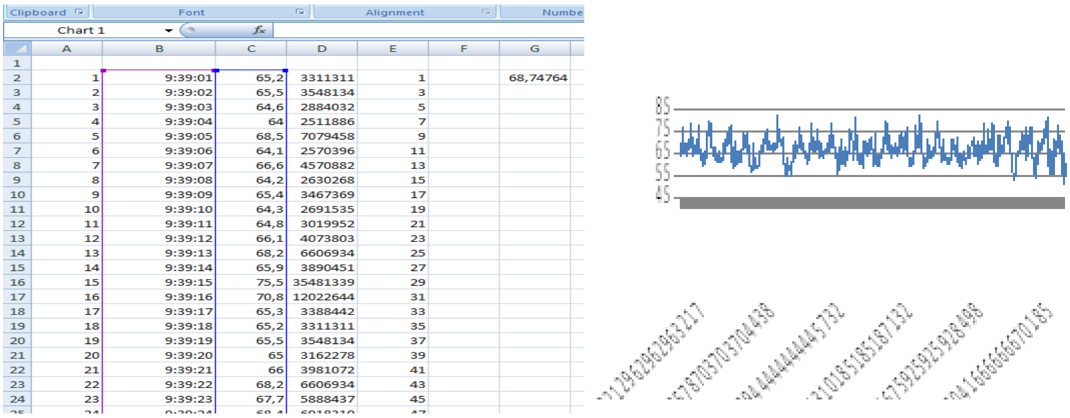
Milutin Milanković boulevard (main city road) approximately 50 m from the hospital for pulmonary diseases “Dr Vasa Savić“.

Instrument was 5m from the road.
Altitude on which the instrument was: 1,5 m.
Time frame for each measument (day, dusk and night): 30 minutes
Day: 10:26 h – 10:56 h
Evening: 19:25 h – 19:55 h
Night: 23:01 h – 23:31 h

RESULTS OF MEASUREMENT

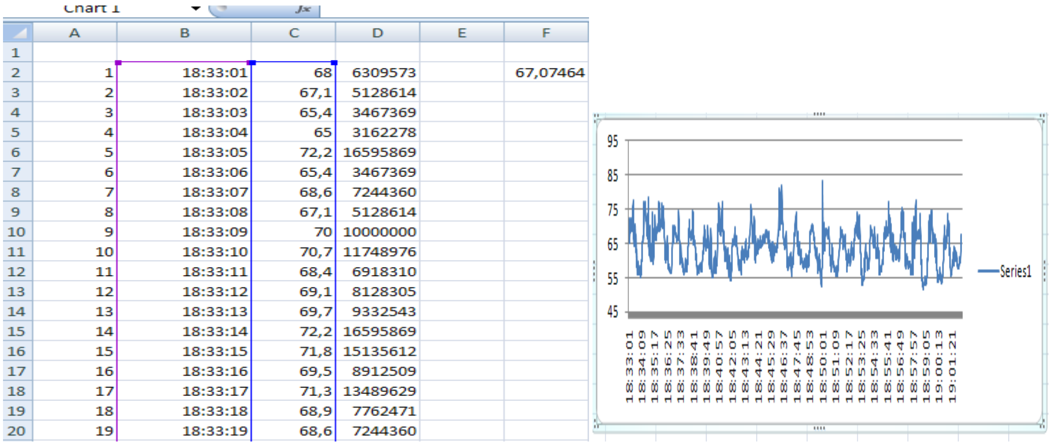
When the measurement is performed, in the set time intervals, values measure by the instrument are methodised, sorted, and analysed. Process for the equipment used for this thesis is following: computer is connected to the instrument by the cable which is the part of the equipment, and the previously installed software on the computer processes the data that instrument measures. Measured values for every second of the process are entered in Microsoft Excel table, which displays all measured values. Programme then calculates mean value for every measurement and makes a graphical chart of measured values.

Results for location 1 are given in Figures 3-5. Tables shown for both locations were representative only (every table has approximately 1700 rows).



	A	B	C	D	E	F	G
1							
2	1	9:39:01	65,2	3311311	1		68,74764
3	2	9:39:02	65,5	3548134	3		
4	3	9:39:03	64,6	2884032	5		
5	4	9:39:04	64	2511886	7		
6	5	9:39:05	68,5	7079458	9		
7	6	9:39:06	64,1	2570396	11		
8	7	9:39:07	66,6	4570882	13		
9	8	9:39:08	64,2	2630268	15		
10	9	9:39:09	65,4	3467369	17		
11	10	9:39:10	64,3	2691535	19		
12	11	9:39:11	64,8	3019952	21		
13	12	9:39:12	66,1	4073803	23		
14	13	9:39:13	68,2	6606934	25		
15	14	9:39:14	65,9	3890451	27		
16	15	9:39:15	75,5	35481339	29		
17	16	9:39:16	70,8	12022644	31		
18	17	9:39:17	65,3	3388442	33		
19	18	9:39:18	65,2	3311311	35		
20	19	9:39:19	65,5	3548134	37		
21	20	9:39:20	65	3162278	39		
22	21	9:39:21	66	3981072	41		
23	22	9:39:22	68,2	6606934	43		
24	23	9:39:23	67,7	5888437	45		

Figure 3. Part of table with measured data for day measurement interval and graphic chart of results (Lakatus, 2014)



	A	B	C	D	E	F
1						
2	1	18:33:01	68	6309573		67,07464
3	2	18:33:02	67,1	5128614		
4	3	18:33:03	65,4	3467369		
5	4	18:33:04	65	3162278		
6	5	18:33:05	72,2	16595869		
7	6	18:33:06	65,4	3467369		
8	7	18:33:07	68,6	7244360		
9	8	18:33:08	67,1	5128614		
10	9	18:33:09	70	10000000		
11	10	18:33:10	70,7	11748976		
12	11	18:33:11	68,4	6918310		
13	12	18:33:12	69,1	8128305		
14	13	18:33:13	69,7	9332543		
15	14	18:33:14	72,2	16595869		
16	15	18:33:15	71,8	15135612		
17	16	18:33:16	69,5	8912509		
18	17	18:33:17	71,3	13489629		
19	18	18:33:18	68,9	7762471		
20	19	18:33:19	68,6	7244360		

Figure 4. Part of table with measured data for evening measurement interval and graphic chart of results (Lakatus, 2014)

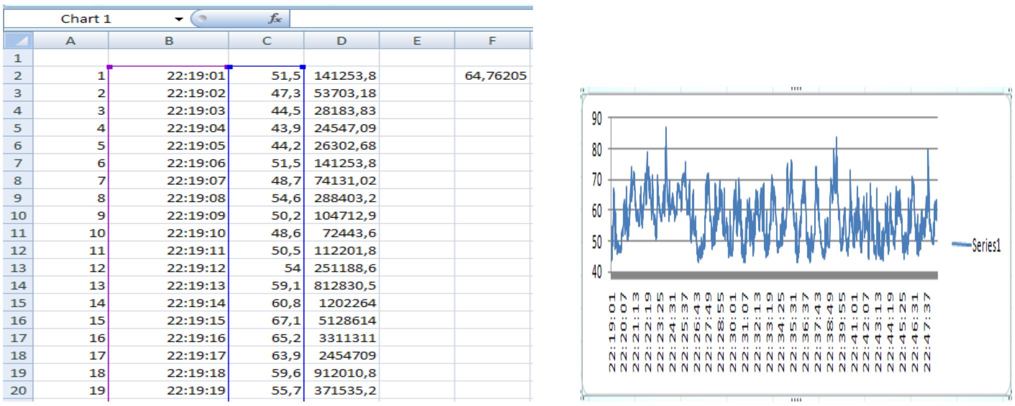


Chart 1

	A	B	C	D	E	F
1						
2	1	22:19:01	51,5	141253,8		64,76205
3	2	22:19:02	47,3	53703,18		
4	3	22:19:03	44,5	28183,83		
5	4	22:19:04	43,9	24547,09		
6	5	22:19:05	44,2	26302,68		
7	6	22:19:06	51,5	141253,8		
8	7	22:19:07	48,7	74131,02		
9	8	22:19:08	54,6	288403,2		
10	9	22:19:09	50,2	104712,9		
11	10	22:19:10	48,6	72443,6		
12	11	22:19:11	50,5	112201,8		
13	12	22:19:12	54	251188,6		
14	13	22:19:13	59,1	812830,5		
15	14	22:19:14	60,8	1202264		
16	15	22:19:15	67,1	5128614		
17	16	22:19:16	65,2	3311311		
18	17	22:19:17	63,9	2454709		
19	18	22:19:18	59,6	912010,8		
20	19	22:19:19	55,7	371535,2		

Figure 5. Part of table with measured data for night measurement interval and graphic chart of results (Lakatus, 2014.)

All representative data are for location 1 – Žitni square, Nikola Pašić street corner. Calculation for practical measured values will be presents later in the thesis after data for Location 2, for clarity of data and better analysis of calculated values of both locations.

Results for location 2 are given in Figures 6-8.

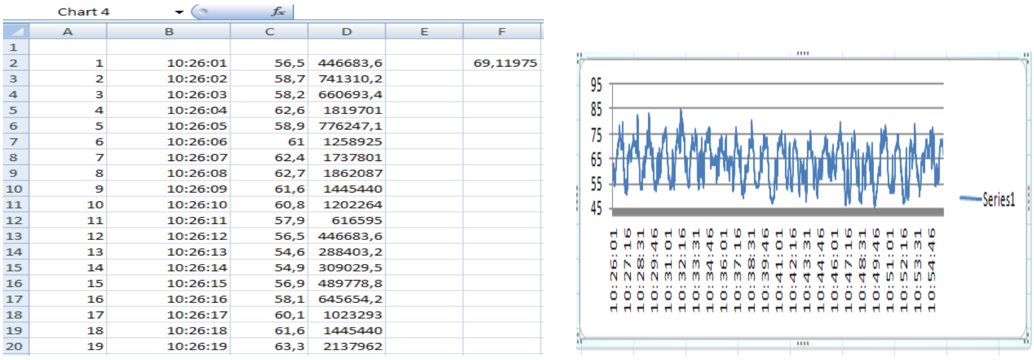


Chart 4

	A	B	C	D	E	F
1						
2	1	10:26:01	56,5	446683,6		69,11975
3	2	10:26:02	58,7	741310,2		
4	3	10:26:03	58,2	660693,4		
5	4	10:26:04	62,6	1819701		
6	5	10:26:05	58,9	776247,1		
7	6	10:26:06	61	1258925		
8	7	10:26:07	62,4	1737801		
9	8	10:26:08	62,7	1862087		
10	9	10:26:09	61,6	1445440		
11	10	10:26:10	60,8	1202264		
12	11	10:26:11	57,9	616595		
13	12	10:26:12	56,5	446683,6		
14	13	10:26:13	54,6	288403,2		
15	14	10:26:14	54,9	309029,5		
16	15	10:26:15	56,9	489778,8		
17	16	10:26:16	58,1	645654,2		
18	17	10:26:17	60,1	1023293		
19	18	10:26:18	61,6	1445440		
20	19	10:26:19	63,3	2137962		

Figure 6. Part of table with measured data for day measurement interval and graphic chart of results (Lakatus, 2014.)

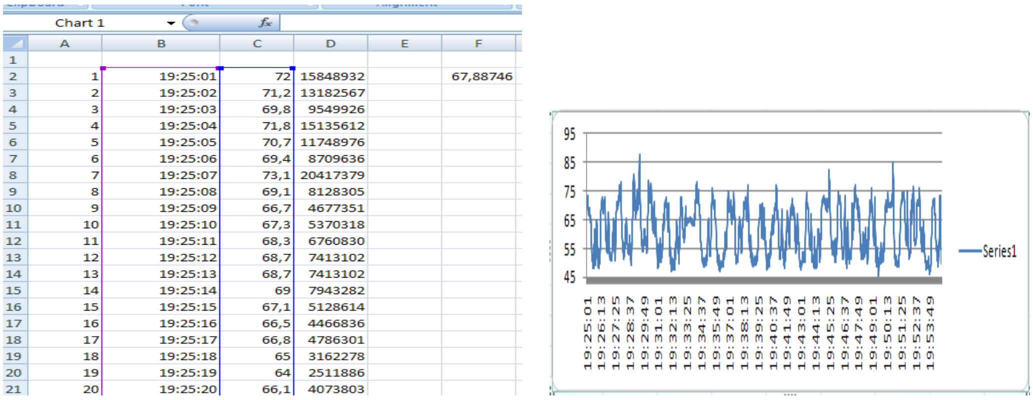


Chart 1

	A	B	C	D	E	F
1						
2	1	19:25:01	72	15848932		67,88746
3	2	19:25:02	71,2	13182567		
4	3	19:25:03	69,8	9549926		
5	4	19:25:04	71,8	15135612		
6	5	19:25:05	70,7	11748976		
7	6	19:25:06	69,4	8709636		
8	7	19:25:07	73,1	20417379		
9	8	19:25:08	69,1	8128305		
10	9	19:25:09	66,7	4677351		
11	10	19:25:10	67,3	5370318		
12	11	19:25:11	68,3	6760830		
13	12	19:25:12	68,7	7413102		
14	13	19:25:13	68,7	7413102		
15	14	19:25:14	69	7943282		
16	15	19:25:15	67,1	5128614		
17	16	19:25:16	66,5	4466836		
18	17	19:25:17	66,8	4786301		
19	18	19:25:18	65	3162278		
20	19	19:25:19	64	2511886		
21	20	19:25:20	66,1	4073803		

Figure 7. Part of table with measured data for evening measurement interval and graphic chart of results (Lakatus,2014.)

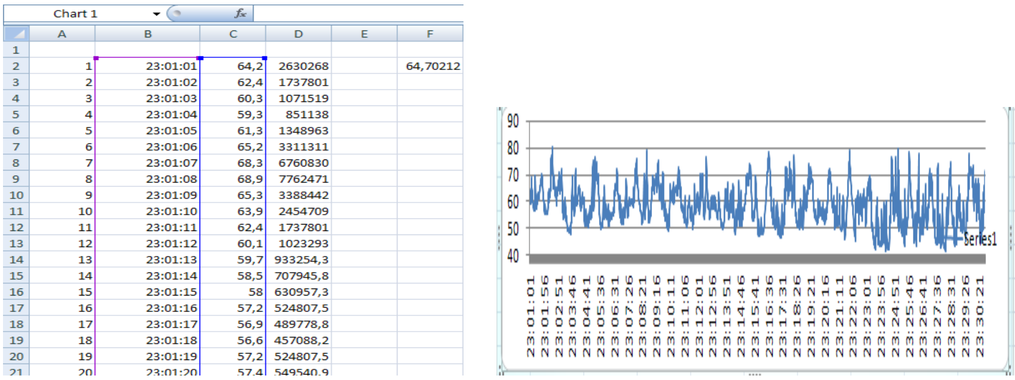


Chart 1

	A	B	C	D	E	F
1						
2	1	23:01:01	64,2	2630268		64,70212
3	2	23:01:02	62,4	1737801		
4	3	23:01:03	60,3	1071519		
5	4	23:01:04	59,3	851138		
6	5	23:01:05	61,3	1348963		
7	6	23:01:06	65,2	3311311		
8	7	23:01:07	68,3	6760830		
9	8	23:01:08	68,9	7762471		
10	9	23:01:09	65,3	3388442		
11	10	23:01:10	63,9	2454709		
12	11	23:01:11	62,4	1737801		
13	12	23:01:12	60,1	1023293		
14	13	23:01:13	59,7	933254,3		
15	14	23:01:14	58,5	707945,8		
16	15	23:01:15	58	630957,3		
17	16	23:01:16	57,2	524807,5		
18	17	23:01:17	56,9	489778,8		
19	18	23:01:18	56,6	457088,2		
20	19	23:01:19	57,2	524807,5		
21	20	23:01:20	57,4	549540,9		

Figure 8. Part of table with measured data for night measurement interval and graphic chart of results (Lakatus, 2014.)

ANALYTICAL CALCULATION OF NOISE

Calculation of parameter L_{DEN}

Level of noise for day-evening-night $\mathbf{L_{den}}$ (d – day , e – evening, n – night) in decibels dB(A) is defined by the equation below:

$$L_{day} = 10\log\frac{1}{24}\left(12\cdot 10\frac{L_{day}}{10} + 4\cdot 10\frac{L_{evening}+5}{10} + 8\cdot 10\frac{L_{night}+10}{10}\right) \qquad (1)$$

A - Weighted average for long-term levels of noise for specific periods of day is defined by the equation (2).

$$L_{Aeq,T} = 10log\left[\frac{1}{N}\sum_{i=1}^{N} 10^{0,1(L_{Aeq,T})t}\right] \qquad (2)$$

For Location 1, Žitni square, near the shopping centre „Mala Varoš“, on Nikola Pašić street (next to the building and approximately 50 m from the residential building), data for calculation of L_{den} are given in Table 4.

Table 4: Data for calculation of L_{den} (Lakatus, 2014.)

Measurement period	Ruling period	Measured value [dB(A)]
Day	12h	**65,97**
Evening	4h	**63,66**
Night	8h	**56,93**

L_{DEN} = **64,03dB (A)**

For Location 2, Milutin Milanković boulevard, approximately 50 m from the hospital for pulmonary diseases “Dr Vasa Savić“,data for calculation of L_{den} are given in Table 5.

Table 5: Data for calculation of L_{den} (Lakatus, 2014.)

Measurement period	Standard period	Measured value [dB(A)]
Day	12h	**63,68**
Evening	4h	**60,8**
Night	8h	**58,41**

L_{DEN} = **62,04dB(A)**

Standard period is a period of 24 hours and it refers to daytime lasting from 6 till 18h , evening lasting from 18 till 22h and night lasting from 22 till 6h. In the table 6 there are number of hours for every period, for location 1.

NOTE: Parameter L_{den} was calculated based on 1,5 h measurement. This was calculated by summing 30 minute intervals for every period of measurement – day, evening and night.

Table 6: Measured values for location 1(Lakatus, 2014.)

	Laeq [dB(A)]	LAF max [dB(A)]	LAF min[dB(A)]
Day	65,97	81,5	51,7
Evening	63,66	83,2	51,7
Night	56,93	86,6	43,1

LAF max [dB (A)] are maximum measured values of sound pressure
LAF min[dB(A)] are minimum measured values of sound pressure

In the table 7 there are number of hours for every period, for location 2.

Table 7: Measured values for location 2 (Lakatus, 2014.)

	LAeq[dB(A)]	LAF max [dB(A)]	LAF min[dB(A)]
Day	63,68	84,7	45,7
Evening	60,8	87,7	45,5
Night	58,41	80,3	42,1

LAF max [dB(A)] are maximum measured values of sound pressure
LAF min[dB(A)] are minimum measured values of sound pressure

Noise measurement and result analysis were performed in accordance with standards SRPS ISO 1996 – 1 Acoustics -- Description and measurement of environmental noise -- Part 1: Basic quantities and procedure and SRPS ISO 1996 – 2 Acoustics -- Description, measurement and assessment of environmental noise -- Part 2: Determination of environmental noise levels. Calculation of results was also performed in accordance to the above standards above.

ANALYSIS OF THE RESULTS OF NOISE MEASUREMENT IN ZRENJANIN

Traffic parameters that are taken into account while discerning levels of noise are:

- Car frequency
- Tractor frequency
- Heavy vehicle frequency
- Bus frequency
- Motorcycle frequency.

Data on subjective feeling of noise for people living and working in the vicinity of Location 1 and patients in the hospital for pulmonary diseases were collected by unofficial interview of 10 subjects, which gave perspective of the impact that noise has on everyday activities of people exposed to it. NOTE: Data presented below are unofficial and participants will not be named, albeit they are anonymous. Both interviews were made for the purpose of this thesis only and cannot be used otherwise. Results of the interview for Location 1 are given in Table 8.

Table 8: Results of the interview for Location 1 (Lakatus, 2014.)

Ordinal number	Participant's age (years)	Tenant / employee	Noise disturbance – yes or no
1	35	Employee	no
2	34	Tenant	yes
3	60	Tenant	yes
4	42	Tenant	yes
5	52	Employee	no
6	18	Tenant	no
7	73	Tenant	yes
8	49	Employee	yes
9	28	Tenant	yes
10	24	Tenant	no

Based on the interview of 10 participants of different age, it is clear that employees near the Location 1 are not disturbed by the noise; on the other hand the tenants who live in the vicinity of Location 1 stated that the noise disturbs them, especially during periods of extreme temperatures, when the windows are open during the entire day. Also tenants stated that noise disturbs them the most during the night, in the summer and it disrupts their sleep. For employees, noise in the night is not relevant, because they are not in the vicinity of Location 1 in that period.

Results of the interview for Location 2 are given in Table 9.

Table 9: Results of the interview for Location 2 (Lakatus, 2014.)

Ordinal number	Participant's age (years)	Patient / employee	Noise disturbance – yes or no
1	74	Patient	yes
2	60	Patient	yes
3	46	Employee	yes
4	48	Patient	no
5	64	Patient	yes
6	55	Employee	no
7	39	Patient	no
8	28	Employee	no
9	31	Patient	no
10	78	Patient	no

Based on the interview of 10 participants of different age, the results show that intensity of noise on Location 2 does disturbs neither patients nor employees. The reason for this might be the fact that the hospital building is situated behind wall next to a location 2, therefore the wall is a form of acoustic insulation, also hospital entrance is in the other street with less traffic than Milutin Milanković boulevard.

