University of Belgrade
Technical Faculty in Bor
28th International Conference Ecological Truth
& Environmental Research

EcoTER'20

PROCEEDINGS

EDITOR
Prof. Dr Snežana Šerbula

16 - 19 June 2020, Hotel Aquastar Danube, Kladovo, Serbia

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PREFACE

The world today is faced with the rapid changes in technology. The excessive unsustainable consumption of fossil fuels and primary raw materials require a multidisciplinary approach in finding adequate sustainable solutions. That is why environmental research and ecological truth are at the focus of the 28th International Conference Ecological Truth & Environmental Research 2020 (EcoTER'20), which will be held at Kladovo, Serbia, 16-19 June 2020. On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Conference.

We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.

The 28th International Conference Ecological Truth & Environmental Research 2020 is organized by the University of Belgrade, Technical faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, University of Zagreb, Faculty of Metallurgy – Sisak, University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

These proceedings include 51 papers from the authors coming from the universities, research institutes and industries in 7 countries: Russia, Lithuania, Nigeria, Croatia, Bosnia and Herzegovina, Montenegro and Serbia.

As a part of this year's conference, the third student section is being held. We appreciate the research of the students and their mentors who have made a contribution to the conference. Abstracts of the students' papers have been included into the EcoTER'20 proceedings.

Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged.

We appreciate the effort of all the authors who have contributed to these proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the Conference participants for their support to EcoTER'20. Sincere thanks go to all the people who have contributed to the successful organization of EcoTER'20.

On behalf of the 28th EcoTER Organizing Committee,

Snežana Šerbula, Professor

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Plenary Lecture

AMDs FROM COPPER MINES – A DRAMATIC THREAT TO LOCAL WATER FLOWS OR A VALUABLE SOURCE FOR COPPER PRODUCTION

Velizar Stanković[1*]

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Abstract

Maintenance of mining wastes, produced in heavy metal mines (dumps, abandoned mining works, not excavated ore body edges), represents significant costs for a company, as well as a serious concern for society, due to environmental problems closely related to a company's mining activities. Active, closed, or abandoned, metal or nonmetallic mines produce more or less volumes of mine waters, contaminated with dissolved minerals residues. The supposition is that there are >10,000 active or abandoned mines and mining waste sites of different kinds across Europe, discharging spontaneously 5 to 10 bilions m^3*/year of mine waters into surface water streams. These waters need to be purified, which causes a necessity of investing large amount of money for this purpose. Therefore, mine waters remain a major concern, for which neither the European Community, nor the rest of world have found a proper solution yet. This is one of the aspects of the European ecological truth! What is ours?*

Special attention is paid to mine waters, originating from copper mines, known as acid mine drainages (AMDs) containing, besides heavy metal ions, a certain amount of sulphuric acid which makes them acidic. AMDs cause environmental problems on a global level. Some studies suggest that up to ca. 19,300 km of rivers, and around 72,000 ha of lakes and similar water reservoirs around the world have been polluted with various metal-sulphate salts and sulphuric acid.

Situation in the Balkan countries is even worse than the above, because of mining works in more than 20 active heavy metal mines. In each of them there are some AMDs affecting the surrounding water flows heavily and irretrievably. The process of AMD generation is complex and involves chemical, biochemical and electrochemical reactions.

On the other hand, mine dumps, as a cause and AMDs as their consequence, must be considered as valuable secondary raw materials that could be further exploited, in order to extract metal residues from them, and to reduce the existing mine waters overburden on the surface water flows. New approaches are presented in implementation of some emerging technologies, in combination with conventional techniques, for copper mine waters purification.