CONCLUSION

Traffic noise makes about 50% of all sources of noise and therefore the most important tasks for prevention of negative impact on people in general are measurement of levels of traffic noise and its causes (levels of emission) and prevention of exposure of people (immission level) to the higher levels of noise. When it is not possible to reduce the level of existing traffic noise to the legally allowed level, other measures have to be apply, and the most important ones are economic measures. Those measures can reflect in inducing the manufacturers to make "silent" vehicles and "silent" tires, and on the other hand in imposing taxes on existing noisy vehicles and also through costs of appropriate measures for noise prevention that institutions that govern the traffic have. From all the above mentioned facts we can conclude that the size of the noise problem is something that has to have greater importance.

Certain improvements were made on the sources of noise – vehicles (new technologies), but there are no universal solutions to this problem. Every regulation of traffic which is limiting the number of cars can contribute to noise prevention. In this specific case, based on the measured and calculated values of traffic, the best solution for Zrenjanin would be finishing the bypass for heavy vehicles which cannot be allowed to use the main city road in the city centre.

Noise is a part of everyday life, and the longer we endure noise, especially strong noises, the more it affects out health. Higher decibels do not only damage hearing, but also we already mentioned at the beginning of the thesis, they have detrimental effect on the whole human body. As a reminder, constant exposure to the high levels of noise can cause high blood pressure, anxiety, and chronic fatigue syndrome and affects vegetative nervous system. Noise not only causes hearing loss, but also has negative affect on the whole body. According to the WHO (World Health Organisation), environmental noise lessens productivity and learning abilities, increases number of injuries and frequency of sick leaves and can affect increased use of drugs. At work, increased noise combined with complex work tasks can increase the risk of cardiovascular diseases due to increased stress.
Based on the facts that we mentioned in this thesis, local authorities and institutions will have to show that they are aware of the extent of the traffic noise problem with which many of us experience on daily basis. This thesis is a short view on the conditions on the field, specifically locations that were examined in this work, with supporting theory on the harmful effects of noise on human body.

European models for solutions of the traffic noise problems are setting panel barriers near the roads with heavy traffic, planting trees, multiplying lanes, careful planning of traffic lights, changing the quality of the road surface because of friction and gliding and improving of car technology.

This conclusion imposes on us - authorities have to convey all necessary measures in order to protect us from all the sources of noise that threaten our physical and mental health.

REFERENCES

Adamoviç, Z., *Technical diagnostics*, OMO Belgrade, 2001.

Adamovic, Z., Jevtic, M., Savic, N., Josimovic, Lj., Stanojevic, M., Nenadic, D., *Vibrodijagnostic and Tribodiagnostic of machines*, Society for Technical Diagnostics Serbia, Belgrade, 2009.

Adamovic, Z., Bursac, Z., Eric, S., *Vibration and Noise Causes - Diagnosis - protection*, Serbian academic Center, Novi Sad, 2014.

Group of authors, *The noise - basically, analysis, resources and protection*, Faculty of civil engineering, Belgrade

Bruel & Kjaer, *Noise and Vibrations*, 1998.

Todorovic, D., Salom, I., *Acoustics*, Academic Thought, 2006.

Cvetkovic, D., Prascevic, M., *Noise and Vibrations*, University of Nis, Faculty of Occupational Safety, 2005.

Budisavljevic, B.B., *Protection against noise*, seminar of Republican environmental inspectors,Vrnjačka Banja, 1993.

The Law on the Protection of environmental noise ("Off. Gazette of RS", no. 36/2009 and 88/2010)

ISO 1996-1 *Acoustics - Description, measurement and assessment of environmental noise - Part 1: Basic quantities and assessment procedures*

ISO 1996-2 *Acoustics - Description, measurement and assessment of environmental noise - Part 2: Determine the level of environmental noise*

Lakatus, I, *Importance of monitoring road traffic noise in the city of Zrenjanin*, thesis, Technical faculty „Mihajlo Pupin“ Zrenjanin, 2014.

http://www.zrenjanin.rs

http://www.kragujevac.rs/

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BENEFITS OF URBAN GREEN SPACES FOR CITIZENS: ANKARA CASE STUDY

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ABSTRACT

In recent years, the importance of green spaces has emerged as a result of increasing population density and concretization. Parks and open spaces are the areas that satisfy such longing and meet recreational needs in cities. Studies have shown that urban green areas offer a wide range of individual, social, economic and environmental benefits. Green spaces provide opportunities for physical activity for people's well-being in urban landscape. They also procure to fulfill psychological, emotional and spiritual needs. This study aims to reveal the benefits of urban green spaces on people's well-being in Ankara City. The largest green areas were examined in terms of features and physical qualities. The physical activity levels, experienced feelings and opinions about these areas were determined by the surveys, observations and interviews. Results confirm that being in nature such as open green spaces and parks, provide positive effects on physical health, emotional well-being and social interaction. At the end of the study, planning and design suggestions are submitted to increase the quality of life of urban citizens.

Key words: Open Spaces, *Benefits, Parks, Ankara.*

INTRODUCTION

Urban parks and open green spaces have a strategic importance for the quality of life of urbanized society. Increasing empirical evidence, in fact, indicates that the presence of natural assets and components in urban contexts contributes to the quality of life in many ways (Chiesura, 2004)

Parks offer unique settings within the urban landscape, providing opportunities for physical activity, enjoyment of nature, social interaction and escape (Hayward and Weitzer, 1984). Services offered in open spaces provide individuals with various physical, psychological, social, environmental and economic benefits.

Important environmental services such as air and water purification, wind and noise filtering, or microclimate stabilization, natural areas provide social and psychological services, which are of crucial significance for the livability of modern cities and the well-being of citizens (Chiesura, 2004). A park experience may reduce stress (Ulrich, 1981) , enhance contemplativeness, rejuvenate the city dweller, and provide a sense of peacefulness and tranquility (Kaplan, 1985).

Physical benefits of urban green spaces

All people need physical activity to maintain fitness and health. Physical activity increases strength, flexibility, and endurance; relieves symptoms of depression and anxiety; improves mood; and enhances psychological well-being (Gies, 2006).

Ward Thompson (2013) stated that there is particular interest in how the design and management of everyday environments might support and encourage physical activity. If it is possible to create attractive streets, parks and outdoor spaces physical activity level increases. In a survey among park's visitors a significant relation was found between use of the parks and perceived state of health: those who used local parks frequently were more likely to report good health than those who did not (Godbey et al., 1992).

Urban green space also plays a role in improving the social health of their inhabitants. It is not only the cleaning and cooling ability of plants that show direct positive effects on human health by providing shade, reducing heat strain, reducing risks of cancer, and cutting down on noise (Heidt and Neef, 2008).

Psychological benefits of urban green spaces

According to the later studies, natural environments have a positive influence on psychological and mental health. Contemporary research on the use of urban parks and forests, for example, verifies beliefs about stress-reduction benefits and mental health (Conway, 2000; Hartig et al., 1991).

Schroeder (1991) has shown that natural environments with vegetation and water induce relaxed and less stressful states in observers compared with urban scenes with no vegetation. Kuo and Sullivan (2001) stated that greenery helps people to relax and renew, reducing aggression.

Researchers also found that residents with even limited views of trees or grass from their apartments reported less mental fatigue, less procrastination in dealing with life issues, and feeling that their problems were less severe, more solvable, and of shorter duration than residents with no views of nature. Even small amounts of nature, such as a few trees and a bit of grass, were shown to have an impact (Gies, 2006).

Social benefits of urban green spaces

Beside aesthetic, psychological and health benefits, natural features in cities can have other social benefits. Nature can encourage the use of outdoor spaces, increases social integration and interaction among neighbors (Coley et al., 1997). The presence of trees and grass in outdoors common spaces may promote the development of social ties (Kuo et al., 1998). Research shows that residents of neighborhoods with greenery in common spaces are more likely to enjoy stronger social ties than those who live surrounded by barren concrete (Gies, 2006).

Urban green spaces serve as a nearby resource for relaxation and recreation for inhabitants. Green areas in cities provide contact with nature, for example, marking the rhythm of the changing of the seasons: autumn when leaves fall, the flowering of plants and trees in spring, the presence of seasonal birds. Thus green spaces and trees provide an emotional warmth and softness to city life, as opposed to the hardness of concrete and pavement. They can also add a sense of privacy. Urban green spaces are also educational resources, providing locations for structured and informal lifelong learning about nature, and ecological and environmental processes (Heidt and Neef, 2008).

Green spaces are very useful in urban planning, because they are elements that bring order to the surrounding area. They imbue the area with aesthetic dignity and they often serve as a link between various neighborhoods. They often becoming an aesthetic or symbolic reference point, making streets and neighborhoods more alive. In addition, parks serve as links between neighborhoods, often becoming a place to socialize and bringing people together (Heidt and Neef, 2008).

Environmental benefits of urban green spaces

Parks and greenways can mitigate air pollution and increased temperatures. Mature tree canopies can reduce air temperature five to ten degrees, helping to counteract the urban heat island effect and trees filter pollutants out of the air. One of the common health problem is respiratory disease resulting from increased air pollution (Gies, 2006). Urban green space ameliorates the climate; filters the air, water, and soil of many pollutants; and provides a habitat for fauna and flora (Heidt and Neef, 2008).

Green spaces also provide locations where unsealed soils exist, thus simultaneously decreasing excessive surface run-off and combined sewer flows that damage local streams, and reducing the urban heat-island effect via greater evapotranspiration. The effects of vegetation on the urban climate are important even in the case of small green spaces, like neighborhood parks (Heidt and Neef, 2008).

Meyer (1997) reported that a small park with both trees and shrubs can bind up to 68 metric tons of dust per hectare per year. A street with trees and small parks contain about 25% and 20% of the atmospheric dust load found in city centers without trees Even some trees in high-density neighborhoods decrease the amount of dust in the air. Trees in a street also produce small air circulations, which dilute pollutants and so reduce the risk of inversions and smog. Green spaces of 50 to 100 m depth improve air quality up to 300 m away in their neighborhoods (Heidt and Neef, 2008).

In a research conducted in Ankara, temperature changes were measured in different areas in August. The highest average of daily temperature was determined at the area which has least green space. Also the lowest average of daily temperature was determined at the area which has most green space (Yüksel and Yılmaz, 2008).

Economic benefits of urban green spaces

Beside the social and psychological benefits mentioned above, the functions of urban nature can provide economic benefits for both municipalities and citizens. Air purification by trees, for example, can lead to reduced costs of pollution reduction and prevention measures. Furthermore, aesthetic, historical and recreational values of urban parks increase the attractiveness of the city and promote it as tourist destination, thus generating employment and revenues (Chiesura, 2004).

Indicators are very strong that green space and landscaping increases property values and the financial returns for land developers. Studies have found increased financial returns of 5% to 15% depending on the type of project (McMahon, 1996). Also, 70% to 80% of consumers rated natural open space as the feature they desired most in a new home development (McMahon, 1996).

Using vegetation to reduce the energy costs of cooling buildings has been increasingly recognized as a cost-effective reason for increasing green space and tree plantings in cities (Fezer, 1995). Even small green spaces decrease temperatures in urban environments in manifold ways (Heidt and Neef, 2008):

1. They produce small-scale air circulations. These air movements, due to wind or thermal upswing, cause air exchange.
2. Even though a park may be exposed to solar radiation throughout the morning, evaporation from the grass surface and trees create lower ground surface temperatures and consequently lower air temperatures in the park than in the surrounding urban area. With strong winds, a cooler park can significantly contribute to the reduction of the heat intensity in the town. For example, a park of 1.2 km × 1.0 km can produce an air temperature difference between the park and the surrounding city that is detectable up to 4 km away (Takashi and Vu Than, 1998).
3. Urban vegetation counteracts the urban heat-island effect by providing shade. Even single trees, strategically planted to shade homes, can reduce air conditioning bills significantly. Up to 227 kWh can be saved by each tree through cooling by evapotranspiration and 61 kWh through direct shading of a home (McPherson et al., 1999). Simulations of energy saving benefits for the cities of Sacramento and Phoenix found that three mature trees around homes cut annual air conditioning demand by 25% to 40% (McPherson et al., 1999).

MATERIAL AND METHOD

The study was conducted across the five big sub-provinces of Çankaya, Keçiören, Yanimahalle, Mamak and Altındağ in Ankara (Figure 1). According to TÜIK (Turkish Statistical Institute) data Çankaya’s population is 914.501. There are 256 parks with a total area of 1.592.517 m^2. Keçiören’s population is 848.305 and there are 412 parks. The total size of these parks is 2.381.777 m^2. The population of Yenimahalle is 591.462 and there are 409 parks with a total area of 2.952.042 m^2. Mamak has a population of 568.396. There are 232 parks with a total area of 1.100.028 m2 in Mamak. The population of Altındağ is 359.597 and the total area of parks is 2.106.854 m^2 (Table 1).

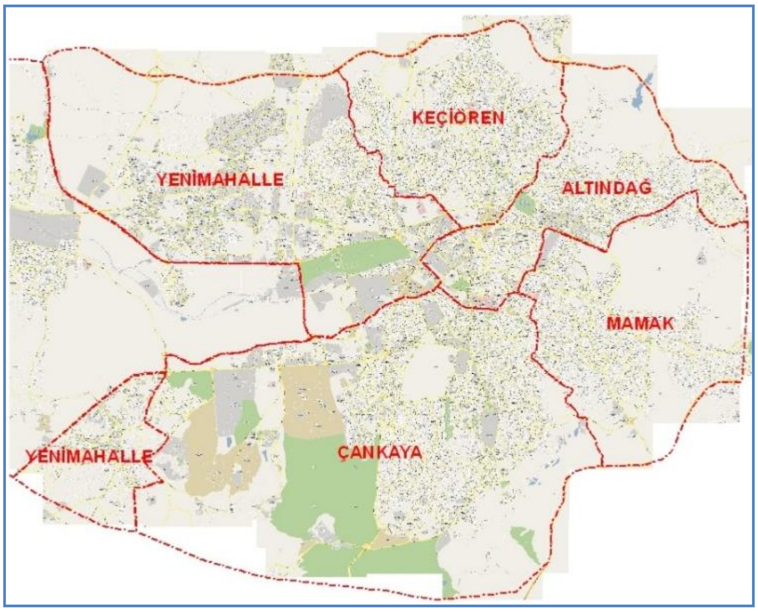

Figure 1. The location of the sub-provinces in the study area

Table 1: Characteristics of sub-providences

Sub-providence	Population	Size of parks (m^2)
Çankaya	914.501	1.592.517
Keçiören	848.305	2.381.777
Yenimahalle	591.462	2.952.042
Mamak	568.396	1.100.028
Altındağ	359.597	2.106.854

The research was conducted in the biggest parks I n these sub-provinces. Dikmen Vadisi Park has a total area of 175.000 m^2 and Ahlatlıbel Park has an area of 180.000 m^2 in Çankaya. Gökçek Park is located in the area of 46.000 m^2 in Keçiören. 50. Yıl Park has 135.000 m^2 of green areas in Mamak. And Altınpark is located in 640.000 m^2 area (Figure 2).

The current study that aims to determine the benefits of urban green spaces used questionnaire, observations and interview tools. Accordingly, the number of survey samples were determined as 320 participants, taking into consideration a confidence level of 95% and a deviation of (α=0,05) +5.5%. It is aimed to investigate user’s demographic details, existing park habits and effects of green spaces. Benefits of green spaces were tested with questions about physical health, psychological benefits, social benefits and environmental benefits. Respondents were asked to indicate on a three-point Likert scale. The items were rated on a response scale 1- “disagree” and 3-“agree”.

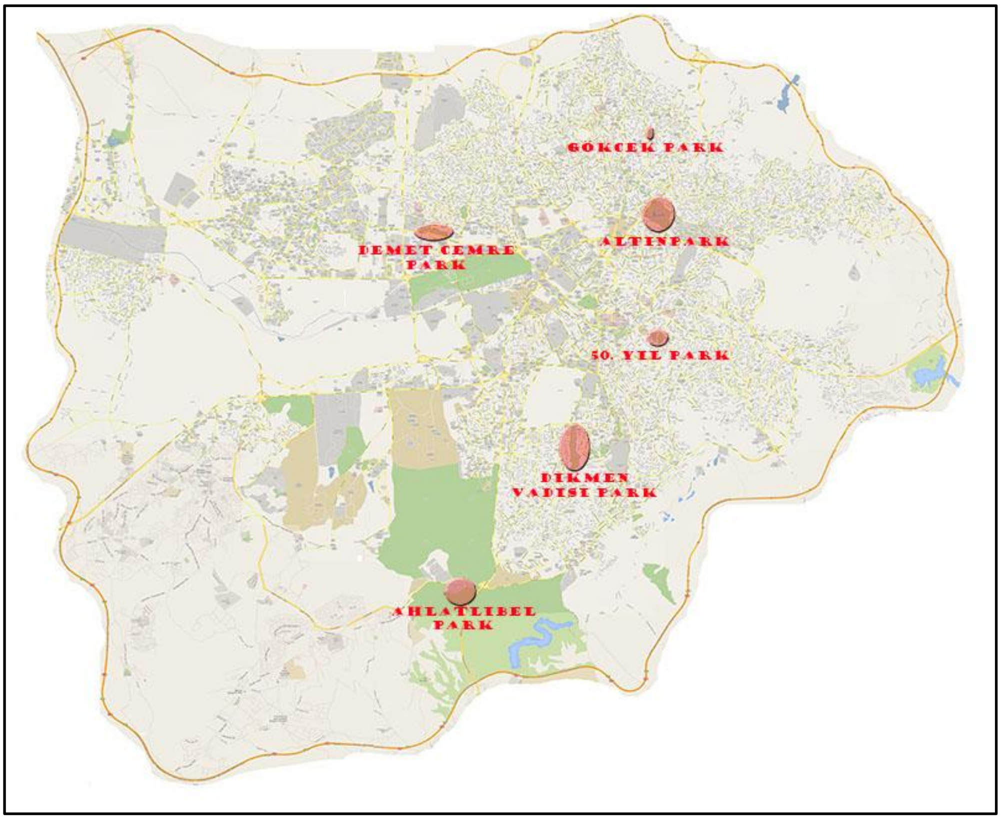

Figure 2. The location of the sub-provinces in the study area

FINDINGS

Out of 320 questionnaire the participants, 145 were female and 175 were male. As the age groups were analyzed, 94 were between the ages of 18-25, 112 between the ages of 26-39, 62 were between the ages of 40-59, and 52 were 60 and above (Table 2).

Table 2: Characteristics of participants

Sample Demographics	N	%
Sex		
Female	145	45,3
Male	175	54,7
Age		
18-25	94	29,3
26-39	112	35,0
40-59	62	19,4
60 and above	52	16,3
N=320		

Table 3: Frequency of visiting parks

Frequency	N	%
Everyday	84	26,2
Few times a week	48	15
Once a week	113	35,3
Every other week	42	13,1
Once a month	28	8,8

Other	5	1,5

% 35,3 of respondents visit parks once a week, %26,1 visit everyday. %81,3 high level of respondents visits parks and green spaces at day time (Table 3). Participants spend time with walking %71, doing exercise %35, with team sports (basketball, volleyball etc.) %18, in cafes %42, with friends/family %79 in parks.

As their opinions about benefits of urban green spaces examines, participants mostly stated that viewing nature in the workplace reduce perceived job stress, and improve job satisfaction (M=2,53), natural areas improve psychological well-being, provide physical exercise and social interaction (M=2,50), being in natural areas feels them more energetic (M=2,44), residents who have nature nearby have greater neighborhood satisfaction, overall health and life satisfaction (M=2,41), they prefer walking in natural areas (M=2,38), green spaces helps to feel tranquil and at peace (M=2,38) and they can spend time with friends at urban green spaces (M=2,34) (Table 4).

Table 4: Items and scale means and standard deviations for benefits of urban green spaces dimensions

	Mean Value	sd
I prefer natural areas for walking	2,38	,751
I have more opportunity to do exercise in the park.	2,03	,695
Spending time in natural areas makes me feel more energetic.	2,44	,669
I prefer doing exercise at green space rather than in the gym.	2,28	,729
Green spaces helps me to feel tranquil and at peace.	2,38	,660
Being in nature improves concentration and positively affects mood state.	2,13	,660
Being in nature improves performance in attention demanding tasks.	2,06	,669
Viewing nature in the workplace reduce perceived job stress, and improve job satisfaction.	2,53	,567
I can spend nice time with my friends in this park.	2,34	,701
I can meet up with my neighbors/friends in this park.	1,94	,669
In this area I can get away from the noise and air pollution of the city.	2,19	,644
Residents who have nature nearby have greater neighborhood satisfaction, overall health and life satisfaction than residents who do not.	2,41	,665
Natural areas improve psychological well-being, provide physical exercise and social interaction.	2,50	,568

According to the interviews and observations done in the research area, the benefits of green spaces could be summarized as follows:

- Parks and green spaces which have walking paths and fitness equipment are more preferred by citizens,
- Parks and green spaces which have non-traffic density around and have more green space, have been visited more.
- People do exercise regularly in open spaces with adequate equipment.
- Citizens prefer parks which are larger and have more green space, rather than small ones in the city.
- Citizens are satisfied with using sports equipment free of charge in urban green spaces, rather than pay for a gym.
- Especially in summer days, people visit green spaces in order to cool off.

CONCLUSION

Urban green spaces have an important role on health, environment and economic. Green spaces contribute to physical activity and psychological health as well as social health of citizens. As the conditions are sufficient, people are encouraged to increase physical activity levels. High levels of physical activity was observed in parks with adequate sports fields and equipment in the study area.

Survey results showed increase of green spaces facilitates relaxation, enhances physical and psychological well-being and social interaction. In study area some parks has higher level of concretization and it was determined that these parks counteracts these effects.

Study conducted in Ankara report that green spaces have lower temperature than other areas in summer days. As a result of this, people prefer visiting urban natural areas in Ankara especially in summer.

More green spaces are required in order to fulfill people’s recreational needs in Ankara. Planning proposals should be presented to meet demands and needs of local community in these areas. Parks must offer various play fields, fitness areas and walking paths for different age groups. Also, silent, tranquil and natural areas must be created in parks.

REFERENCES

Chiesura, A. (2004). The role of urban parks for the sustainable city. *Landscape and urban planning, 68*(1), 129-138.

Coley, R. L., Sullivan, W. C., & Kuo, F. E. (1997). Where does community grow? The social context created by nature in urban public housing. *Environment and behavior, 29*(4), 468-494.

Conway, H. (2000). Parks and people: the social functions. *The Regeneration of Public Parks’, E&FN Spon, London*.

Fezer, F. (1995). Das Klima der Städte. Gotha: Justus Perthes Verlag.

Gies, E. (2006). The Health Benefits of Parks. *The Trust for Public Land*.

Godbey, G., Graefe, A. R., & James, S. W. (1992). *The benefits of local recreation and park services, a nationwide study of the perceptions of the American public*: National Recreation and Park Association Ashburn (VA).

Hartig, T., Mang, M., & Evans, G. W. (1991). Restorative effects of natural environment experiences. *Environment and behavior, 23*(1), 3-26.

Hayward, D. G., & Weitzer, W. H. (1984). The public's image of urban parks: Past amenity, present ambivalance, uncertain future. *Urban Ecology, 8*(3), 243-268. doi: http://dx.doi.org/10.1016/0304-4009(84)90038-X

Heidt, V., & Neef, M. (2008). Benefits of urban green space for improving urban climate *Ecology, Planning, and Management of Urban Forests* (pp. 84-96): Springer.

Kaplan, R. (1985). The analysis of perception via preference: a strategy for studying how the environment is experienced. *Landscape planning, 12*(2), 161-176.

Kuo, F. E., Bacaicoa, M., & Sullivan, W. C. (1998). Transforming inner-city landscapes trees, sense of safety, and preference. *Environment and behavior, 30*(1), 28-59.

Kuo, F. E., & Sullivan, W. C. (2001). Environment and crime in the inner city does vegetation reduce crime? *Environment and behavior, 33*(3), 343-367.

McMahon, E. T. (1996). Green enhances growth. from http://plannersweb.com/1996/04/green-enhances-growth/

McPherson, E. G., Simpson, J., Pepper, P., & Xiao, Q. (1999). Benefit-cost analysis of Modesto’s municipal urban forest. *Journal of Arboriculture, 25*(5), 235.

Meyer, J. (1997). *Die zukunftsfähige Stadt: Nachhaltige Entwicklung in Stadt und Land*: Werner.

Schroeder, H. W. (1991). Preference and meaning of arboretum landscapes: Combining quantitative and qualitative data. *Journal of Environmental Psychology, 11*(3), 231-248.

Takashi, A., & Vu Than, C. (1998). Case study: effects of vegetation on the climate in the urban area: In: Breuste, J., Feldmann, H., and Uhlmann, O.(eds.) Urban Ecology: Springer, Berlin.

Ulrich, R. (1981). Natural versus urban scenes some psychophysiological effects. *Environment and behavior, 13*(5), 523-556.

Ward Thompson, C. (2013). Activity, exercise and the planning and design of outdoor spaces. *Journal of Environmental Psychology, 34*, 79-96. doi: 10.1016/j.jenvp.2013.01.003

Yüksel, Ü. D., & Yılmaz, O. (2008). Ankara kentinde kentsel isi adasi etkisinin yaz aylarinda uzaktan algilama ve meteorolojik gözlemlere dayali olarak saptanmasi ve değerlendirilmesi. *Gazi Üniversitesi Mühendislik-Mimarlık Fakültesi Dergisi, 23*(4).

DEVELOPMENT OF URBAN ECOLOGY THROUGH EDUCATIVE AND INFORMATION ACTIVITIES

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OPERATIONAL PARAMETERS OF SUN COLLECTORS

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ABSTRACT

In order to efficiently solve the problems created by the deepening energy crisis affecting Europe and the world, governments cannot neglect the opportunities of using the energy produced by sun collectors. In many of the EU countries there are sun collectors producing heat energy, e.g. in 2011 in the area of EU27 (countries which belong to European Union) + Switzerland altogether 37519126 m^2 were operated, which are capable of producing 26.3 GWh heat energy. The energy produced by these sun collectors is utilized at the place of production. In the near future governments will have to focus more on spreading and using sun collectors. Among the complex problems of operating sun collectors, this article deals with determining the optimal tilt angle, directions of sun collectors. We evaluate the contamination of glass surface of sun collector to the produced energy. Our theoretically results are confirmed by laboratory measurements. The purpose of our work is to help users and engineers in determination of optimal operation parameters of sun collectors.

Keywords: *heat energy, direction of sun collector, contamination of surface*.

INTRODUCTION

In order that the surface of the sun collectors should be able to convert as much as possible from the energy transported by the arriving sun rays we must be familiar with the Sun-Earth movements (Duffie and Beckman, 1980). When determining the geometry of the Sun-Earth movement we tried to use the simplest formulas possible that engineers and enterprises designing the sun collectors may be able to work with. Figure 1 shows the geometric relationships of sun collectors placed on the Earth’s surface.

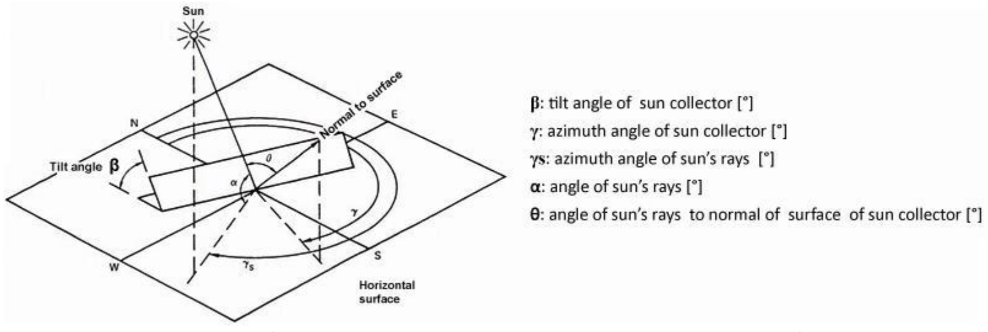

Figure 1. Relationships of the incident beam radiation and a tilted surface (Dickinson and Cheremisinooff, 1980)

The amount and intensity of the radiation arriving at the surface of the sun collector also depend on the relative position and movement of the Earth-Sun (Patkó, 2010). Figure 2 depicts the movement of the Sun and Earth in relation to each other, the so-called sun paths at 48˚ north longitude (Patkó, 2009).

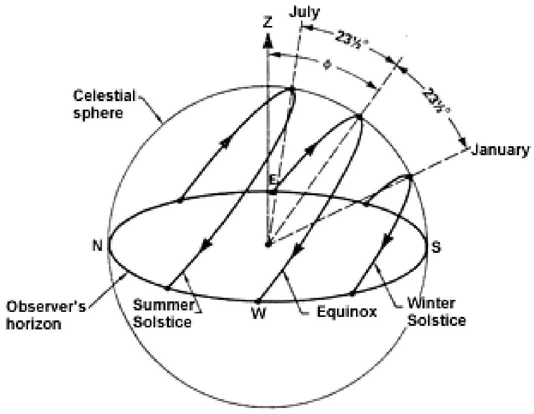

Figure 2. Visualization of the sun paths (Dickinson and Cheremisinooff, 1980)

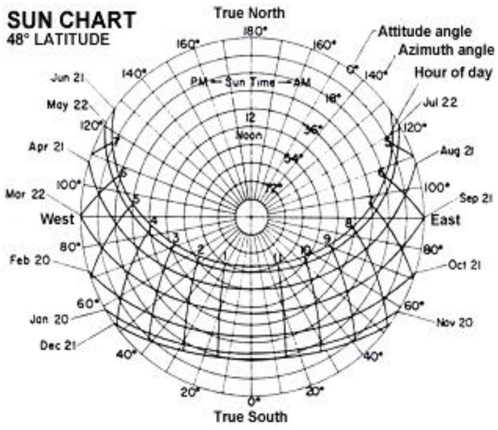

Figure 3. Sun charts (Dickinson and across the sky Cheremisinooff 1980)

At 48˚ latitude of the northern hemisphere the figure shows the sun’s movement at the time of the winter and summer solstice and the equinox. If we prepare the top-view picture of this figure, we get the sun chart of this northern latitude (Figure 3) (Patkó, 2009). According to the sun charts (Hand, 1978) the sun gets the closest to the sun collector placed in the centre of the figure i.e. the observation point, at the time of the summer solstice, i.e. at 12.00 June 21st. It is obvious from this figure that if the sun collector is directed in the true south direction, it gets the largest possible radiation energy. During the day the angle of the sun to the normal of the sun collector (θ) changes according to the passage of time (Ibrahim, 2008). If we want the sun to reach the surface of the sun collector at the most optimal angle during the day, continuous east-west sun collector adjustment must be provided. In our work with change tilt angle β to the horizontal surface and we determine those tilt angles (β) at which, during the year, the collector will be capable of transforming the largest energy deriving from the sun. This means that the tilt angle of the (β) should be modified according to the movement of the sun each day of the year.

This is technically unimaginable and impracticable; therefore in this section of our article we determine the most optimal tilt angle values at the tested geographical location (N 47.5°):

- for the whole year
  (the tilt angle of the collector (β_{year}) is not modified during the year),
- seasonally
  (the tilt angle of the collector is modified according to the four seasons. Therefore four tilt angles will be defined (β_{summer}, β_{winter}, β_{autumn}, β_{spring})).

The Earth orbits the Sun in an elliptical orbit with an eccentricity of 3%. The Earth makes a full circle in a year. The Earth does not only go around the Sun but it also rotates around its own axis at a speed of one rotation per day. Its own axis is tilted at δ=23.5° from the axis of the orbit around the Sun. In this way during its orbit around the Sun, the northern hemisphere gets closer to the Sun in the summer than the southern hemisphere, and this is changed in winter. In spring and autumn the tilting of the Earth’s axis (δ) is such that the distance of the northern hemisphere and the southern hemisphere relative to the Sun is the same. This is shown in Figure 4.

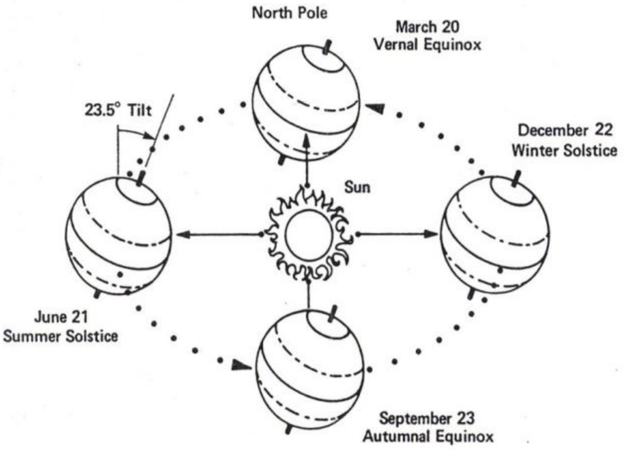

Figure 4. Diagram of the Earth's orbit around the Sun
(Dickinson and Cheremisinooff, 1980)

On the basis of our theoretical (Patkó et al., 2013) considerations and experience we have accepted that – globally, regarding a whole year – the tilt angle of the sun collector equals the value of the northern latitude, i.e.:

- $\beta_{year} = \Phi$

so at the test site, in Budapest, (47.5° N):

- $\beta_{year} = 47.5°$

According to [1] $\beta_{year} = \Phi$ should be modified in the following way:

- $\beta_{year} = \Phi + (10° \div 20°)$

We disregard this assumption, proposal during our tests. The – theoretical – values of seasonal tilt angles are the following according to Figure 6.

- $\beta_{summer} = \Phi - \delta$
- $\beta_{winter} = \Phi + \delta$
- $\beta_{autumn} = \Phi$
- $\beta_{spring} = \Phi$

The tilt angles of the sun collectors at the test site, in Budapest, (47.5°N):

- $\beta_{summer} = 24°$
- $\beta_{winter} = 71°$
- $\beta_{autumn} = 47.5°$
- $\beta_{spring} = 47.5°$

We made some measurements in order to verify the correctness of the values.

MATERIAL AND METHODS

Laboratory measurements

We made a series of measurements with glass covered flat collectors in order to determine the ideal collector tilt angles (β) in the area of Budapest (47.5°N). The main point of the measurement is to determine the optimal tilt angles (β) as a result of comparative series of measurements. We measured the thermal characteristics of two sun collectors parallel, at the same time. We had set the tilt angle of one collector to a value – which we defined – relating to the whole year (β_{year}) and we did not change that during the series of measurements. This collector was marked collector B. The tilt angle of the other collector marked A was modified according to the seasonal values defined by us (β_{summer}, β_{winter}, β_{autumn}, β_{spring}) during the measurements. Figure 5 depicts the collectors.

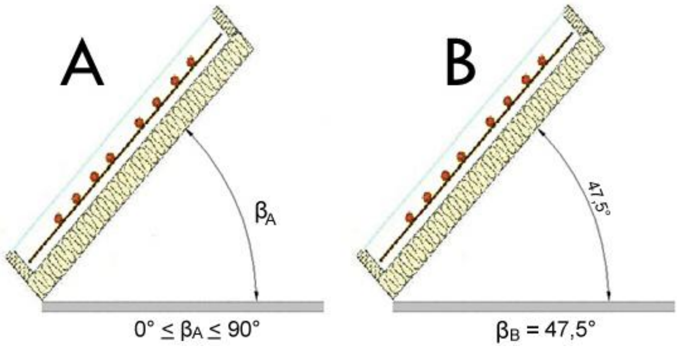

Figure 5. Tilt angles of collectors

During the measurements the thermal characteristics of both collectors were measured and we made our conclusions by comparing these. The measurements were made in the summer, autumn and winter of 2011. In our opinion the autumn and spring measurements – relative to each other – must produce the same result, so we did not make any measurements in spring. This conclusion is supported by Figure 6 as well.

Description of the measuring equipment

In order to confirm and support by experiments the sun collector tilt angles (β) determined theoretically in the previous sections, a special measurement station was created at Óbuda University (Budapest, Hungary) and installed on the roof of the building. With the measurement equipment – which is fully automated and controlled by a computer – we were able to continuously measure the thermal characteristics of the sun collector in summer, autumn and winter. The conceptual layout of the measuring equipment is shown in Figure 6. The equipment incorporates two (2.0 m^2) glass covered flat collectors (marked A and B) witch were developed by us. The system has two loops. The primary loop which consists of the sun collector and the liquid heat exchanger placed in the solar tank is filled up with antifreeze liquid medium. The secondary loop utilizes the heat content of the water in the solar tank. Measurement points were established in the measuring equipment to measure the water and liquid material temperature, and the mass flow of water and liquids. In order to increase the safety and reliability of the measurements, we measured the amounts by MBUS and PLC systems. The measurements were processed by a monitoring computer and presented them on the screen by VISION system. During the measurements great care was taken to make sure the temperatures and mass flows of the medium entering the collectors – in the case of both collectors – should be equal. This was ensured by keeping the secondary loops and the tank temperatures at a constant value. The characteristics of the external atmosphere were measured by a meteorological station located on the roof and equipment measuring solar radiation, and the results were entered into the monitoring computer. Special care had to be taken of the winter measurements. The system had to be protected against freezing in a way that by the beginning of the – daily – measurement the temperature of the solar tank should not be higher than 2÷3°C. The conceptual layout of the measuring equipment is shown in Figure 6.

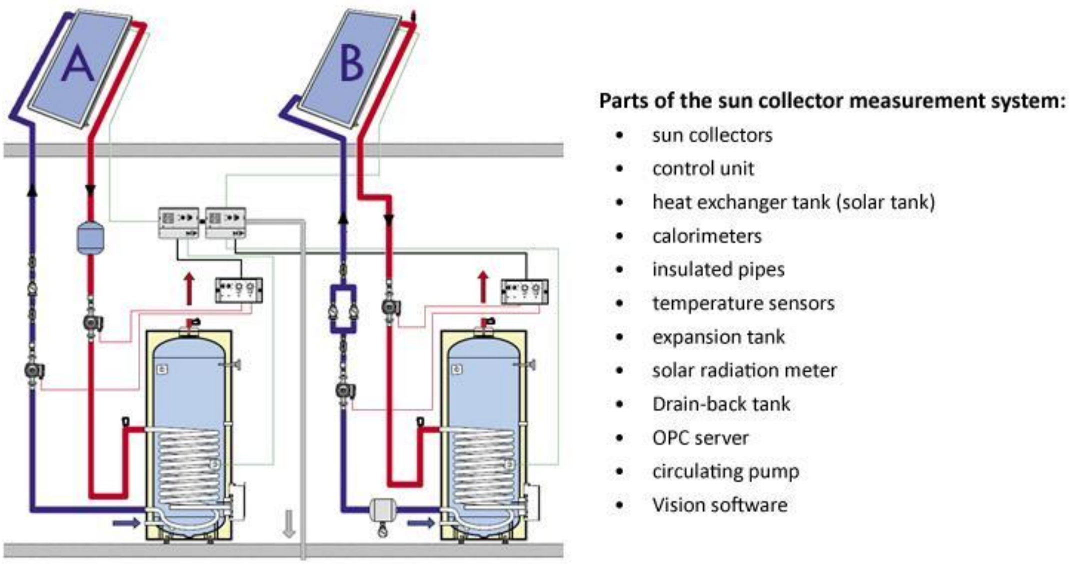

Figure 6. Sun collector measurement system

Measurements of optimal tilt angel (β)

We set the tilt angle of collector B to β_{year} = 47.5° and kept it at the same angle during the measurements. We set the tilt angle of collector A to three values in each season. These values are the seasonal values which we determined, i.e.:

- $\beta_{summer} = 24°$
- $\beta_{winter} = 71°$
- $\beta_{autumn} = 47.5°$

During the measurements we measured the temperature and the mass flow of the liquids entering and leaving the sun collectors, the temperature of the solar tank, the amounts of heat carried off the solar tank as well as the data of the external atmosphere and solar radiation. During the measurements it was ensured that the temperatures and mass flows of the medium entering the collectors should be equal.

According to the previous chapters the value of entry temperatures of both sun collectors and the value of mass flows of the medium flowing through the collectors were the same during the measurements. In such cases if we want to compare the power of the collectors (P_A, P_B).

The power relation ($R_{PA}/_{PB}$) of the two tested collectors should – approximately – equal the relations of the exit temperatures of the collectors, which were determined in our earlier paper [14].
The determined power relations tilt angle β_A of collector A (with modified tilt angle) and the deviation of the calculated power relations – according to the seasons – were given in Table 1.-Table 3.

Table 1: Summer, $\beta_B = 47.5°$

β_A [°]	$R_{PA/PB}$ [%]	Deviation
24	141	7.23
47.5	100	2.59
71	86	2.46

Table 2: Autumn, $\beta_B = 47.5°$

β_A [°]	$R_{PA/PB}$ [%]	Deviation
24	80	1.55
47.5	100	1.83
71	81	3.37

Table 3: Winter, $\beta_B = 47.5°$

β_A [°]	R $_{PA}$/ $_{PB}$ [%]	Deviation
24	80	5.54
47.5	102	4.12
71	110	5.49

These diagrams shows – approximately – the R $_{PA}/_{PB}$ change of the power relation of collectors A and B at angles β_A and β_B = 47.5°=constant value per season.

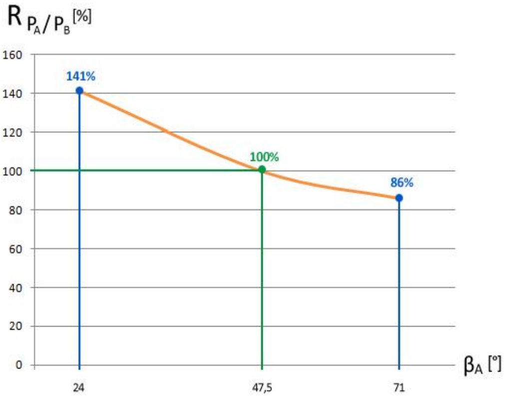

Figure 7. Power relations of collectors in summer, β_B = 47.5°

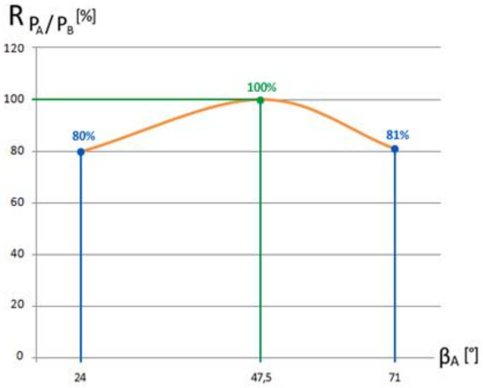

Figure 8. Power relations of collectors in autumn, β_B = 47.5°

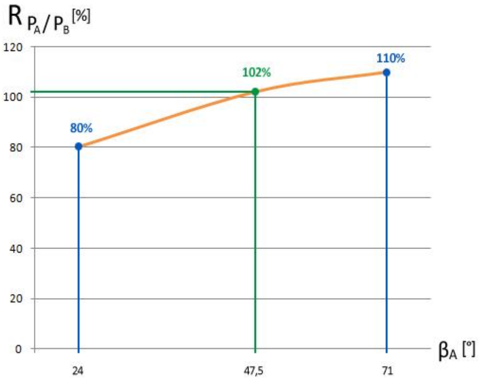

Figure 9. Power relations of collectors in winter, β_B = 47.5°

Measurements of infect of surface contamination

During operation, the surface of solar collectors gets contaminated. Depositing and airborne aerosols deposit on glass surfaces and therefore reduce glass transparency, which results in reduced solar collector power. No literature has been found on the relation between surface contamination of solar collectors and power drop. It is important though to carry out experiments to explain the relation between surface contamination of solar collectors and power drop. By changing surface contamination of solar collector B the different efficiency curves at different contamination rates were determined:

$$\eta = f\left(\frac{t_s - t_a}{I}\right)$$

Where t_s is the solar collector average surface temperature, t_a is ambient temperature, and I is irradiance. To model surface contamination, carbon black was spread on the surface. In the course of measurements solar collector efficiency curves were taken at 4 different degrees of contamination: 0

g/m^2, 75 g/m^2, 150 g/m^2, and 225 g/m^2. Figure 10 shows the characteristic curves determined by measurements.