Conference Papers

THE EFFECT OF EFFLUENT ON THE WATER QUALITY IN THE NIŠAVA

Slavica Stevanović[1*], Jovana Krstić[1], Branka Stojanović[1], Dušan Paunović[1],
Danica Dimitrijević[1], Jasmina Veličković[1]

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Abstract

From a general perspective, the sewage system in Niš is a combined type system. After mixing with fecal and atmospheric water effluent is discharged directly into the Nišava via the two main outlets (the left and right collectors). This research presents the influence of untreated wastewater on the recipient's quality (surface water). Surface and wastewater quality testing is carried out in accordance with the relevant directives, national and international regulations. Physical (temperature, turbidity, pH and electrical conductivity) and chemical (chlorides, ammonia, nitrites, nitrates, sulfates, iron, manganese and chromium in the form of Cr^{6+} *and* Cr^{3+} *ions) parameters are analyzed as indicators of quality. Yearly sample quality monitoring indicated river degradation, which necessitates wastewater treatment in the left and right collectors before the discharge into the Nišava.*

Keywords: wastewater, surface water, monitoring, spectrophotometry

INTRODUCTION

During recent years, there has been an increasing awareness and concern about water conservation all over the world. Hence, new approaches towards achieving sustainable development of water resources have been advanced internationally [1].

Due to industrial development, domestic effluent and urban run-off account for the bulk of the wastewater generated in Niš. Domestic sewage contains a wide variety of dissolved and suspended impurities and is the primary source of pathogens (disease-causing microorganisms) and putrescible organic substances. Because pathogens are excreted in feces all sewage from cities and towns is likely to contain pathogens of some type, potentially presenting a direct threat to public health. Putrescible organic matter has posed a different sort of a threat to water quality in recent years.

India is recognized as having major problems with water pollution, predominantly, due to untreated sewage. Rivers such as the Ganges and the Yamuna, all flowing through highly populated areas, are polluted. 80% of the sewage in India is untreated and flows directly into the nation's rivers, polluting the main sources of drinking water. Indian cities produce nearly 40,000 million liters of sewage every day and barely 20 percent of it is treated. Hence, treatment of sewage and its reuse is the need of the hour [2].

From a general perspective, the Niš sewage system is a combined type system. A large section of the city, in particular, the central region of the city on the left and right banks of the Nišava possesses general (mixed) type collectors whereas for Niška Banja and certain peripheral and newly-built parts of the city a separation system was constructed. After mixing with fecal and atmospheric water wastewater is discharged directly into the river Nišava via the two main outlets: outlet 1 - the left collector in Ivan Milutinović street and outlet 2 - the right collector in Beograd mahala.

The purpose of this study is to estimate the effect of untreated sewage effluent on the recipient's water quality (the Nišava) via physical and chemical water quality indicators.

MATERIALS AND METHODS

Water quality is tested according to the corresponding directives and regulations of national and international authorities –regulations (Official Gazette of RS, No: 33/2016; 67/2011, 48/2012 1/2016; 50/2012; 24/2014; 74/2011 and Official Gazette of SRS, No. 31/82).

The Nišava water quality is also monitored following drinking water regulations (EU Council Directive 98/83/EC 1998; Official Gazette SRJ No: 42/1998, 44/1999, 28/2019; WHO 2011a; US EPA 1999a; US EPA 2012) considering that river water (at the entrance to the city) is used as the water intake.

The quality analysis of the wastewater in the left (L) and right (R) city collectors and the Nišava water quality analysis before (N- the water intake) and after the discharge of the left city collector (Nk - around 300 m downstream), was carried out in the laboratory of the sanitary control sector with the PUC 'Naissus' laboratory in Niš. The laboratory is accredited according to the standard SRPS ISO/IEC 17025:2006.

The water samples for physico-chemical examinations were taken by experts in accordance with the standards: SRPS EN ISO 5667-1:2008, SRPS EN ISO 5667-3:2017, SRPS EN ISO 5667-4:1997, SRPS EN ISO 5667-6:1997, SRPS EN ISO 5667-10:1997.

The analysis of wastewater and surface water encompassed the appointment of the following parameters:

Physical parameters (methods): water temperature (SRPSH.Z1.106:1970), turbidity (EN ISO 7027: 1999), pH value (EN ISO 10523: 2008) and electrical conductivity (SRPS EN 27888:2009).