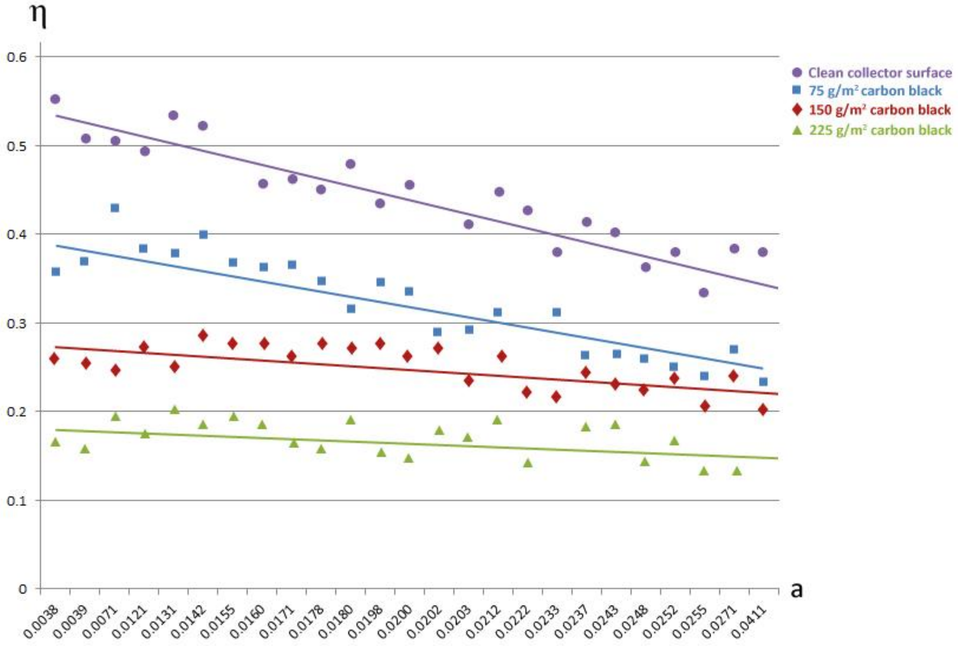

Figure 10. Relation between surface contamination and collector efficiency

According to Figure 10 it can be established that the more the surface of solar collector is contaminated the further efficiency curves are drifted toward lower efficiency value ranges. Experimental values are summarized in table 4.

Table 4: Surface contaminations and efficiency curve data

No.	Contamination [g/m^2]	Deviation R^2 [-]	Regression line
1	0	0.4215	$\eta = -0.0079a + 0.5147$
2	75	0.1828	$\eta = -0.0057a + 0.3917$
3	150	0.1901	$\eta = -0.0021a + 0.2749$
4	225	0.0847	$\eta = -0.0013a + 0.1808$

where: $$a : \frac{t_s - t_a}{I}$$

Theoretical approach to the orientation of sun collectors

Orientation is of great importance in terms of solar collector performance. In the literature papers studying orientation have assumed solar collectors are faced to the true north in the South Hemisphere or the true south in the North Hemisphere. Figure 1 shows that the angle between the vertical projection of sunlight on the ground and the true north (γ_S) is called the azimuth of sun, while the angle between the vertical projection of the normal of collector surface and the true north (γ) is called the azimuth of collector. β is tilt angle of solar panel, and θ is the incidence angle of sunlight.

If the observer is located at or near the Equator, then the orientation of solar panels needs not to face the right direction (Calabro, 2009). Figure 1 clearly suggests that solar collectors work at optimum performance if $\gamma = \gamma_s$ and θ values minimum, that is $\theta = \theta_{min}$.

Sun path and collector tilt angle (β) also affect θ. Theoretical considerations and findings in the literature suggest that solar collector power will decrease if panels are not oriented to the true south

(γ=180˚) in the Northern Hemisphere. According to our experiments, power at a given tilt angle (β) may drop by 20-60%, depending to the rate of deviation from the true south. Considering that solar collector surface is exposed not only to direct radiation (I_{dir}) but also diffused radiation (I_{diff}), the total irradiation of surface is $I_{total} = I_{dir} + I_{diff}$ (Chang, 2008). Taking Sun constant (1353 W/m^2) and atmospheric losses (57%) into account, the value of direct radiation is I_{dirmax} = 582 W/m^2. Based on experimental values, diffuse radiation (I_{diff}) is $I_{diff} = I_{dirmax}$ *(0.4-0.8). It means that with γ=180˚ and at $\beta = \beta_{opt}$. the irradiation solar collector surfaces are exposed to be:

$$I = I_{dir} + I_{dirmax}\,(0.4\text{-}0.8)$$

At $\gamma = 90^o$ or $\gamma = 270^o$, or at orientation to the west or east, respectively, the irradiation solar collector surfaces are exposed to is:
$I = 0 + I_{dirmax}$ (0.4-0.8), which results in a power drop by 20-60%. This expected drop in performance is seen in Figure 11, where ΔP is the change in solar collector power caused by deviation in orientation.

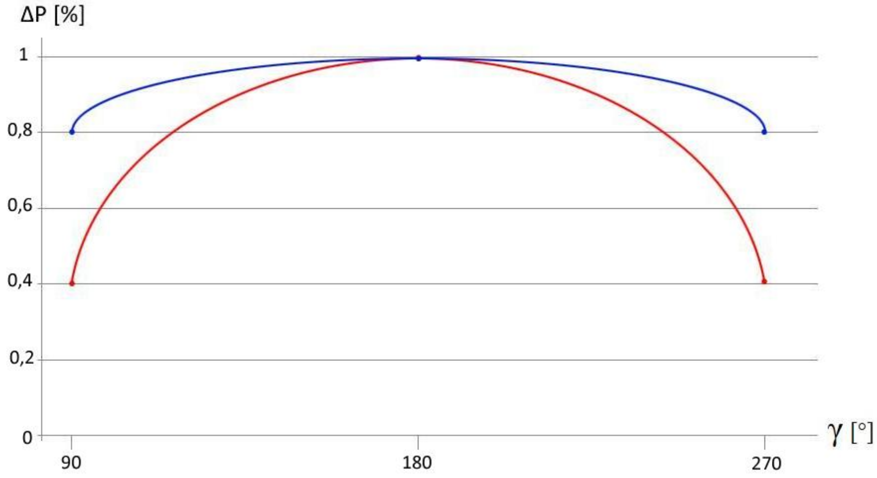

Figure 11. Optimum tilt angle (β_{opt}) drop in solar collector power in function to azimuth angle (γ)

CONCLUSION

Considering the efficient operation of sun collectors Óbuda University established a special measurement station capable of measuring the thermal characteristics of several sun collectors at the same time. Based on the laws of the Sun – Earth relative movement published in the specialist literature we determined the optimal tilt angle of the sun collectors at which the energy producing capability of the collector is optimal. In this way we determined a set-up angle for a whole year and the collector tilt angles for the four seasons (autumn, winter, spring, summer). Through laboratory measurements we confirmed our conclusions made theoretically. Our measurements made it clear that if the sun collector is not set at the right angle, the power of collector falls by up to 10-20%. Figure 7 – Figure 9 graphically depict this decrease in power due to improper tilt angles. If the tilt angle of the sun collector is not modified during the year, the power of the collector in summer – when the possibility of energy transformation is the best – is up to 20-30% less than the optimal value. In spring and autumn the operation and energy producing capability of the sun collector is optimal at this tilt angle ($\beta = \phi$ = 47.5°).

For the measurements we used a special sun collector developed by we, whose construction cost is lower compared to the commercial sun collectors available in Hungary. In the future we find it necessary to repeat our measurements under more precise circumstances, with more tilt angles and at least four collectors in parallel. We hope that those results will give us more accurate information how to modify the tilt angles of sun collectors. The effect of contamination of solar collector surface on collector performance and collector efficiency characteristic curve were determined. Based on theoretical considerations the expected drop in solar collector power was determined with collectors not facing the true south (in the northern hemisphere).

REFERENCES

Duffie, J. & Beckman, W. 1980. Solar energy thermal processes. California: Wiley.

Dickinson, W. & Cheremisinooff, P. (1980). Solar energy technology handbook. New York: Marcel Dekker.

Patkó, I. (2010). Integrating renewable energies into the national energy system with special regard to the thermal utilization of solar energy. Conference of the Hungarian Technical Experts; Hungarian Academy of Science; Budapest.

Patkó, I. (2009). Renewable energies. University book. Budapest: BMF Publishing Inc.

Hand, I. F. (1978). Charts to obtain solar altitudes and azimuths. Heating and Ventilating, October, 86-88.

Patkó, I., Szeder, A. & Patkó, Cs. (2013). Evaluation the impact tilt angel on the sun collectors. *Energy Procedia*, 32, 222-231.

Ibrahim, R. & Andreas, A. (2008). Solar position algorithm for solar radiation applications. Colorado. Technical Report NREL.

Calabro, E. (2009). Determining optimum tilt angel of photovoltaic panels at typical north-tropical latitudes. *Journal of Renewable and Sustainable Energy*, 1.

Chang, T. P. (2008). Study on the optimal tilt angle of solar collector according to different radiation types. *International Journal of Applied Science and Engineering*, 6, 151-161.

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EDUCATIONAL TRAININGS WITHIN THE TEMPUS NETREL PROJECT

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ABSTRACT

NETREL (Network for education and training for public environmental laboratories) project is based on a core-network of academic research institutes from EU countries (UK, CZ, SK) dealing with analytical chemistry, environmental sampling and monitoring of environmental pollutants and universities and reference laboratories from Serbia and Bosnia & Herzegovina with proven experience in the field of environmental issues. Within NETREL, six learning courses and six training courses will be organized. After 18 months from the beginning of the TEMPUS NETREL Project, five training courses have been completed. At EU universities, four practical trainings were organized for university staff of Serbia (University of Novi Sad, University of Belgrade) and Bosnia & Herzegovina (University of Sarajevo, University of Banja Luka). The learning courses were held in parallel in Serbia and Bosnia & Herzegovina, and three of six have already been done. The first training course organized from the university staff for public environmental laboratories was held on September, 2014, in Novi Sad, Serbia. The grant holder of the Project is Slovak University of Technology (STU) and Prof. Spanik is Project manager. This type of educational courses organized on so called two levels (from EU Universities to academic staff in Serbia and Bosnia & Herzegovina and from academic staff to public environmental laboratories) was suggested for the first time within NETREL TEMPUS Project.

Key words: *training courses, learning courses, environmental matrices.*

INTRODUCTION

TEMPUS Training Network NETREL aims to train researchers and experts in Serbia and Bosnia & Herzegovina in environmental analytical techniques required to meet the major challenges in the monitoring, assessment and management of pollution and emission of toxic compounds in Western Balkan countries. NETREL action will allow the development and implementation of state-of-the-art methodologies to enable and improve Western Balkan capabilities for monitoring of environmental pollutants. These will be comparable to those already used in EU member states. Moreover, it will provide a unique opportunity to share already developed protocols, validated analytical methods and harmonised chemical and biological monitoring methods (including sampling methodology, sample treatment, QC/QA) for determination of environmental pollutants regulated by various EU legislation.

The public laboratories in Serbia and Bosnia & Herzegovina monitor the quality of raw water and drinking water. Monitoring parameters include only the basic physical chemical parameters and metals. Considering organic pollution, only trihalomethanes, anion-active detergents and phenols are monitored. The major reasons for the lack of accredited methods for environmental analysis and for absence of systematically monitoring programmes indicated by public laboratories are insufficient experience and up-to-date knowledge in sampling, sample treatment and analytical methodology.

OBJECTIVES OF PROJECT

An important overall objective of NETREL is to establish a cluster of academics and other experts in Serbia and Bosnia & Herzegovina in the area of environmental monitoring. At the end of the project the trained expert teams will be capable to further disseminate the obtained know-how and expertise to public institutions/laboratories in the region that are active in environmental protection. In the Western Balkan region, there is a broad pool of experts dealing with general physical chemical parameters and inorganic analysis of water, but a very limited number of scientists in academia or governmental organizations with experiences, knowledge and skills necessary to provide adequate support of regulatory bodies in monitoring of priority and emerging environmental pollutants (WFD, NORMAN, 2014). Thus, it is essential to train experts with the understanding of the modern monitoring practices, state-of-the-art analytical techniques used in environmental monitoring programmes, as well as ensuring a quality control and quality assurance of obtained analytical results and finally improve a capability of interpreting monitoring data in terms of legislative requirements, assessments of risk, and the need for intervention to prevent further deterioration or to enhance water quality. All these could be achieved through the appropriate training opportunities within this proposal that would enhance the development of Western Balkan region.

NETREL project is based on sharing up-to-date knowledge gathered during development of EU environmental policies with academia experts from partner Western Balkan countries, which will further be transferred to staff in public laboratories. This main objective requires active cooperation between academia, public authorities and decision makers in Western Balkan countries with possibility to open it to private companies and other stakeholders in the environmental sector. NETREL network also keeps in mind the perspective and future of region, and thus will open courses also to young talented students from Serbia and Bosnia & Herzegovina. The gained knowledge in the fields of QA/QC, analytical methods, environmental monitoring and management would be helpful for their later career development. Finally, in order to maintain project sustainability after its completion, already developed courses will be presented to major stakeholders, private laboratories and companies. Bringing together stakeholders and the formed high quality training network will further facilitate the exchange of knowledge and expertise and produce a generation of young scientists that would easily bridge gaps between the various environmental sectors and will maintain cross-sectoral long-term collaboration.

EDUCATIONAL TRAININGS

The proposed NETREL training programme is based on a well-balanced mixture of different training elements. The academia experts from Serbia and Bosnia & Herzegovina will take part in extensive training through participation in lecture courses and seminars at the participating host institution. The major benefit of the visits of partner country academic staff to the EU partners is practical hands on training and laboratory visits. Lecture courses and seminars taking place in partner country will be aimed to provide general lectures and establishment of standard operating procedures and validation of analytical methods on purchased equipment. The offered lecture courses together with seminars w be organised in first half of project duration under supervision of academia experts from all EU partner countries. Additionally, in order to maximise the project efficiency, defined courses offered by individual partners will be available for partner experts at their home institution. The offered courses will cover all aspects of environmental monitoring including sampling, introduction and advanced training in analytical methodologies, data handling and QA/QC. All those activities will be supported by hands on training that will allow experts to benefit from the high level expertise available within the network team. The hands on training will be aimed on development of expert skills in generally used analytical methods in environmental monitoring (Spanik et al, 2013).

In addition to lectures, practical exercises are offered to actively involve the fellows in discussions, exercises, and problem solving cases. One of the five days of each event will be reserved for the provision of complementary skills, provided by professional trainers. The obtained knowledge will be transferred into public laboratories in Serbia and Bosnia & Herzegovina through free of charge training courses (during project duration) organised by trained academia experts from universities in Serbia and Bosnia & Herzegovina under EU partner supervision. This educational activity is the first step for establishing long life learning (LLL).

Learning course “Sampling of environmental pollutants” was prepared in a close collaboration of two expert scientists in the field of environmental chemistry.

The aims of the learning course were to provide project partners from Western Balkan state universities with state of the art information on sampling of environmental pollutants required by the current European legislation

- to understand key aspects of current water policy in Europe and how this affects the monitoring of environmental pollutants,
- to understand what are priority and emerging pollutants and their environmental fate,
- to give attendees a sound theoretical knowledge of how to sample a wide range of key environmental pollutants in water, sediments and biota,
- to have a practical knowledge of how to plan and undertake a field monitoring study for key environmental pollutants, and have an appreciation of the quality control and quality assurance aspects of environmental sampling.

The topics covered by the course included: Water policy and management in Europe; Objectives and principles of the Water Framework Directive (WFD); Monitoring requirements of the WFD; Compliance with the WFD; Fate of toxic compounds in the environment; Environmental quality standards and their derivation; Priority pollutants and river basin specific pollutants (RBSP); Assessment of ecological and chemical status under WFD; Marine Strategy Framework Directive; Emerging pollutants; Monitoring tools and methods for priority and River Basin Specific Pollutants; Sampling: Traditional methods and new approaches; Classical methods in monitoring; Continuous methods; Portable instruments; Test kits; Sensors; Chemical monitoring in biota; Biological early warning systems; Test kits: bioassays; Biosensors: integrated systems; Principles of passive sampling; Partition passive sampling; Adsorption based passive sampling; Passive sampling of metals; Comparison of passive sampling with monitoring in biota; Example of passive sampling from BIH: monitoring of Bosna river; Sediment sampling techniques; Sieving and freeze drying of sediments; Data normalisation and assessment in sediment analysis; introduction to QA/QC in environmental sampling.

Learning course “Sample preparation of environmental matrices” was prepared in a close collaboration of two expert scientists for EU countries in the field of environmental analytical chemistry.

The aims of the learning course were to provide project partners from Western Balkan state universities with state of the art information on sample preparation in analysis of environmental pollutants required by the current European legislation in the water sector, namely:

- to understand key aspects of treatment of environmental matrices for further analytical determination of WFD pollutants with main focus on surface water,
- to understand basic principles of the most frequently used sample treatment methods used for extraction of organic pollutants from environmental matrices,
- to have basic knowledge about parameters that need to be optimized prior to sample treatment procedure and their influence on overall process,
- to give attendees basic information about methods development process,
- to give attendees a sound theoretical knowledge of how to treat samples containing a wide range of environmental pollutants with various physico-chemical properties.

The topics covered by the course included: Overview of Water Framework Directive pollutants; general introduction to sample treatment methods; volume reduction; derivatisation in sample treatment; general theory of extraction; liquid – liquid extraction – single step, multi step and counter current; perspectives and current trends in liquidliquid extraction; overview of liquid-liquid extraction methods for extraction of WFD pollutants; sorptive extraction methods – introduction and general theory; sample treatment methods for volatile organic pollutants; stir bar sorptive extraction; extraction using monolith materials; solid phase microextraction; solid phase extraction – introduction and general theory; perspectives and current trends of sorptive sample treatment methods; overview of sorptive extraction methods for extraction of WFD pollutants; sample treatment methods for solid matrices; sieving and normalization of sediments; drying and lyophilisation of solid matrices; Soxhlet extraction; supercritical fluid extraction; accelerated solvent extraction; superheated water extraction; microwave extraction; automation in sample treatment; methods for determination of WFD pollutants – summary.

The program of the courses was formally divided into five days. The lectures covering various aspects of environmental monitoring and sampling of environmental pollutants in aquatic environment, accomplished by a halfday trip to river field site to practically demonstrate monitoring techniques discussed in the classroom (Learning course on sampling of environmental matrices) or by a practical demonstration of various sample preparation techniques discussed in the classroom (Learning course on sample treatment of environmental matrices). The speed of the course was intended to be driven by the attendees. The quality of the course was assessed by an anonymous questionnaire filled in by participants at the end of the course.

CONCLUSIONS

Project participants are from strong interdisciplinary fields of expertize. In this way, achieved skills and obtained knowledge will be used for understanding the significance of the monitoring process in the function of the aquatic pollution management from multidimensional and interdisciplinary approach and aspects. This will enable more proficient transfer of knowledge and practical experience to the beneficiaries, which are the staff of public environmental laboratories. Based on the detailed review of the original project proposal, the conclusion was made to increase the number of participants, especially the groups of various levels of knowledge and interests, which are dealing with environmental issues. In future all activities will be oriented towards higher inclusion of people from different institutions, universities, research institutes, as well as private and governmental organizations. The process of dissemination of results gained within NETREL Project is actively included in finalization of Project.

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REFERENCES

Directive 2013/39/EU. Water Framework Directive (WFD), Official Journal of the European Community.

NORMAN (accessed 2 May 2013).http://www.norman-network.net/index_php.php

I. Spanik, M. VojinovićMiloradov, B. Jovančićević, T. Muhić Šarac, B. Kukavica, G.Gajica, J. Radonić: Development of network for education and training of public environmental laboratories within the TEMPUS project Netrel. 14th European Meeting on Environmental Chemistry, Budva, Montenegro, December 04-07, 2013, p. 128.