Chemical parameters (methods): chloride (SRPS ISO 9297/1:2007 revision 1), ammonia (SRPS.H.Z1.184:1974), nitrite (SRPS ISO 26777:2009), nitrate (Standard methods for testing hygienic correctness "Drinking water"1990), sulfate (USEPA 375.4:1978), iron (SRPS ISO 6332:2003), manganese (Standard methods for testing hygienic correctness "Drinking water"1990) and chromium in the form of Cr^{6+} and Cr^{3+} ions (ISO 11083:1994(E)).

The wastewater and surface water quality analysis was conducted from January to December 2017 with a monthly sampling frequency.

RESULTS AND DISCUSSION

The results of the physical and chemical parameters are shown in Tables 1-3.

The highest surface water and wastewater temperatures were measured in the wastewater samples (R) 23.8°C in August while the lowest water temperature was measured in the samples of surface water at the water intake location (N) 6.4°C in December (Table 1). No national or international standards have been set for the temperature of surface water and wastewater, because they don’t have an immediate effect on human health, but they influence the chemical and microbiological processes in water.

Table 1 *Yearly temperature, turbidity, pH values and electrical conductivity in surface and wastewater: (N) the Nišava- water intake, (L) the left city collector, (R) the right city collector, (Nk) the Nišava downstream from the left collector*

Month	Temperature °C				Turbidity NTU		pH value				Electrical conductivity µS/cm			
	N	L	R	Nk	N	Nk	N	L	R	Nk	N	L	R	Nk
January	11.2	14.0	14.1	13.8	22.1	28.9	7.90	7.96	7.95	8.02	352	886	1062	468
February	6.5	13.2	15.6	8.9	12.6	10.4	8.18	8.00	8.00	8.30	375	922	1072	400
March	8.0	14.9	13.8	9.5	15.2	27.0	7.79	7.60	7.95	7.90	354	727	933	412
April	9.8	16.2	15.1	11.4	5.2	11.1	8.02	7.61	7.82	8.06	384	870	1184	398
May	12.0	15.9	16.1	14.3	17.1	25.0	8.01	7.90	7.50	8.04	372	860	1022	407
June	17.2	18.1	17.7	19.1	16.1	16.7	8.10	7.92	7.52	8.39	467	803	1027	513
July	19.5	21.8	22.5	21.7	11.1	30.0	8.04	7.80	7.87	8.30	457	840	1045	522
August	16.9	18.8	23.8	18.2	6.0	26.0	8.00	7.81	7.94	8.10	403	876	1008	464
September	17.4	22.7	23.8	17.7	1.8	4.4	8.08	7.80	7.94	8.20	411	884	970	460
October	13.2	17.6	14.7	13.8	4.3	4.4	8.05	7.65	7.62	8.06	471	886	1289	491
November	8.2	14.4	13.8	8.6	10.2	15.2	7.96	7.88	7.65	7.72	380	823	840	405
December	6.4	12.4	11.3	6.7	18.3	25.1	7.98	7.85	7.94	8.20	307	890	792	328

The turbidity values measured in each surface water sample ranged from 1.80 NTU (Nephelometric turbidity units) - at the water intake area to 30.00 NTU in the Nišava downstream from the wastewater discharge point (Table 1), which points to a deterioration of river water quality.

The toxicity of many components depends on the pH value. For instance, HCN toxicity increases with the decline of pH values while the toxicity of NH_3 grows with the elevation of pH values. Simultaneously, with the elevation of pH values, heavy metals in effluent get deposited in the form of their hydroxides. The measured pH values (Table 1) in all effluent and surface water samples with the highest value of 8.39 are within the recommended values.

The electrical conductivity of water depends on the geology of the area through which water flows and the ionizing particles in it. The highest values of electrical conductivity in the wastewater were 1289 µS/cm (the right collector), which did not affect the drastic increase of conductivity in the surface water: from the highest value 471 µS/cm at the water intake (N) to the highest value of 522 µS/cm in the river downstream from the discharge point (Nk) (Table 1). The EU directive (1998) limited conductivity to 2500 µS/cm at 20°C under the condition that the water is not aggressive. In Turkey, in 177 samples of groundwater electrical conductivity is within the interval of 332 µS/cm to 3004 µS/cm with the average value of 1573 µS/cm [3].

Table 2 *Yearly chloride and ammonia ion concentration in surface and wastewater: (N) the Nišava-water intake, (L) the left city collector, (R) the right city collector, (Nk) the Nišava downstream from the left collector*

Month	Cl^- mg/l				NH_4^+ mg/l			
	N	L	R	Nk	N	L	R	Nk
January	<5.0	45.8	67.5	12.8	0.2	35.6	30.6	7.9
February	6.6	53.7	62.7	7.5	0.1	26.7	30.1	0.6
March	<5.0	62.6	84.0	5.2	0.1	35.6	28.9	0.5
April	<5.0	46.8	81.9	5.1	0.1	30.8	34.4	6.1
May	6.5	45.5	63.1	7.4	0.2	45.3	60.0	3.9
June	6.7	42.8	50.9	8.5	0.1	24.7	28.3	0.7
July	6.5	40.8	77.5	6.6	0.1	25.6	26.5	6.2
August	5.3	42.0	55.0	14.7	0.1	31.2	35.1	6.7
September	6.5	54.3	59.5	12.2	0.1	23.5	27.4	1.4
October	6.6	57.3	140.5	11.4	0.1	33.5	42.9	2.3
November	5.2	41.2	92.8	5.1	0.1	26.2	36.2	0.4
December	<5.0	44.8	107.2	<5.0	0.1	29.1	39.2	2.3

Chloride concentrations in all the river water samples (N and Nk - Table 2) are below the maximum allowed concentration values of 100 mg/l. Chloride concentration increases with the rise of mineral content. Chloride increases water's electrical conductivity and thus corrosiveness in water is also increased [4]. Wastewater samples (L and R) contain chloride in higher concentration, but lower than 100 mg/l (Table 2). In Banat, Serbia, groundwater has low chloride content ranging from 5 mg/l to 50 mg/l [5].

The presence of ammonia in concentrations higher than the geological level is an important factor for fecal contamination and can be utilized for the assessment of overall water quality [6,7]. Ammonia nitrogen concentrations (NH_4^+-N) in all wastewater samples ranged between 23.5 (L) to 60.00 mg/l (R) (Table 2) and this affected the increase of this parameter in the river: from 0,1 mg/l (at the water intake) to 7.9 mg/l in the Nišava after the wastewater discharge, which is considerably higher than the maximum allowed concentration in a river.

Nitrates and nitrites in wastewater and surface water can appear naturally but anthropogenic processes like the overuse of inorganic nitrogen fertilizers, municipal wastewater, septic tanks, farm runoff, industrial effluent, and others comprise the most common causes. Inorganic nitrogen analysis enables the assessment of these activities influence on water quality [8]. The highest nitrate concentration (NO_3-N) of 21.3 mg/l and nitrite nitrogen (NO_2-N) concentration of <2.24 mg/l in the Nišava (Table 3) show water quality deterioration after the discharge of untreated wastewater into the river. These values are above the maximum allowed concentration for surface water. In the United States of America, Texas, a region that aside from oil and natural gas production also engages in agriculture, the groundwater nitrate concentration varies from <0.44 mg/l to 149 mg/l whereby in 3 out of 40 water samples nitrate concentration exceeds the national standard of 44 mg/l. Statistics show that nitrate concentration drops with well depth [9].