M. Vojinovic Miloradov, I. Spanik, J. Radonic, M. Turk Sekulic, M. Stosic, D. Milovanovic, N. Senk: Environmental laboratory practice based on up to date education, knowledge and training. Challenges and trends. Abstracts book, SETAC Europe 23rd Annual Meeting, Glasgow, UK, May 12-16, 2013, p. 187.

http://www.netrel.uns.ac.rs/

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DESIGN OF SOFTWARE FOR VALIDATION OF TEHNICAL SOLUTIONS FOR MOBILE PRESS

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ABSTRACT

A design of software is process divided into phases and activities. Each phase has own specific inputs, realizations, output, resources and controls. On other side, software for validation of technical solutions has special features related to object, i.e. mobile vehicle press.In the paper are presented model of software for validation of technical solution for mobile automotive press based on requirements analysis, value based approach, and principles of software engineering.

Key words: *design of software, validation, technical solutions, mobile vehicle press.*

INTORUCTION

Software is specific product with own life cycle. The first phase in life cycle is design.

Input in design of software is requirements analysis. According Young (2004) system life cycle is divided into 15 requirements – related activities: (1) identifying the stakeholders, (2) understanding customers' and users' needs, (3)identifying requirements, (4) clarifying and restating the requirements, (5) analyzing the requirements, (6) defining the requirements to be some for all stakeholders, (7) specifying the requirements, (8) prioritizing the requirements, (9) deriving requirements, (10) partitioning requirements, (11) allocating requirements, (12) tracing requirements, (13) managing requirements, (14) testing and verifying requirements, and (15) validating requirements.

During realization of project TR-35033 "Sustainable development of technologies and equipment for the recycling of motor vehicles" all 15 requirements related activities are performed and it was one input to software design.

The second input to software design is value approach (Setijono and Dahlgard, 2007) which is incorporated in defining the decision trees and rules for decision. For validation of software solutions are emphasized three values: (1) profitability, (2) quality, and (3) productivity. Using AHP approach are defined hierarchy of values, and needed information and preferences of decision makers.

The software solution is realized as three level web application. It is portable for different ICT platforms. The software solution is tested for three different variants of technical solutions of mobile vehicle press.

The research results is yet in initial stage because there are not performed benchmarking with other methods, software solutions, and technical solutions. Real validation bee in practice.

The paper is structured as fallowing.

After introduction in second part is presented basics of requirements analysis. In third part is presented base model of value engineering with using AHP, and in fourth part characteristic of designed software. At the end is presented discussion and concluding remarks.

BASIC OF REQUIREMENTS ANALYSIS

A requirements engineering is well known approach (Young, 2004; Groody, 1993). A requirements analysis covers different types of requirements:
business requirements,
user requirements,
environmental requirements,
unknowable requirements.

In this paper we will concerned on business requirement related to ELV recycling system. According Arsovski *et al.* (2014) total requirement analysis is presented in figure 1.

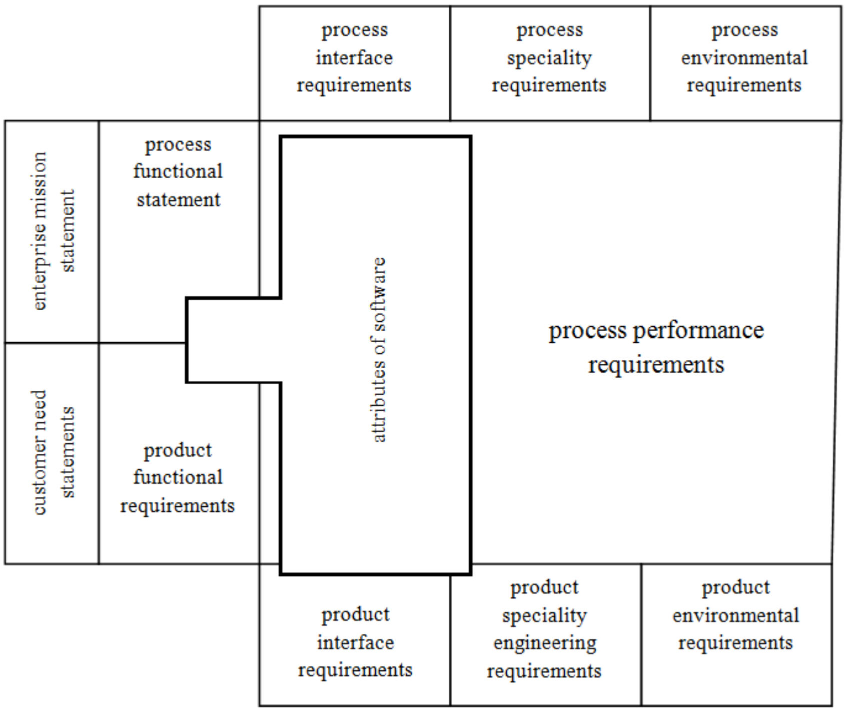

Figure 1. Total requirements taxonomy

Business requirements is gathered through following activities:

- review related historical information about ELV recycling system,
- review related organization polices of ELV recycling centers and agencies,
- identify stakeholders and their needs and requirements related to vehicle press,
- develop a strategy to involve customers and software users through the software development process,
- write project scope,
- develop a requirement plan,
- provide for peer reviewers and inspection of all requirements related work products,
- initiate a project glossary and a project acronym list,
- decide about the life-cycle approach to be used during the project,
- begin tailoring the corporate (or other) requirement process,
- establish a mechanism to evaluate the real requirements for the stated requirements,

- provide requirement-related training sessions for project participants, including customers and users, and for RAs,
- rewrite the high-level system or software requirements as you proceed through the initial steps,
- initiate development of the real requirement based on the stated requirements,
- initiate documenting the rationale for each requirement,
- establish a mechanism to central changes to requirements and new requirements,
- perform V & V planning,
- select the practice, methods, and techniques that will be used to gather the requirements, etc.

There are over 40 requirements elicitation techniques, as interviews, document analysis, brainstorming, requirements workshop, prototyping, use cases, scenarios, modeling, performance and capacity analysis. In our approach we used combination of use cases, modeling, interviews and performance and capacity analysis.

For identified requirements is conducted risk analysis related to:

- stability requirements,
- completeness requirements,
- clarity requirements,
- validity requirements,
- feasibility requirements,
- procedural requirement,
- design performance requirement,
- design testability requirements,
- hardware constraints requirement,
- integration and testing requirements,
- engineering specialties, reliability, security and safety requirements,
- development process formality requirements,
- development process requirements,
- development system requirements.

Because the project is in first phase, we analyzed first four requirements for Serbian ELV recycling organizations.

VALUE BASED VALIDATION OF TECHNICAL SOLUTIONS

Value based approach is very appropriate for validation of technical solutions (Wagner, 2013; Tian, 2005). It is based on different subjective preference of decision makers (Locher, 2008; Cohen and Wawrick, 2008; Iyer, 2009; Holweg, 2004).

A simultaneous rating approach is the simplest method based on subjective preference of various values by the decision maker. For ***ELV*** recycling these values are:

Profitability:	The amount of expected present value of net profit achieved from development or application of desired technology portfolio in next 5 years.
Quality:	Technology related quality characteristics, as waste rate, reliability, mean time to failure, flexibility through faster adaptation on changes etc.
Productivity:	The amount of present worth of added value divided with total costs.

Analytical Hierarchy Process (***AHP***), as second and very popular approach, which starts with set up the hierarchy of values. In figure 2 is presented the hierarchy of values for ***ELV*** technology portfolio. (Tadic *et al.*, 2010; Yu, 2006; Al-Hakim, 2006)

Next steps in ***AHP*** approach are:

- set up a standard scale for pair-wise comparison,
- develop an comparison matrix w for n values in a hierarchy,
- estimate the average preferences of weights of the n value in a hierarchy,
- check matrix consistency,
- revise the pair-wise comparison for consistency and
- distribute the relative preference of a value to values through a sub-hierarchy.

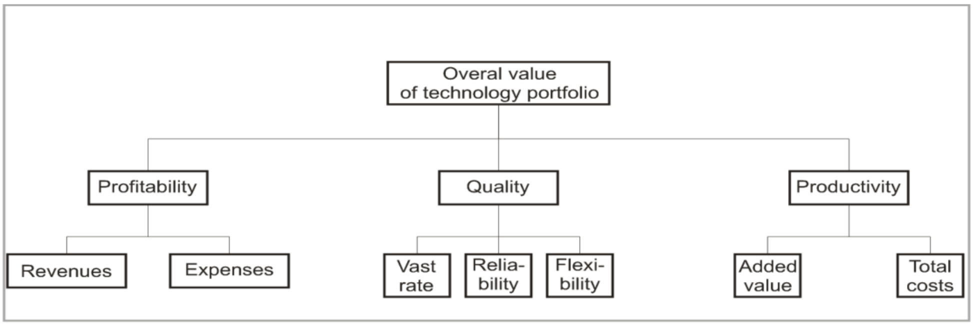

Figure 2. The hierarchy of values for technology portfolio

The third modern method is based on utility theory by *Neuman and Morgensen*. In area of ***ELV*** technology portfolio utility theory is related to money and risk attitude. The risk premium determine prevalent utility function (figure 3) .

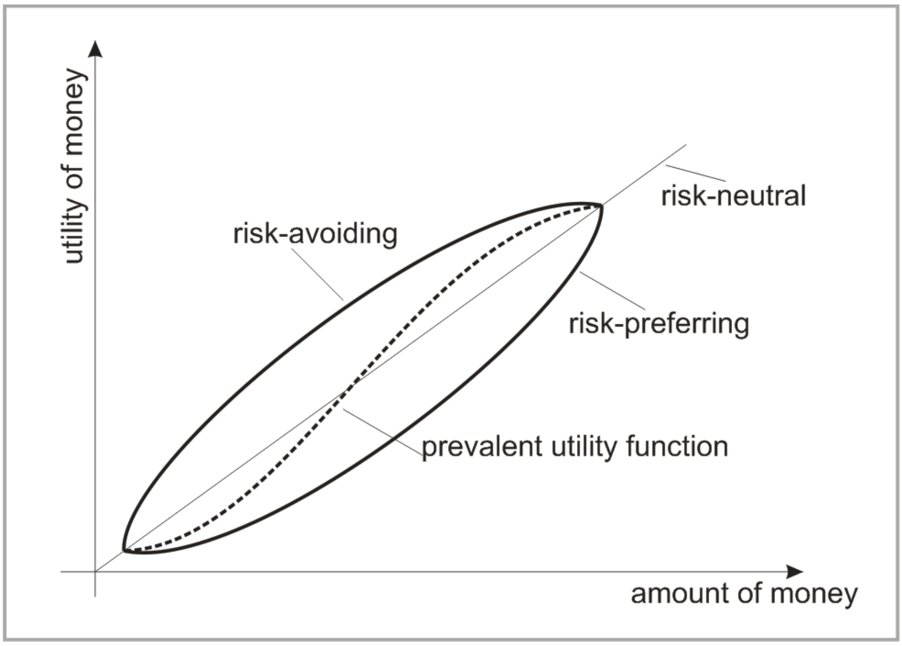

Figure 3. Risk attitude forwards money

These three approaches are related, using other approaches as *Fuzzy*, simulation, etc. (Tadic, et al., 2010; Arsovski et al., 2012).

According to the project management principle and *ISO 10006* for project management (*End-of-Life Vehicle*). Phase of product development process are:

1. overview and opportunity identification/selection,

2. concept generation,
3. concept/project evaluation,
4. development, and
5. launch.

First, is necessary to define technology platform as a set of systems and interfaces that form a common structure. It is basis for all individual technology projects within a family of products (i.e. technical solutions).

Opportunity identification is next step based on six societal trends (table 1).

Table 1: Opportunities

No	Trend	Related Technology Opportunities
1	Just – in Time Life	Exists high pressure for technological solutions
2	Sensing consumers (users)	Ecological and societal specific needs and requests
3	Transparent Self	Available on different places and platforms
4	In search of “enoughness”	Enhancing a quality of life
5	Virtual made real	Connecting with web
6	Co – creation	Cooperation with users in technology development

Next step is to corporate strategic planning of technology portfolio using appropriate matrix *(table 2)*.

Table 2: Degree of innovativeness

Risk		Change in operation/marketing mode		
		name	Some	great
Change in use	Name	Low	Low	Medium
	Some	Low	Medium	High
	Great	Medium	High	Dangerous

Because of that, only 2% of technologies are completely new for new products (table 3).

Table 3: Degree of innovativeness

Technologies	Products			∑ (expected using different references)
	Old	Modified	New	
Old	40	30	30	100
Modified	30	35	35	100
New	30	35	35	100
∑	100	100	100	

After performing the market old analysis of products we find products 70%, modified 25% and 5% new products (present situation). That means, totally new technology in new products has share of 35 x 0.05 = 1.75%, what is extremely low level of new technologies.

At this moment we expect enhancement through new technologies development (Table 4).

Table 4: Strategic technology portfolio model

	Low Market Newness	High Market Newness
Low Product Newness	Improvement of Existing Products (30%)	Additions to existing product lines (30%)
Medium Product Newness	Cost Reduction (15%)	New Product Lines (15%)
High Product Newness	Repositioning (5%)	New – to – the World product

For purpose of development of four families of products with different technologies, we emphasized medium product newness with cost production (15%) and new product lines (15%).

In *table 5* is presented basic data for generic development of mobile vehicle press.

Table 5: Project schedule

No	Phase	Activity completion time (months)			
		Optimistic a	Likely m	Pessimistic b	variance
1	Overview and opportunity identification	5	6	9	2
2	Concept generation	6	8	10	3
3	concept project evaluation	5	6	8	2
4	development	8	10	12	4
5	launch	12	15	18	3

Using *MS* project is simulated project activities and defined expected time for completion of project in amount of 30 months. In figure 4 is presented cumulative project completion cost as a function of project completion time.

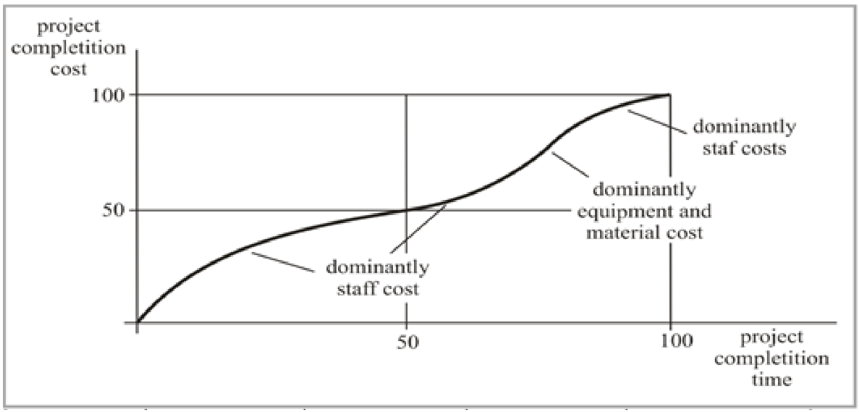

Figure 4. Cost function

Because the project is in phase of concept generation dominantly are staffs cost.

Between project competition costs and project competition time can find relation, as presented in figure 5.

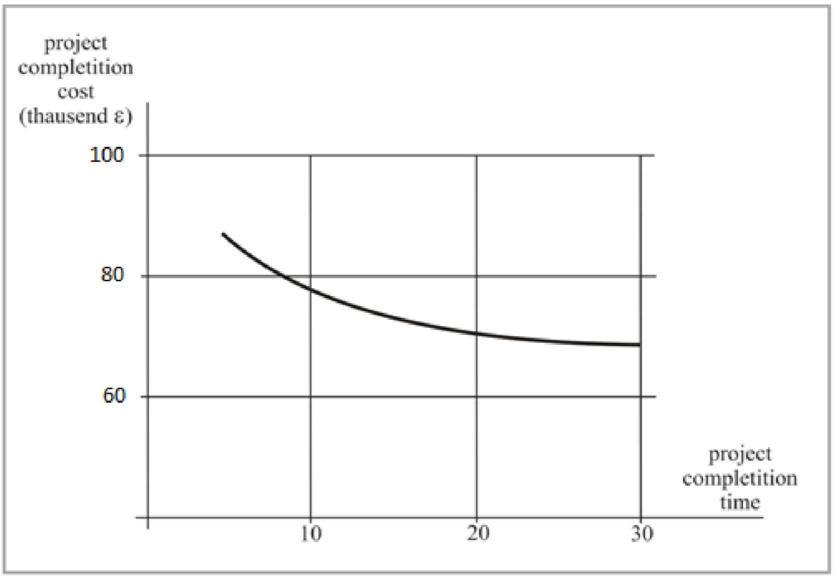

***Figure 5**. Relation between project competition time and costs*

Project team concluded that expected time of 30 months is with minimum of costs. Because of risk of the project, contracted time for project was 36 months.

CHARACTERISTICS OF VALUATION SOFTWARE

Presented mathematical model of valuation software has been described and tested within the case studies on five recycling centers. For the purposes of implementation of case studies software SETSELVR (software for evaluation of technical solutions ELV recycling) was developed which is based on a fuzzy mathematical model.

The basic idea in the realization of fuzzy mathematical model a software solution (Arsovski *et al.*, 2014; Arsovski *et al.*, 2012) was to provide faster and efficient means to determine the optimal solution of ELV recycling system.

During the development of the architecture of software solutions, the set of user requirements had to be met:

- It is necessary that the software is easy to install and maintain,
- the specific requirement is that software have clearly defined structures which is expressed through layers of presentation, application and database, and it is necessary to enable the use of various databases
- it is necessary that the user interface is simple, intuitive and easy to use (user friendly), that is, you do not need special training for binding software, and
- it was recommended a web-based solution so that application may be accessed from remote locations

The software is implemented as a three-layer, web application where access to the database made by the use of abstract layer to realize the software that is portable to different bases and platforms. Software used the PDO extension for formalized connection to databases using a single interface. For the purposes of creating software SETSELVR it was chosen environment with javascript, php and mysql development tools. This environment was chosen because of its openness to different types of databases and the ability to exercise technical and technological independence.

In the process of software design, following requirements were expressed:

- The existence of multiple user types with different set of powers,
- System of software protection has been realized using the RDBMS access and regulating access rights which are divided into two main sets of rights,

- full (administrator) - allows you to create, modify, delete, and read the parameters and setting and creating new patterns,
- user - allows only input parameters and use the results,
- Providing the flexibility of introduction of indicators to determine the optimal technology portfolios, vulnerability and sustainability of ELV recycling system, group A - profitability, group B - quality and C – productivity,
- If necessary, it is a simple and easy way to add the required parameters and elements for the evaluation of these parameters,
- The possibility of saving scenarios and determine the optimal technology portfolios, vulnerability and sustainability of ELV recycling system along with all the entered indicators. This is necessary to enable the monitoring of the condition of the optimal portfolio of technology, vulnerability and sustainability of ELV recycling system in the desired time period,
- The possibility of monitoring and comparing the optimal technological portfolios, vulnerability and sustainability of ELV recycling system between two or more recycling centers. One of the main purposes, of models and software will enable an objective evaluation and comparison of the optimal technological portfolios, vulnerability and sustainability of the system of recycling ELV observed recycling centers,
- Enabling intuitive and clear evaluation times certain system performance, with no apparent need for a high expertise in the respective field.

All of the above requirements, which were the result of the analysis of the needs and specificities of constructed models, built in the SETSELVR software so that has a range of tools that are inherent to all modern software solutions. The user is first enabled to log on as an administrator and user, to be able to exploit a predefined set of rights and functionality.

The difference between the two sets of rights is that administrator can perform the reconfiguration of the system according to the requirements given in the above. In both cases, the user can open a previously stored scenario or to define a new scenario. In the case of defining new scenarios the user enters basic parameters defined indicators capacity for recovery. In general, the user can use the predefined set, the administrator can change the set parameters. In both cases, can be evaluated set of defined indicators to determine the optimal technological portfolios, vulnerability and sustainability of the recycling system group A - profitability, Group B - quality and C – productivity.

Each of the individual indicators can get their self-worth and their self-description. The next steps, regardless of whether it comes to the old or the new scenario corresponding to a set of steps described in the mathematical model and the resulting assessment of ELV recycling system together with the signified strategic directions for its improvement. The system supports basic commands (new-creating new scenarios, open-open the old save-capture, save-as recording under a different name, print-print, close-to-close applications).

After starting a new project, carry out the evaluation of system parameters using the drop-down menu. The user defines the linguistic expressions for determining the weight of indicators and processes that underpin the matrix pairs comparison of processes and sustainability ELV recycling system. Particular indicator selecting is done by the system wizzard that allows easier evaluate certain parameters.

After determining the weight of indicators and processes, the software calculates the steps of the algorithm developed fuzzy model. Results of calculations that are displayed in the user interface include:

- Ranking process in the analyzed company,
- Determining the extent of the belief that process is in second place in the ranking according to indicators of technical solution has worse performance than the designation process, which are the first in the range,

- Ranking process in the analyzed company respecting indicators optimal system of technical solution,
- Determining the overall sustainability of technical solution at the recycling center

The use of the developed software SETSELVR gives managers the opportunity to analyze the situation of recycling centers and make strategic decisions based on data obtained in an exact manner (Burton and White, 2011). It is believed that the decision-making that is less burdened by subjective views of members of management teams can facilitate sustainable development centers for recycling, reduce their vulnerability and enhance technological portfolio.

CONCLUSION

In the paper are described basic approach of valuation of technical solutions. For one special technical object, i.e. mobile vehicle press is developed appropriate software based on comprehensive ICT. A lot of technical variants is analyzed using the developed software and using value based approach is chosen the optimal solution for different input parameters (profitability, quality, and productivity). The software is yet in testing phase related to objects, verification vs validation, timeline, defect detection, testing environment, ICT tools, stakeholders needs and roles, and testers.

In next period we expect to pass all needed verification activities and to make broader the software in modular sense to cover other technical objects used in ELV recycling.

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REFERENCES

Al-Hakim, L., (2006). *Information quality management: theory and applications*, Idea group publishing, London

Arsovski, S., Pavlović, M., & Lazić M. (2012). An approach to monitor and change the technology portfolio of ELV recycling, *6th International Quality Conference June 08th 2012 Center for Quality, Faculty of Engineering, University of Kragujevac, 2012*, 25-30

Arsovski, S., Pavlovic, M., & Puskaric, H. (2014). Software Development For Design Of Optimal Portfolio Of ELV Recycling System, *8th International Quality Conference, Kragujevac, Serbia, May 23th 2014.*, 501-506, ISBN 978-86-6335-004-5

Arsovski, Z., Arsovski, S., Stefanovic, M., & Lula P. (2012). Value Based Recycling of ELV, *7th International Conference ICQME 2012, University of Montenegro, Faculty of Mechanical Engineering, Center for Quality, Tivat, Montenegro, Proceedings, September 19-21, 2012* 105-116, COBISS.CG-ID 20844560, ISBN 978-9940-527-28-0,

Bruton, G., & White, M. (2011). *Strategic Management of Technology and Innovation*, South-Western, Cengage Learning, ISBN 13: 978-0-538-48173-1

Cohen, B., & Warwick, M. (2008). *Value-driven Business: how to change the world, make money, and have fun*, Berett-Koehler Publishers. Inc., San Francisco.

Groody, J. (1993). *System requirements analysis*, McGrow Hill, New York.

Holweg, M., & Pil, F. (2004). *The Second Century: Reconnecting Customer and Value Chain through Build-to-Order*, The MIT Press, Cambrdge, Massachusetts

Iyer, S. (2009). *Managing for Value*, New Age International (p) Limited, Publishers, New Delhi.

Locher, D. (2008). *Value Stream Mapping for Lean Development: A How - to Guide for Streamling Time to Market*, CRC Press, A Productivity Press Book.

Setijono, D., & Dahlgard, J. (2007). Customer Value as a key performance indicator (KPI) and key improvement indicator (KII), Measuring Business excellence, 11(2), 44-61,

Tadić D., Arsovski, Z., Stefanović, M., & Aleksić, A. (2010). *A fuzzy AHP and topsis for ELV dismantling selection*, International Journal for Quality Research, 4(2), 139-144

Tadic, D., Arsovski, A., Stefanovic, M., & Aleksic, A., (2010). *A fuzzy AHP and TOPSIS for ELV dismantling*, International Journal for Quality Research, 4(2)
Tian, J. (2005). *Software product quality engineering*, IEEE computer Society Publications
Wagner, S. (2013). *Software product quality control*, Springer.
Young, R. (2004). The requirements engineering handbook”, Artech House, Boston.
Yu, O. (2006). Technology portfolio planning and management: practice concepts and tools, Springer

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LOGICAL PROGRAMMING IN ECOLOGY

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ABSTRACT

Logical programming and software tools from artificial intelligence area could help scientists in thinking and reasoning on huge amount of data. Our paper shows how Prolog as well known language from artificial intelligence area can be used for analyzing air pollution data. This data for air pollutant concentrations were collected from Internet and transformed in a form suitable for processing in Prolog system. A set of reasoning rules for analyzing air pollutants concentration were defined in order to discover when concentrations of pollutants are greater than it is allowed with standards or to calculate average values of air pollutants. At the end the results of making goals in Prolog are presented.

Key words: *Logical programming, Prolog, ecology.*

INTRODUCTION

Scientists and researchers in the field of ecology have a variety of software tools for collecting and analyzing data, but relatively small number of tools that enable reasoning. The ecological data and knowledge bases are already extremely large and growing continually. This growing knowledge and huge amount of data challenges researchers to develop new and more efficient ways of organizing, processing and analyzing knowledge. Results, methods and tools from artificial intelligence area may provide computerized tools, methods and techniques that aid ecologists in thinking and reasoning to solve real problems (Zhu et al., 1996). Expert systems are a well-known area of the artificial intelligence that has in recent year’s appliance in ecology. Expert systems as a decision support tool, database, and a geographical information system as advanced information technologies were combined for air quality modeling found in (Karatzas et al., 2000). The use of this tools and methods was focused on emission reduction scenario formation and evaluation. An expert system for evaluating the ecological quality of streams and rivers is presented in (Scardi et al., 2008). The paper (Oprea et al., 2010) presents an expert system developed for environmental diagnosis within three modules: for air pollution analysis and dispersion assessments, for surface water pollution analysis, and for soil erosion risk assessments. Fuzzy expert systems and their applications can be found in ecological planning done by (Zhu et al., 1996) or for power system diagnosis (Cho et al., 1997). The aim of the expert system presented in (Hatzikos et al., 2007) is to help in the decision-making process in the battle against pollution of the aquatic environment, which is vital for public health and the economy. This fuzzy expert system monitors sea water quality and pollution through a sensor network. Knowledge-based systems and their applications as another part of artificial intelligence were used in ecology by (Rodionov et aj., 1999) for climate forecasting, for environmental protectio (Gomolka et al., 2000), and for wastewater treatment (Baeza et al., 2000). In paper (Neagu et al., 2002) authors propose a neuro-fuzzy knowledge-based system, an efficient decision support system that could function as a predictive tool in an air quality operational center.

LOGICAL PROGRAMMING WITH PROLOG

Logical programing was done with SWI-Prolog, a free version of Prolog that was developed at University of Amsterdam as an open Prolog environment (SWI-Prolog, 2014; Wielemaker, 2012). The most popular software in the field of logical programing and artificial intelligence is Prolog and the author was Alan Kalmero. Name of Prolog is an abbreviation of the English word "PRO (gramming) and LOG (ic)," which means that it is a programming language that is primarily intended logical programming. Prolog is based on the first order predicate calculus. The search solutions in Prolog is based on Robinson's resolution rule for automated theorem proving from 1965, with the modification of the principle of Horne's clauses. These are the clauses that contains at least one positive literal (without logical negation). This modification was made because of the lack of working with literals, and a method of performing and reading the evidence is extremely unnatural to man, which is far closer working with the implication form of sentences. (Hotomski, 2004)

SWI-Prolog version is distributed freely through the Internet, and it has the possibility to interactively edit and reload a program even while the program is running, it supports the commonly found set of compiler warnings: syntax errors, singleton variables, predicate redefinition, system predicate redefinition and discontinuous predicates, it enables quick tests on the completeness of the loaded program, predicates are categorized as exported, called and not called, the Prolog Navigator provides a hierarchical overview of a project directory and its Prolog files.

In the Prolog, there are three types of sentences: facts, rules and goals. The rules are formulas containing implication, where the conclusion is a positive literal, and assumptions literals with or without negation. Implication form of rules is transformed into clauses form where the conclusion is the head of rules and assumptions are body clause. The fact is, according to the present clause, empty body, which consists only of the head of the rule. The facts include data from real world and because of that we collected data about air pollution that has been measured by monitoring station.

Air pollution monitoring is carried in order to obtain reliable and good quality data on environment. It provides raw measurements of air pollutant concentrations and with appropriate analysis and interpretation these measurements can be transformed into useful information about air quality. The data measurement was carried out by monitoring with automatic measuring station in city of Zrenjanin (Republic of Serbia), in urban zone, on 75m of attitude. This station has a code RS10005 and it is designed to monitor pollution levels with referent method of measuring in residential and commercial zone that comes primarily from traffic and other sources. Monitoring data are stored and published at Internet portal of Provincial Secretariat for Protection of Environment and Sustainable Development of Vojvodina region, in Serbia. We use a public access of these data from location with the following url: http://www.eko.vojvodina.gov.rs. This data shows values for the following components: ozone, oxides of nitrogen - nitrogen monoxide, nitrogen dioxide, sulfur dioxide, carbon monoxide, particulate matter (PM_{10}, $PM_{2.5}$), hydrogen sulfide, benzene, toluene, o-xylene and ethyl benzene. Creating facts as an internal base of available air monitoring data that are required for processing in Prolog system requires a new predicate that we called “airdata”. This predicate has thirteen arguments, in a following form:

```
airdata(S,D,H,X1,X2,X3,X4,X5,X6,X7,X8,X9,X10).
```

where:

- S is station code number,
- D is date of the measurement,
- H is time of the measurement,
- X1 is sulfur-dioxide concentration (SO_2),
- X2 is hydrogen sulfide concentration (H_2S),
- X3 is ozone concentration (O_3),
- X4 is benzene concentration (B),
- X5 is toluene concentration (T),

- X6 is ethyl benzene concentration (E),
- X7 is particulate matter concentration (MP_X),
- X8 is o-xylene concentration (O_X),
- X9 is particulate matter concentration (PM_{10}),
- X10 is a concentration of carbon monoxide (CO).

Collected data about air pollution that has been measured by monitoring station was transformed into more than 700 facts for a month of May in 2014, in Zrenjanin urban region street. A part of these facts are shown in a list presented below with measured values from 0 am to 12 am in one day. Values for nitrogen dioxide are not present in this list of arguments, because the station does not measure concentrations for this pollutant in observed period.

```
airdata(‘RS10005’,2014-05-01,00:00:00,3.83,1.72,19.03,3.39,3.98,0,1.07,1.42,2.92,0.58).
airdata(‘RS10005’,2014-05-01,01:00:00,4.02,1.37,29.48,2.9,3.94,0.75,2.33,1.16,1.68,0.37).
airdata(‘RS10005’,2014-05-01,02:00:00,3.54,1.15,34.84,0.97,1.12,0.86,0.82,0.59,3.44,0.25).
airdata(‘RS10005’,2014-05-01,03:00:00,3.82,1.44,30.53,1.37,1.69,0,1.07,1.36,2.63,0.34).
airdata(‘RS10005’,2014-05-01,04:00:00,4.07,1.55,18.54,1.85,2.72,0.72,1.19,3.91,1.11,0.45).
airdata(‘RS10005’,2014-05-01,05:00:00,3.73,1.17,28.09,1.36,1.53,0,0.77,1.89,2.4,0.34).
airdata(‘RS10005’,2014-05-01,06:00:00,3.85,1.46,22.59,1.28,0.92,0,0,0,3.31,0.44).
airdata(‘RS10005’,2014-05-01,07:00:00,3.86,1.18,38.89,1.39,1.29,0.73,1.76,0,4.54,0.33).
airdata(‘RS10005’,2014-05-01,08:00:00,3.76,0.95,61.21,0.8,0.48,0,0,0,1.33,0.4).
airdata(‘RS10005’,2014-05-01,09:00:00,4.02,0.98,82.39,0.88,0.97,0,0,0,1.14,0.52).
airdata(‘RS10005’,2014-05-01,10:00:00,4.4,1.1,101.91,1.08,1.33,0.51,0.78,0,1.14,0.54).
airdata(‘RS10005’,2014-05-01,11:00:00,4.16,1.18,115.53,0.7,2.28,0.51,1.34,0,3.12,0.44).
airdata(‘RS10005’,2014-05-01,12:00:00,3.32,0.97,110.26,1.13,0,0,0,0,1.62,0.5).
```

Creating reasoning rules was based on regulations on limit values and measuring methods of emissions, criteria for creation of measuring points and data records are defined at Legal Clinic for the Protection of the Environment, Faculty of Law, University of Novi Sad. This regulation allows the following maximum concentrations of air pollutants in urban region (Regulations, 2014):

- PM_{10} - for one hour 50 µg/m3 and for three hours 150 µg/m3,
- NO_2 - for one hour 150 µg/m3 and for one day 50 µg/m3,
- O_3 - for one hour 150 µg/m3 and for one day 85 µg/m3,
- CO - for one hour 10 mg/m3 and for one day 5 mg/m3,
- SO_2 - for one hour 350 µg/m3 and for one day 150 µg/m3,
- T - for one hour 7,5 g/m3,
- B - for one hour 5 g/m3.

Reasoning rules are created from Serbian regulations for air pollutants maximum allowed concentrations (Regulations, 2014). It has been created four reasoning rules for every air pollutant. List of rules are presented only for ground ozone.

Reasoning rule 1 – Determinates and displays when the concentration of air pollutant was greater than it is allowed by regulative (Regulations, 2014):

```
pollutionO3(DAY,HOUR,O3):-airdata(_,DAY,HOUR,_,_,O3,_,_,_,_,_,_,_),O3>150.
```

Reasoning rule 2 – Calculating the average concentration of air pollutant in whole observed period:

```
avg O3(AV):-findall(O3,airdata(_,_,_,_,_,O3,_,_,_,_,_,_,_),LP),
sumlist(LP,SP),length(LP,L),AV is SP/L.
```

Reasoning rule 3 – Calculating the average concentration of air pollutant in one day:

```
avgdayO3(AV,DAY):-findall(O3,airdata(_,DAY,_,_,_,O3,_,_,_,_,_,_,_),LP),
sumlist(LP,SP),length(LP,L),AV is SP/L.
```

Reasoning rule 4 - Calculating the average concentration of air pollutant in one hour from whole period:

```
avghourO3(AV,HOUR):-findall(O3,airdata(_,_,HOUR,_,_,O3,_,_,_,_,_,_,_),LP),
sumlist(LP,SP),length(LP,L),AV is SP/L.
```

where:

- AV, HOUR, DAY, O3, LP, SP, and L are variables,
- findall, sumlist, length, and airdata are predicates.

Goals with only one literal are called queries. We have done four kinds of queries in Prolog based on previously presented rules. These rules are different in used arguments and variables that contain values of measured air pollutant.

First example of query for rule 1 – “When were the concentrations of carbon monoxide higher than it is allowed with standards?”

```
?- pollutionCO(DAY,HOUR,CO).
false.
```

Answer for this query is “false”. So we can conclude that the concentration of this pollutant was not high in searched period because all measured values for this pollutant were smaller from the given value in the rule.

Second examples of query for rule 1 – “When were the concentrations of benzene higher than it is allowed with standards?”

```
?- pollutionB(DAY,HOUR,B).

DAY = 2014 - 5 - 6
HOUR = 6 : 0 : 0
B = 5.45 ,

DAY = 2014 - 5 - 9
HOUR = 22 : 0 : 0
B = 5.38 ,

DAY = 2014 - 5 - 10
HOUR = 21 : 0 : 0
B = 6.34 ,

DAY = 2014 - 5 - 10
HOUR = 22 : 0 : 0
B = 10.41 ,

DAY = 2014 - 5 - 10
HOUR = 23 : 0 : 0
B = 12.09 ,

DAY = 2014 - 5 - 11
HOUR = 0 : 0 : 0
B = 5.62 ,

DAY = 2014 - 5 - 13
HOUR = 22 : 0 : 0
B = 5.69 ,

DAY = 2014 - 5 - 18
HOUR = 21 : 0 : 0
B = 6.97 ,

DAY = 2014 - 5 - 18
```

```
HOUR = 22 : 0 : 0
B = 6.49 ,
```

Answer for the second query was created with multiple use of the unification process. Prolog listed all values for variables defined in query that displays day, hour and concentration for this pollutant when it was greater from the given value in the rule.

Third example of query is for rule 2 – “What is average concentration of ground ozone in whole period?”

```
?- avgO3(AV).
AV = 89.95913888888889.
```

Fourth example of query is for rule 3 – “What was the average concentration of ground ozone for May 1st in 2014?”

```
?- avgdayO3(AV,'2014-05-01').
AV = 73.99624999999999.
```

Fifth example of query is for rule 4 – “What is average concentration of ground ozone in 15 hour for all days in observed period?”

```
?- avghourO3(AV,'15-00-00').
AV = 130.396.
```

RESULTS

Average values for SO_2, CO, O_3, PM_{10}, B, H_2S and T concentrations per day, calculated with reasoning rule 3 are presented in Table 1.

Average concentrations for air pollutants in May 2014 calculated with reasoning rule 2 are: for sulfur dioxide 5.44 µg/m3, hydrogen sulfide 0.96 µg/m3, particulate matter 21.76 µg/m3, carbon monoxide 0.48 mg/m3, ozone 89.96 µg/m3, toluene 1.94 g/m3 and for benzene 1.39 g/m3.

Average values for SO_2, CO, O_3, PM_{10}, and T concentrations for every weekday are calculated from data presented in Table 1 and shown on Figure 1 and Figure 2. It can be concluded that the average values of this six air pollutants are not greater than it is allowed with standards in Republic of Serbia (Regulations, 2014).

Table 1: Average concentrations of air pollutants

	SO_2	**CO**	**O3**	**PM_{10}**	**B**	**T**	**H_2S**
00:00:00	4.57	0.47	67.14	31.73	1.52	2.15	1.17
01:00:00	4.17	0.40	69.72	27.38	1.33	1.93	1.06
02:00:00	4.21	0.34	71.11	13.24	1.06	1.37	1.00
03:00:00	4.49	0.31	69.43	11.55	0.90	1.16	0.95
04:00:00	5.05	0.34	64.17	13.13	0.97	1.12	1.02
05:00:00	5.25	0.41	55.98	16.66	1.07	1.19	1.02
06:00:00	5.09	0.49	60.03	32.23	1.30	1.59	1.01
07:00:00	5.73	0.54	66.83	33.25	1.54	2.20	0.99
08:00:00	5.51	0.54	76.08	21.67	1.60	2.11	0.97
09:00:00	6.29	0.54	86.89	24.89	1.59	2.17	0.99
10:00:00	6.74	0.54	98.31	21.35	1.65	2.38	0.97
11:00:00	6.52	0.51	109.54	19.30	1.57	2.31	0.88
12:00:00	6.44	0.49	118.16	29.97	1.23	1.57	0.88

13:00:00	6.68	0.49	121.58	29.65	1.19	1.66	0.87
14:00:00	6.86	0.50	126.79	17.79	1.12	1.55	0.87
15:00:00	6.43	0.48	130.40	20.04	1.09	1.56	0.87
16:00:00	6.28	0.46	128.78	15.34	1.01	1.34	0.88
17:00:00	6.15	0.46	127.45	14.81	0.99	1.42	0.85
18:00:00	6.02	0.50	117.89	23.72	1.11	1.59	0.87
19:00:00	5.51	0.53	100.33	23.84	1.43	2.09	0.87
20:00:00	4.93	0.54	82.96	13.77	1.69	2.50	0.91
21:00:00	4.69	0.62	68.42	18.41	2.18	3.30	1.08
22:00:00	4.51	0.59	68.80	24.32	2.33	3.47	1.10
23:00:00	4.51	0.47	72.24	24.02	1.87	2.78	1.00
Average:	5.44	0.48	89.96	21.76	1.39	1.94	0.96

Results of executing queries based on reasoning rule 1 shows concentrations of air pollutants when the measured values were greater than it is allowed by regulative: for ozone it was 47 hours when concentrations were greater than 150 µg/m3, for toluene 14 hours > 7.5 g/m3, for benzene 9 hours > 5 g/m3, and for PM_{10} 75 hours > 50 µg/m3. For CO and SO_2 it hasn’t been found greater concentrations of pollutants.

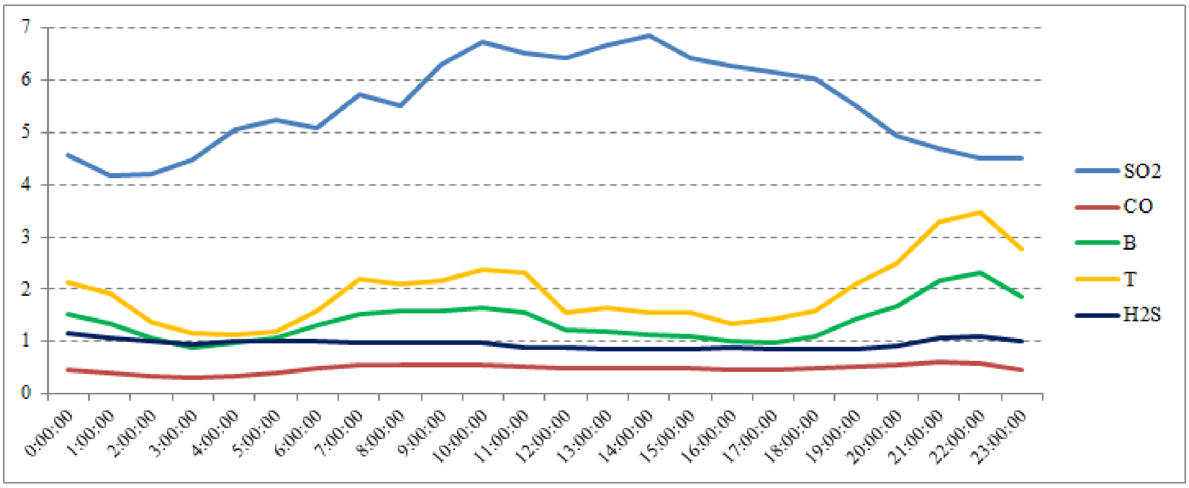

Figure 1. Average concentrations for sulfur dioxide, carbon monoxide, benzene, toluene, and hydrogen sulfide

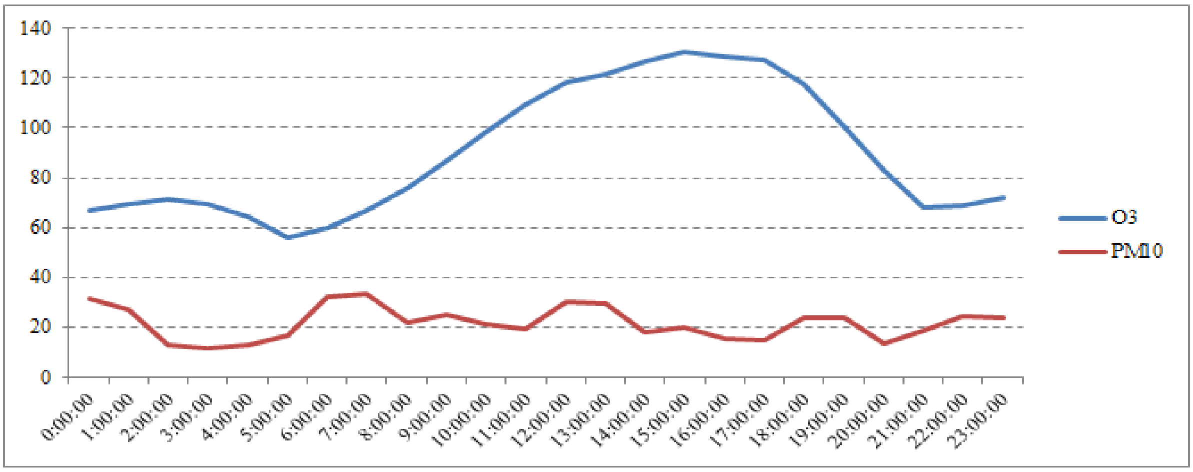

Figure 2. Average concentrations for ground ozone and particular matter

CONCLUSION

Results of executing program with ecological data in Prolog shows that the average concentrations for air pollutants in Zrenjanin were not greater than it is recommended. With reasoning rules we discovered that in some hours in May 2014 ground ozone, PM_{10}, toluene and benzene concentrations were greater than it is allowed. Further development of the high performance computing and knowledge management potentials in ecology associated with artificial intelligence techniques is desired in environmental informatics. Our paper shows that the program with a bit of intelligence knowledge, like Prolog program could help ecologists in working and analyzing specific data.

ACKNOWLEDGEMENT

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REFERENCES

Zhu, A.X., Band, L.E., Dutton, B., & Nimlos, T.J. (1996). Automated soil inference under fuzzy logic, *Ecological Modeling*, Vol. 90, pp. 123–145.

Karatzas, K., & Moussiopoulos, M. (2000). Development and use of integrated air quality management tools in urban areas with the aid of environmental telematics, *Environmental Monitoring and Assessment*, Vol. 65, pp. 451–458.

Scardi, M., Cataudella, S., Di Dato, P., Fresi, E., & Tancioni, L. (2008). An expert system based on fish assemblages for evaluating the ecological quality of streams and rivers, *Ecological Informatics*, Vol. 3, pp. 55–63.

Oprea, M., & Dunea, D. (2010). SBC-MEDIU: A multi-expert system for environmental diagnosis, *Environmental Engineering and Management Journal*, Vol. 9, no. 2, 2010, pp. 205-213.

Cho, H.J., & Park, J.K. (1997). An expert system for fault sectiondiagnosis of power systems using fuzzy relations”, *IEEE Transactions on Power Systems*, Vol. 12, pp. 342–348.

Hatzikos, E.V., & Bassiliades, N., Asmanis, L., & Vlahavas, I. (2007). Monitoring water quality through a telematic sensor network and a fuzzy expert system, *Expert Systems*, Vol. 24, no. 3, pp. 143-161.

Rodionov, S.N., & Martin, J.H. (1999). An expert system-based approach to prediction of year-to-year climatic variations in the north atlantic region, *International Journal of Climatology*, Vol. 19, pp. 951–974.

Gomolka, Z., & Orlowski, C. (2000). Knowledge management in creating hybrid systems for environmental protection”, *Cybernetics and Systems: An International Journal*, Vol. 31, pp. 507–529.

Baeza, J.A., & Ferreira, E.C., & Laufuente, J. (2000). Knowledge-based supervision and control of wastewater treatment plant: a real-time implementation”, *Water Science and Technology*, Vol. 41, pp. 129–137.

Neagu, C.D., Avouris, N., Kalapanidas, E. & Palade, V. (2002). Neural and neuro-fuzzy integration in a knowledge-based system for air quality prediction”, *Applied Intelligence*, Vol. 17, pp.141–169.

SWI-Prolog: history and focus for the future, Jan Wielemaker Web and Media group, VU University Amsterdam, http://www.cs.nmsu.edu/ALP/wp-content/uploads/2012/06/ swi25.pdf (18.7.2014)

Wielemaker, J. (2012). An overview of the SWI-Prolog programming environment, *Web and Media group, VU University Amsterdam*, http://www.cs.nmsu.edu/ALP/wp-content/uploads/2012/06/swi25.pdf (18.7.2014)

Hotomski, P. (2004). Artificial intelligence (book on Serbian), *University of Novi Sad, Technical faculty “Mihajlo Pupin”*, Zrenjanin, Serbia, 2004.

Regulations on limit values and measuring methods of emissions, criteria for creation of measuring points and data records, Faculty of Law, University of Novi Sad, Legal Clinic for the Protection of the Environment, www.ekologija.pf.nas.ac.rs (1.7.2014)

APPENDIX

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IMPACTS OF SOME ENVIRONMENTAL FACTORS ON THE N_2O AND CO_2 PRODUCTION OF CULTIVATED SOIL IN CLOSED MICROCOSM EXPERIMENTAL SYSTEM

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ABSTRACT

Because of increasing the soil pollution with heavy metal due to the human activities, there was a reducing in the soil quality and soil fertility. That is the reason for the following task. In closed microcosm containing 200 g agricultural brown forest soil (Keszthely, Hungary) of 60% water holding capacity and pH(KCl) 7.55. The experiment was conducted to estimate the impacts of different concentrations of Cd and Pb ions on the emission of N_2O and CO_2 at incubation temperatures (15 and 37°C). The CO_2 and N_2O concentrations were analysed by gas chromatographic methods. The results indicated that N_2O gas production increased up to the 5th day of incubation and then the amount of the gas production gradually reduced. The production of CO_2 increased but not significantly by the increasing time of incubation up to the 15th day and then it decreased gradually. The amount of gas emission in Pb- contaminated soil samples was more than that of Cd-contaminated soil samples. The results indicated that the trace gases more emitted at 37°C than at 15°C, and the high concentration of Pb more inhibited the emission process than Cd concentration. The results demonstrated that the production of gases were significantly depending on the soil C:N ratio.

Keywords: *N_2O, and CO_2 emission; heavy metal; microcosm; temperature; soil contamination.*

INTRODUCTION

Nitrification is the oxidation of NH_4^+ to NO_3^-, denitrification is the anaerobic reduction of NO_3^- to gaseous forms of N. Consequently, different nitrogen (N) forms can have different effects on soil N transformations and N_2O emissions, as they kinds of soil microorganisms. Because of increasing the soil pollution with heavy metal due to the human activities, there was a reducing in the soil quality and soil fertility. N_2O is involved in global warming and the destruction of stratospheric ozone (Bouwman, 1990). Heavy metals known to influence the activity of soil microbial communities, affecting the soil respiration, soil biomass, N-mineralization and nitrification (Giller et al., 1998). The application of fertilisers is essential to optimal nutrient supply of plants in agriculture but the extended use of N-fertilisers induce problems in soil-plants-animals/people food chain. The NO_3 leaching into surface and groundwater and accumulation in plants has harmful human effects. The negative impact of overdose also causes agricultural problems e.g. overturning the balance between pests and their parasites in soil ecosystem (Nádasy & Nádasy, 2006).

Studies on denitrification and the production of nitrous oxide (N_2O) have indicated that denitrification might inhibited by heavy metals (Sakadevan et al. 1999, Holtan-Hartwig et al., 2002). Denitrification enables soil to reduce the harm of nitrate leaching (Szili-Kovács & Németh, 2006), but a higher denitrification activity produces rising N_2O and CO_2 emission which contributes to global climate change. Therefore suitable agricultural technologies e.g. conservation technologies (Gyuricza et al., 2005) should developed. In the future, the use of methods resulting in reduced CO_2 emission may also have an important economic advantage when the CO_2 emission rights become saleable and purchasable (Béres, 2005). Although the overall impact of most parameters affecting these processes is largely known, the fine details, for example how the heavy metals affects denitrification, nitrification and emission rates are still insufficiently understood. It is involved in ozone decomposition in the stratosphere and exerts a significant greenhouse effect with a global warming potential 320 relative to CO_2 (Kester et al., 1996). Ambus et al. (2006) investigated the quantitative and qualitative relationships between N-cycling and N_2O production in European forests in order to evaluate the importance of nitrification and denitrification for N_2O production. Increased nitrification in response to accelerated N inputs predicted for forest ecosystems in Europe may thus lead to increased greenhouse gas emissions from forest ecosystems. N_2O mainly produced by nitrification, denitrification and nitrifier denitrification (Wrage et al., 2001, 2004). Also, other biological processes involved in the N_2O emission. Each of these processes, and N_2O emission might affected by heavy metals. Little information is currently available concerning the impact of increased heavy metal concentrations on the generation of trace gases (Sakadevan et al., 1999; Holtan et al., 2002).

Vásquez-Murrieta et al. (2006) mentioned that there was a significant negative correlation between production rates of CO_2 and concentrations of Pb. The fertiliser and manure substituting employment of sewage sludge and compost amended sewage sludge means new opportunities in agriculture. Soil temperature depends on location, climate, weather, soil type, soil cover and soil bioactivity. Low rates of denitrification have been reported at -2°C (Dorland & Beauchamp, 1991) and -4°C (Malhi et al., 1990), but higher temperatures > 5°C, are usually required for a significant denitrification rate (Aulakh et al., 1983; Benckiser et al., 1986). The effect of increasing soil temperature on denitrification rate has been investigated in many laboratory studies. The reported differences reflect to some extent bacterial adaption to local conditions (Malhi et al., 1990). At temperatures > 50°C chemodenitrification may be the major mechanism (Keeney et al., 1979). Denitrification stops at temperatures of 75 to 85°C (Keeney et al., 1979). However, such high temperatures are of little practical interest as soil temperatures will mostly be below 60°C, at least where water is present. The temperature increases, the N_2O/N_2 ratio declines. This inverse relationship has been demonstrated by several authors in laboratory incubations of soil (Keeney et al., 1979). The optimum temperature range for nitrification in soil types usually between 25 and 35°C (Bock et al., 1986; Haynes 1986). However, it seems that indigenous nitrifiers have temperature optima adapted to their climatic regions.

Heterotrophic nitrification can probably occur at even higher temperatures (Haynes, 1986). The aims of this research were: (1) to evaluate the effect of different concentrations of Cd or Pb on trace gases emissions; (2) to evaluate differences in the trace gases emissions from heavy metals contaminated soil samples incubated at low and high temperatures. (Rabenarivo et al., 2014). Studies how such agricultural practices affect greenhouse-gas emissions from a loamy Ferralsol previously used as a pasture. We conducted an experiment under controlled laboratory conditions combining cattle manure, crop residues (rice straw), and mineral fertilizers (urea plus NPK or di-NH_4-phosphate) to mimic on-field inputs and examined soil CO_2 and N_2O emissions during a 28-d incubation at low and high water-filled pore space (40% and 90% WFPS). Emissions of N_2O from the control soil, i.e., soil receiving no input, were extremely small (< 5 ng N_2O-N (g soil)$^{-1}$ h^{-1}) even under anaerobic conditions. Soil moisture did not affect the order of magnitude of CO_2 emissions while N_2O fluxes were up to 46 times larger at high soil WFPS, indicating the potential influence of denitrification under these conditions. Both CO_2 and N_2O emissions were affected by treatments, incubation time, and their interactions. Crop-residue application resulted in larger fluxes of CO_2 but reduced N_2O emissions probably due to N immobilization.

MATERIAL AND METHODS

The microcosm experiment was conducted in glass vessels covered gas tightly by silicone septa. 200 g homogenised (< 2 mm) slightly alkaline solonchak arable land soil samples of low humus content were placed into the vessels of 1200 cm^3.

The most important physical and chemical properties of the soil are the next: pH (KCl): 7.55, total salt content: 0.054%, humus: 1.48%, C total organic: 1.08 %, N – total: 0.08 %, NH_4^+-N: 0.53mg (100g)$^{-1}$,

NO_3^-—N: 0.18mg $(100g)^{-1}$, K_2O (AL): 136 mg (100g) $^{-1}$, P_2O_5 (AL*): 130mg (100g) $^{-1}$, density: 2.45g cm^{-3} and C/N ratio: 13.15.

The soil samples were treated by the addition of plant residue, manure and inorganic N-source singly or in combination form as well as different doses of heavy metal (Cd, Pb) $Pb(CH_3COO)_2.3H_2O$: 40,80 and 160 mg Pb kg^{-1} soil and $CdCl_2.2.5H_2O$: 6, 12 and 24mg Cd kg^{-1} soil salts at 60 % of water holding capacity. The treatments were applied in three replications.

The vessels were incubated in a laboratory thermostat at 37 °C temperatures during 30 days. The most important features of the treatments applied in the experiment performed in 2006 are summarised in Table 1.

Table 1: The most important features of the treatments applied in the different experiments.

Label of treatments	Meaning of treatments	Treatments Additives (doses)
C	Control soil	–
C+N1	Control soil amended with KNO_3	• KNO_3: 500 kg N ha^{-1}
C+N2	Control soil amended with NH_4NO_3	• NH_4NO_3: 500 kg N ha^{-1}
R	Control soil amended with plant residue	• Maize straw: 0.5 t ha^{-1}
R+N1	Control soil, plant residue and KNO_3	• KNO_3: 500 kg N ha^{-1} • Maize straw: 0.5 t ha^{-1}
R+N2	Control soil, plant residue and NH_4NO_3	• NH_4NO_3: kg N ha^{-1} • Maize straw: 0.5 t ha^{-1}
M	Control soil amended with manure	• Manure: 52 t ha^{-1}
M+N1	Control soil, manure and KNO_3	• KNO_3: 500 kg N ha^{-1} • Manure: 52 t ha^{-1}
M+N2	Control soil, manure and NH_4NO_3	• NH_4NO_3: kg N ha^{-1} • Manure: 52 t ha^{-1}
Pb	Control soil amended with Pb-acetate	• $Pb(CH_3COO)_2.3H_2O$: 80 mg Pb kg^{-1} soil
Cd	Control soil amended with Cd-cloride	• $CdCl_2.2.5H_2O$: 12 mg Cd kg^{-1} soil

During the experiments, N_2O and CO_2 concentrations of gas samples taken from the headspace of each vessel were determined regularly by gas chromatographic method. 250 – 250 □l gas sample was taken by gas tight Hamilton syringes and was injected from each vessel to the HP 5890 gas chromatograph. Packed columns (Porapak Q) were used to separate the different constituents of gas samples. Electron Capture Detector (ECD) and Thermal Conductivity Detector (TCD) detected N_2O and CO_2 concentrations, respectively. Each gas content was analysed three times per day whenever measurements were carried out using external standard and one point linear calibration. The soil samples experiments were conducted with cultivated brown forest soil samples collected from Keszthely, Hungary. The soil samples were collected from the upper 200-250 mm layer after removing the top 20-30 mm from a sample site. Soil samples were dried for one week and Milling soil grinding to determine the effect of temperature and moisture and addition of heavy metals (Cd, Pb) and N_2O, CO_2 productions.

The physical and chemical characterization of the soil samples was determined according to the applied methods for soil analysis in the Department of Soil Science and Agrochemistry, in Szent

István University, Gödöllő. The physical and chemical characteristics of the above-mentioned soils are mentioned in table 2.

Table 2: The physical and chemical analysis of used soils

Properties	**Keszthely**
PH $_{(KCl)}$	7.55
Total salt (%)	0.054
$CaCO_3$ (%)	0
Humus (%)	1.48
C (%)	1.08
N%	0.08
NH_4^+-N (Mg/100g)	0.53
NO_3^--N (Mg/100g)	0.18
K_2O (AL*) Mg/100g	136
P_2O_5 (AL*) Mg/100g	130
Density (g/cm³)	2.45
C/N	13.15

Measured by the ammonium-lactate method

Applied treatments

The microcosms experiment was conducted in glass vessels of 1.2 litres covered by septa. Each vessel contained 200g dry clay-cultivated brown forest soil sample. different additives and 11ml, 9.05ml and 5.51ml distilled water were added to the soil samples in each vessel. This amount of water was equivalent to about 60 % and 30% of the water holding capacity.

Table 3: The most important characteristics of GC measurements

GC analysis of gas samples	HP 5980 Series II type gas chromatography	
Analysed gases	N_2O	CO_2
Carrier gases and flow rates	N_2: 23 ml/min	He: 27 ml/min
Temperature of Injector	70°C	
Columns (oven temperature is 50°C)	Porapak Q (80/100 mesh, 6 ft)	
Detectors (temperature)	ECD (250°C)	TCD (150°C)
Calibration	external standard	
Calibration gas mixture contains	7.9 vpm N_2O	9.7 v/v% CO_2
Evaluation of chromatograms	HP 3390 Ser. II integrator, HP CHEM	

Statistical evaluation

Analytical data were processed by a 2-way variation analysis (Sváb, 1981) by using SPSS 10.0 statistical programme. Correlations were tested between the measured CO_2 and N_2O concentrations, time of sampling and the different agrotechnological treatments. The 12 levels of factor “A” were: 1st, 8th, 15th, 22nd, 29th, 36th, 43rd, 50th, 57th, 64th, 71st and 78th day. The 6 levels of factor “B” were: C, N, Cd, O, ON and OCd. (Labels are used according to table 2, i. e. C= control soil, N=soil treated by N-fertiliser, Cd= soil treated by cadmium-compound, O= soil containing organic matter, ON= soil treated by organic additives and N-fertiliser, OCd= soil treated by organic additives and cadmium compound.)

As a starting stipulation normality investigation of data populations was performed (Baráth, 1996). For the measured CO_2 and N_2O concentration data only slightly differed from the curve required, the data can be considered normal distribution.

Modelling of kinetics

Considering the $NO_3^- \rightarrow NO_2^- \rightarrow \frac{1}{2}\ N_2O$ transformations and the decomposition of the organic matter content of soil, which can be well described by first order rate kinetics (Paul and Clark, 1989), it seemed to be reasonable to model the gas concentration-time curves by using the differential equations of consecutive processes consisting of first order reactions. As the simplest possibility, the equations of a complex reaction consisting of two consecutive basic reactions ($A \xrightarrow{k_1} B \xrightarrow{k_2} C$) of first-order were solved.

$$-\frac{d[A]}{dt} = k_1 [A]$$

(In the first reaction *A* concentration decreases.)

$$\frac{d[B]}{dt} = k_1 [A] - k_2 [B]$$

(Concentration of the intermediate matter *B* increases because it is formed from *A* and decreases because it is transformed into *C*.)

$$\frac{d[C]}{dt} = \frac{1}{2} k_2 [B]$$

(Concentration of product *C* continously increases in the second reaction.)

The differential equation system was solved by using a software named Maple 8 [Waterloo Maple Inc. 2002]. In the function of time the concentrations can be written as

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = -\frac{(-k_1 + k_2)[B]_0 e^{-k_2 t}}{k_1 - k_2} - \frac{k_1 e^{-k_1 t} [A]_0}{k_1 - k_2}$$

$$[C] = \frac{1}{2} \frac{e^{-k_1 t} [A]_0 k_2 - e^{-k_2 t} [B]_0 k_1 + e^{-k_2 t} [B]_0 k_2 + 2 [C]_0 k_1 - 2 [C]_0 k_2}{k_1 - k_2}$$

where k_1 and k_2 are rate constants.

RESULTS AND DISCUSSION

During the nitrification, the N of the NH_4^+ ion is transformed into NO_2^- and NO_3^--N. Soil NO_3^- and NH_4^+ content during the experimental period were decreased. Generally the temperature of incubation is a key factor controlling the origin of trace gases emissions. For all treatments, denitrification was the main source of trace gases emissions during the incubation period, because WFPS was 60% on most days. In the first period of the experiment both the N_2O and CO_2 emissions from soil raised due to the increase of microbiological activity and the acceleration of soil organic matter mineralization after drying and rewetting of soil.

Production of N_2O

Denitrification was the main process responsible for total N_2O emissions from soil. N_2O emissions were influenced by the contamination of soil by Cd or Pb and several peaks were registered for each treatment during the experimental period at low (15°C) and high (37°C) incubation temperatures (Figures 1 and 2, respectively). The highest N_2O emission was observed in Cd amended soil between 1st and 10th day of incubation at 37°C. The gas emission flux from microcosms during the incubation period did not show significant differences ($P < 0.05$) at low incubation temperature and between the metal contaminated soils compared to the high incubation temperature. The rate of N_2O produced in the microcosms incubated at 37°C was decreased (statistically is not significantly) with increasing either Cd or Pb concentrations. Fig. 1 shows that in the microcosms containing Pb contaminated soil with 40 mg Pb kg^{-1} soil stimulated the production rate of the N_2O compared with control soil. However, the increasing Pb concentration, the rate of the emission was decreased. On the other hand, Cd stimulated the gas production at all concentrations especially 6 mg Cd kg^{-1}. Figure 2. illustrates that the rate of N_2O produced in the microcosms containing Pb contaminated soil incubated at 15°C was reduced by 50% in comparison with the production rate at 37°C. But the reduction of gas emission in coil contaminated with Cd was 65%. The results indicated that under similar conditions, temperature is significant factor in the production of the gas. Higher gas emission in soil amended with Cd than in Pb contaminated soil was observed. However, predicting gaseous losses of soil N, such as N_2O, is difficult because of the complexity of the N-cycling processes. The rate of gas emission primarily depends on the availability of a mineral N source as a substrate of nitrification and denitrification, O_2 supply, soil moisture, soil temperature, pH, salinity and availability of labile organic compounds (Smith et al., 2003). Our results are in an agreement with the conclusion of Smith et al. (2003). However, in most soils the dominance of nitrification or denitrification as main source of N_2O is not static and can switch very rapidly as the soil aeration state within the biologically active sites changes due to soil physical and chemical properties, climatic changes or increased O_2 demand caused by the presence of easily mineralizable organic matter. In accordance to the effect of heavy metals on nitrification and denitrification, to some extent we agreed with Hinojosa et al. (2004). The different steps in the reduction of NO_3^- to N_2 in denitrification appear to differ in their heavy metal tolerance. Holtan et al. (2002) mentioned that the immediate effect (one day of application) of heavy metals on denitrification. Increases in total Pb decreased the production of N_2O attributed to nitrification by the inhibition method, while increases in pH and total N increased it. Cela and Summer (2002) and Rusk et al. (2004) noted that Pb did not inhibit nitrification. However, this effect was observed in our experimental model, in case of Cd (Figures 1 and 2) and only Pb at 40 mg kg^{-1} soil stimulates the N_2O emission attributed to nitrification by the inhibition method. Sakadevan et al. (1999) mentioned that the effect of heavy metal addition on surface wetland sediments receiving wastewater found that the addition of 500 and 1000 mg Cd kg^{-1} sediment significantly inhibited denitrification. Taking the results shown in Figs 1 and 2 together, it seems very likely that more frequent measurement of soil temperature would have given an even better prediction of N_2O emission fluxes from the soil under the stress of heavy metals. Conen et al. (2000) concluded that the emission flux of N_2O is depended on WFPS, soil temperature and mineral N content. However, it seems likely that this our results is confirmed by the conclusion of Conen et al. (2000).

Production of CO_2

High significant differences in the production rates of CO_2 recorded between microcosms contaminated with Cd or Pb soil and incubated at 37°C (Figure 3) or 15°C (Figure 4). The incubation of microcosms at 37°C stimulated three times the production rates of soil contaminated with Cd or Pb over the production rates at 15°C. Comparatively, no significant difference in the production rates of CO_2 observed between microcosms contaminated with Cd or Pb soil. Also, no significant difference found in the production rates of CO_2 between the various concentrations of Cd or Pb. The results demonstrated that 40 mg Pb kg^{-1} soil stimulate the production rate of the gas compared with control (Figure 3). Moreover, the all applied Cd or Pb concentrations improved the emission of CO_2 from the contaminated soils than control. During the first 28 days of the incubation, no significant differences were observed between the heavy metal treatments and the rates of gas emission especially at 15°C (Figure 4). The results indicated that at 15°C, Pb had more toxic effect on the rate of gas production in comparison to Cd at the same incubation temperature. Here, the Pb reduced the rate of gas emission and the results at these points were consistent with those of Brookes et al. (1986) and Vásquez-Murrieta et al. (2006). Our explanation on the reduction in the gas emission rate might due to many other factors e.g., the availability of organic matter, the soil characteristics, such as pH, strcture, formation, mineral content and the microbial activity which might inhibited by the contamination with tested heavy metals. The optimum temperature for denitrification seems to range from 30 to 67°C (Mancino et al. 1988; Malhi et al. 1990). According to our findings here, temperature may be play the main role in the gas emission as shown in Figures 1 and 3. As the amount of CO_2 uptake of plants in photosynthesis and the rate of the emitted CO_2 during plant respiration correspond to each other annually (Guo and Zhou 2007), soil microbial processes are presumed to contribute significantly to the agricultural CO_2 emission. Although the basic factors determining the rate of these microbial events are soil moisture, temperature and C and N availability (Ma et al. 2007, Guo and Zhou 2007, Chu et al. 2007, Ruser et al. 2006), the effects of a lot of other factors are studied comprehensively. Our results showed that heavy metals had no high influence on the CO_2 emission rate. Generally, these results not in agreement with Brookes et al. (1986) and Vásquez-Murrieta et al. (2006). The two authors reported that a decrease in CO_2-C evolution in the presence of Cd. Dai et al. (2004) also found that the respiration rate was negatively correlated with Pb and Cd content. In this experiment it was shown that the incubation temperature must be taken into account. This is a limitation of the method because in this case the nitrification fraction would also include a contribution via nitrifier denitrification (Webster and Hopkins 1996). There are limited data on the microbial characteristics of undisturbed soils. Šimon (2005) and Rùžek et al. (2003, 2004, 2006) have determined in a long-term field experiment the influence of different fertilization on microbial biomass and respiration. This is in accordance with our findings with the similar characteristics on the tested soils. In conclusion, it can be stated that the applied microcosm experimental model proved to be a suitable tool for detecting the effect of factors influencing the CO_2 and N_2O release from agricultural soil.

This study underlines the key role of contamination of soil sample with different concentrations of two heavy metals (Cd and Pb) in emissions of N_2O, and CO_2 from 60% WFPS soils with low organic matter contents under different incubation temperatures conditions. The management of soil contamination and the temperature are key considerations for mitigating trace gases emissions from these micro-agroecosystems. It is necessary to take into account the incubation temperature at 37°C increased the production rates of the N_2O, and CO_2 more than at 15°C., Pb concentration over 40 mg kg^{-1} soil caused a reduction in trace gas production. Cd had lower toxicity toward the nitrification or denitrification at all concentrations compared with Pb effects. Cd and Pb significantly reduced the rate of N_2O production especially at 15°C. At 37°C, the higher rates of N_2O production found in Cd contaminated soil at all tested concentrations.

Production of N_2O

Figure 1 shows that the production rate of N_2O in the microcosms incubated at 37 °C. The microcosms containing 40 mg Pb/kg soil stimulated the production rate of the gas compared with control. However, the increasing Pb concentration, the rate of the emission decreased.

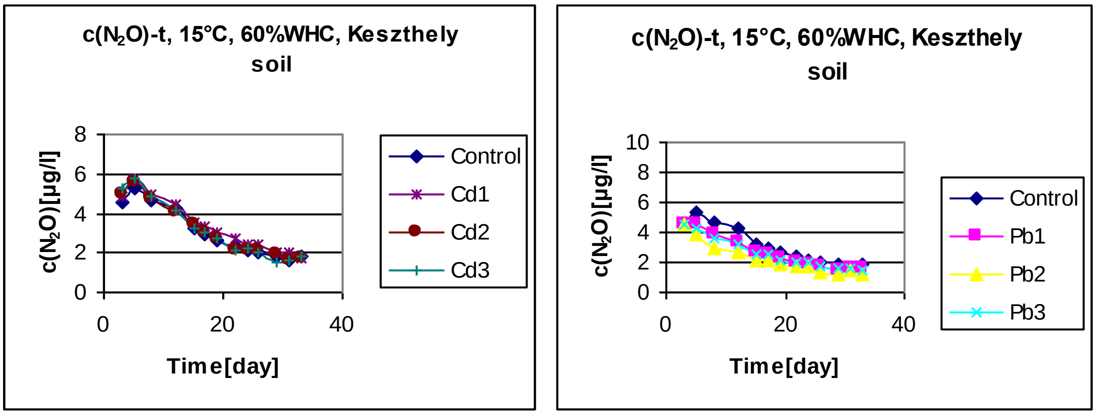

Figure 1. N_2O gas emission vs. time in Experiment. Treated Keszthely soil supplemented by cadmium at 1.5, 3 and 6 ppm and Pb at 40, 80 and 160 ppm.

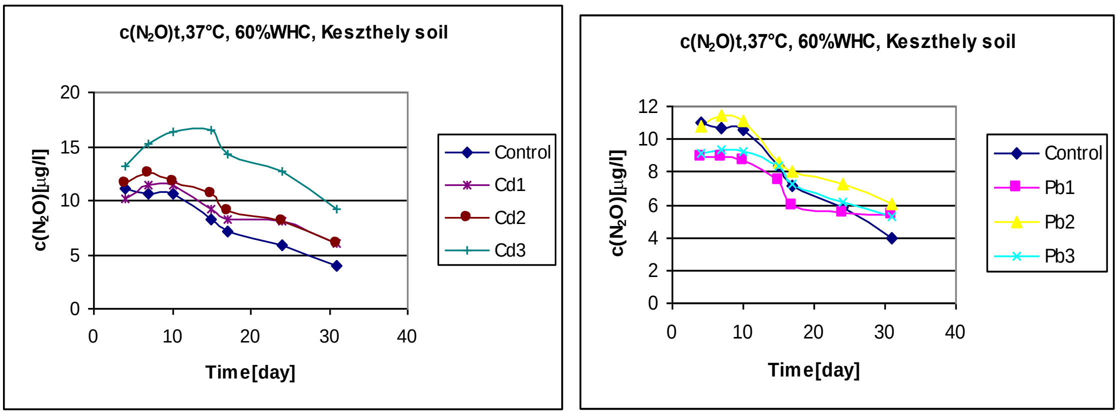

Figure 2. N_2O gas emission vs. time in Experiment. Treated Keszthely soil supplemented by cadmium at 1.5, 3 and 6 ppm and Pb at 40, 80 and 160 ppm.

Production of CO_2

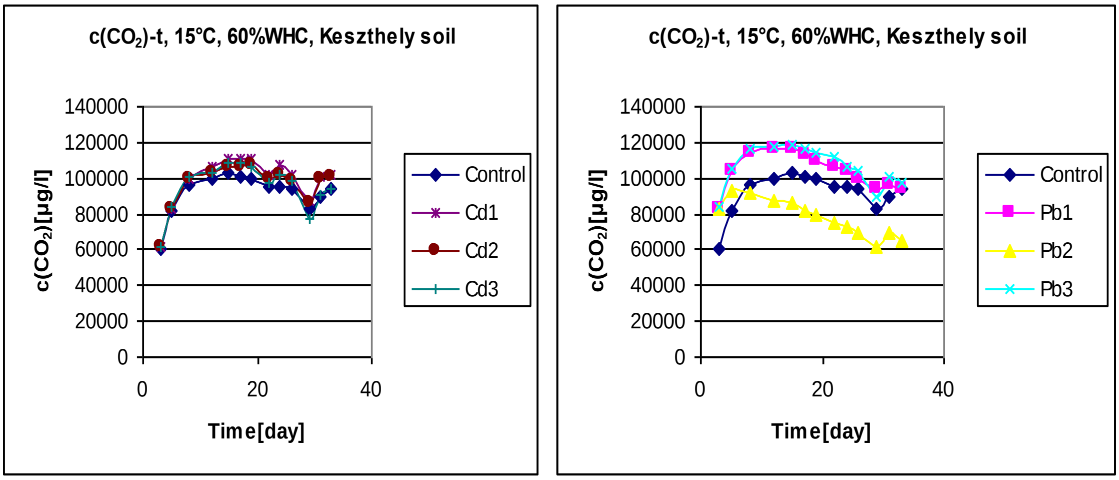

Figure 3. CO_2 gas emission vs. time in Experiment. Treated Keszthely soil supplemented by cadmium at 1.5, 3 and 6 ppm and Pb at 40, 80 and 160 ppm.

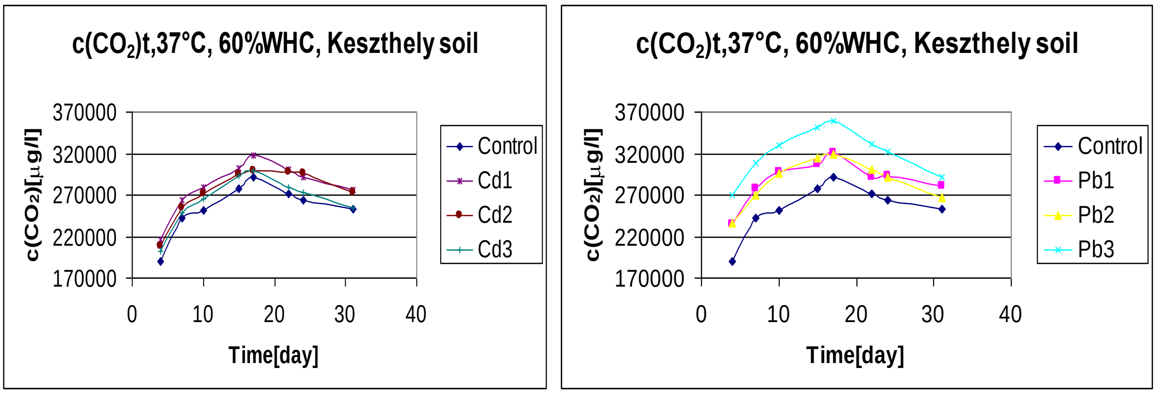

Figure 4. CO_2 gas emission vs. time in Experiment. Treated Keszthely soil supplemented by cadmium at 1.5, 3 and 6 ppm and Pb at 40, 80 and 160 ppm.

REFERENCES

Ambus P., Zechmelster-Boltenstern S., Butterbach-Bahl K. (2006): Sources of nitrious oxide emitted from European forest soil. *Biogeosci*., *3*: 135-145.

Benckiser G., Haider K., Sauerbeck D. (1986): Field measurements of gaseous nitrogen losses from an Alfisol planted with sugarbeets. *Z. Pflanzenernahr. Bodenk*., *149*: 249-261.

Béres K. (2005): Some commercial questions of the CO_2 emission. *Cereal Res. Commun*. **33**: 221-224.

Bock E., Koops H.P., Harms H. (1986): Cell biology of nitrifying bacteria. In: Prosser J.I. (ed.): Nitrification. IRL Press, Oxford: 17-38.

Bouwman A.F. (1990): Exchange of green house gases between terrestrial ecosystem and the atmosphere. In: Bowman A.F. (ed.): Soils and the Greenhouse Effect. J. Wiley, Chichester: 61-127.

Brookes P.C., Heijnen C.E., McGrath S.P. Vance E.D. (1986): Soil microbial biomass estimates in the soils contaminated with metals. *Soil Biol. Biochem*., *18*: 383-388.

Cela S., Summer M.E. (2002): Critical concentrations of copper, nickel, lead, and cadminum in soils based on nitrification. Commun. *Soil Sci. Plant Anal*., *33*: 19-30.

Chu H., Hosen Y., Yagi K. (2007): NO, N_2O, CH_4 and CO_2 fluxes in winter barley field of Japanese Andisol as affected by N fertilizer management. *Soil Biol. Biochem*., *39*: 330-339.

Concen F., Dobbie E., Smith K.A. (2000): Prediciting N_2O emissions from agriultural land through related soil parameters. *Global Change Biol*., *6*: 417-426.

Dai J., Becquer T., Reversat G., Berhard-Reversat F., Lavelle P. (2004): Influence of heavy metals on C and N mineralization and microbial biomass in Zn, Pb, Cu, and Cd contaminated soils. *Appl. Soil Ecol*., *25*: 99-109.

Dorland S., Beauchamp E.G. (1991): Denitrification and ammonification at low soil temperatures. *Can. J. Soil Sci*., *71*: 293-303.

Giller K.E., Witter E., McGrath S.P. (1998): Toxicity of heavy metals to microorganisms and microbial processes in agricultural soil. *Soil Biol. Biochem*., *30*: 1389-1414.

Guo J., Zhou C. (2007): Greenhouse gas emissions and mitigation measures in Chinese agroecosystems. *Agric. Forest Meteorol*., *142*: 270-277.

Gyuricza Cs., Földesi P., Mikó P., Ujj A. (2005): Carbon dioxide emission from arable lands. *Cereal Res. Commun*., **33**: 89-92.

Haynes R.J. (1986): Nitrification. In: Haynes R.J., Orlando F.L. (eds.): Mineral Nitrogen in the Plant-Soil System. Academic Press, New York: 127-165.

Hinojosa M.B., García-Rusíz R., Viňegla B., Carreira J.A. (2004): Microbiologicl rates and enzyme activities as indicators of functionality in soils affected by the Aznlcóllar toxic spill. *Soil Biol. Biochem*., *36*: 1637-1644.

Holtan H.L., Bechmann M., Risnes H.T., Linjordet R., Reier Bakken L. (2002): Heavy metals tolerance of soil denitrifying communities: N_2O dynamics. *Soil Biol. Biochem*., *34*: 1181-1190.

Huang Y., Zou J., Zheng X., Wang Y., Xu X. (2004): Nitrous oxide emissions as influenced by amendment of plant residues with different C:N ratios. *Soil Biol. Biochem*., *36*: 973-981.

Keeny D.R., Fillery I.R., Marx G.P. (1979): Effect of temperature on the gaseous nitrogen products of denitrification in a silt loam soil. *Soil Sci. Soc. Am. J*., *43*: 1124-1128.

Kester R.A., de Boer W., Laanbroek H.J. (1996): Short exposure to acetylene to distinguish between nitrifier and denitrifier nitrous oxide production in soil and sediment samples. *FEMS Microbiol. Ecol*., *20*: 111-120.

Ma W.K., Schautz A., Fishback L.A.E., Bedard H.A., Farrell R.E., Siciliano S.D. (2007): Assessing the potential of ammonia oxidizing bacteria to produce nitrous oxide in soils of a high arctic lowland ecosystem on Devon Island, Canada. *Soil Biol. Biochem*., *39*: 2001-2013.

Malhi S.S., McGill W.B., Nyborg M. (1990): Nitrate losses in soils: effect of temperature, moisture and substrate concentration. *Soil Biol. Biochem*., *22*: 733-737.

Mancino C.F., Torello W.A., Wehner D.J. (1988): Denitrification losses from kentucky bluegrass sod. *Agron. J*., *80*: 148-153.

Nádasy E., Nádasy M. (2006): Some harmful or useful environmental effect of nitrogen fertilisers. *Cereal Res. Commun*., *34*: 49-52.

Rùžek L., Voøíšek K., Strnadová S., Nováková M., Barabasz W. (2004): Microbial characteristics, carbon and nitrogen content in cambisols and luvisols. *Plant Soil Environ*., *50*: 196-204.

Rùžek L., Voøíšek K., Novákova M., Strnadová S. (2006): Microbial, chemical and textural parameters of main soil taxonomical units of Czech Republic. *Plant Soil Environ*., *52*: 29-35.

Rùžek L., Voøíšek K., Vráblíková J., Strnadová S., Vráblík P. (2003): Chemical and biological characteristics of reclaimed soils in the Most region (Czech Republic). *Plant Soil Environ*., *49*: 346-351.

Rabenarivo M .,Wrage-Moennig N .,Jean-Luc C.,Rabeharisoa L .,Razafimbelo Tantely M. and Chapuis-Lardy L (2014): Emissions of CO_2 and N_2O from a pasture soil from Madagascar—Simulating conversion to direct-seeding mulch-based cropping in incubations with organic and inorganic inputs. *Plant Nutr and Soil Sci*., 177: 360-368.

Ruser R., Flessa H., Russow R., Schmidt G., Buegger F., Munch J.C. (2006): Emission of N_2O, N_2 and CO_2 from soil fertilized with nitrate: effect of compaction, soil moisture and rewetting. *Soil Biol. Biochem*., *38*: 263-274.

Rusk J.A., Hamon R.e., Stevens D.P., McLaughlin M.J. (2004): Adaptation of soil biological nitrification to heavy metals. *Environ. Sci. Technol*., *38*: 3092-3097.

Sakadevan K., Zheng H., Bavor H.J. (1999): Impact of heavy metals on denitrification in surface wetland sediments receiving wastewater. *Water Sci. Technol*., *40*: 349-355.

Smith K.A., Ball T., Conen F., Doddie K.E., Massheder J., Rey A. (2003): Exchange of greenhouse gases between soil and atmsphere: interactions of soil physical factors and biological processes. *Euro. J. Soil Sci*., *34*: 779-791.

Šimon T. (2005): Aliphatic compounds, organic C and N and microbial biomass and its activity in long-term field experiment. *Plant Soil Environ*., *51*: 276-282.

Sváb J. (1981): Biometriai módszerek a kutatásban. Mezőgazd. Kiadó, Budapest: 37-355.

Szili-Kovács T., Németh T. (2006): Denitrification of three Hungarian soils treated with ammonium nitrate at different moisture level. *Cereal Res. Commun*., 34: 315-318.

Vásquez-Murrieta M.S., Cruz-Mondragón C., Trujillo-Tapia N., Herrera-Arreola B., Van Cleemput O., Dendooven L. (2006): Nitrous oxide production of heavy metal contaminated soil. *Soil Biol. Biochem*., *33*: 931-940.

Webster E.A., Hopkins D.W. (1996): Contributions from different microbial processes to N_2O emission from soil under different moisture regimes. *Biol. Fertil. Soils*, *22*: 326-330.

Wrage N., Velthof G.L., Benusichem M.L., Oenema O. (2001): Role of nifrifier denitrification in the production of nitrous oxide. *Soil Biol. Biochem*., *33*: 1723-1732.

Wrage N., Velthof G.L., Laanbroek H.J., Oenema O. (2004): Nitrous oxide production in grassland soils: assessing the contribuation of nitrifier denitrification. *Soil Biol. Biochem*., 36: 229-236.

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