***Table 3** Yearly nitrite, nitrate and sulfate concentration in surface and wastewater: (N) the Nišava-water intake, (L) the left city collector, (R) the right city collector, (Nk) The Nišava downstream from the left collector*

Month	NO_3-N mg/l				NO_2-N mg/l	SO_4^{2-} mg/l			
	N	L	R	Nk	Nk	N	L	R	Nk
January	4.7	7.1	10.6	7.5	<0.71	13.2	58.2	50.0	22.9
February	4.5	4.5	6.3	4.8	<0.65	21.3	141.6	178.7	21.2
March	4.5	7.1	11.2	5.4	<0.03	10.0	34.7	18.1	10.9
April	3.8	3.6	3.7	3.7	<0.85	9.4	93.0	143.0	16.5
May	5.4	3.0	4.5	21.3	<0.75	15.3	46.3	71.8	14.1
June	6.5	2.7	2.5	5.5	<1.15	14.9	46.4	65.2	18.9
July	5.0	1.1	1.9	4.9	<2.24	24.5	45.7	70.1	28.7
August	4.9	1.1	0.7	4.5	<0.22	16.9	35.7	47.4	17.3
September	4.3	1.3	6.3	5.4	<0.17	13.6	29.9	16.9	20.4
October	7.7	6.0	4.3	7.7	<0.14	16.4	15.8	28.9	13.1
November	4.8	5.2	6.1	2.2	<0.62	8.4	24.8	19.5	11.6
December	3.8	4.2	8.4	3.9	<0.88	8.9	31.8	29.6	9.1

Studies suggest that in concentrations between 1000 mg/l and 1200 mg/l sulfates have a laxative effect but without diarrhea, dehydration and weight loss (WHO). The highest concentration of sulfate was measured in (R) (178.7 mg/l) in February while the lowest sulfate concentration was measured in (N) (8.4 mg/l) in November. Despite the mild increase of sulfate after the wastewater discharge all measurements in this location are far below the maximum allowed concentration of 100 mg/l for surface water.

Iron concentration in all surface water samples (the Nišava after wastewater discharge) is below the maximum allowed concentration (<0.5 mg/l).

Manganese in water behaves similarly to iron. Manganese concentration in all samples of analyzed surface water is below the method's detection threshold (<0.025 mg/l) and thus satisfies the recommended values and the maximum allowed concentration (0.1 mg/l).

Also, the Cr^{6+} and Cr^{3+} concentrations in all water samples from the river Nišava are below the method's detection threshold (<0.01 mg/l) and therefore meet the recommended values and the maximum allowed concentration (0.05 mg/l).

Even though all of these contaminants have not yet reached toxic levels, they still represent a long term risk to public health [10].

Although the analyzed values of Fe, Mn and Cr are below the method's detection threshold, an increase in river water turbidity, as well as elevated values of nitrogen (ammonia ion, nitrates), indicate that the untreated wastewater discharge continually deteriorates the Nišava water quality. Due to higher values of ammonia ions, which indicate fecal contamination, there is a risk of pathogenic bacteria.

Numerous studies [11] show the efficacy of various technical and technological wastewater treatment processes. They mostly refer to filtration, aeration, disinfection [12] and other processes depending on the degree and type of wastewater contamination. This is certainly applicable to the wastewater in Niš and the result would be the preservation of the environment and river quality.

CONCLUSION

The physical and chemical analysis of the wastewater and surface water quality indicates deterioration in the Nišava after the discharge from the city wastewater collectors. Contaminant concentration in the effluent has been a factor in the deterioration of the recipient's water quality. This can be stated because of the elevated turbidity values and fecal contamination indicators (ammonia ion, nitrates) in the river after the discharge from the collectors. These values are considerably increased in comparison to the values before the discharge of wastewater and in comparison to the limit values for a good ecological status according to the regulation on contaminant limits in surface water, groundwater, sediment and the time limit for reaching them (Official Gazette RS no 50/2012) - for a good ecological status, i.e. class II - river type 2; natural level.

As the aforementioned regulations stipulate time limits for reaching the threshold values, in the following period it is necessary to adjust the emissions of contaminants to the threshold values. To achieve this, a central wastewater facility must be constructed with the view of preserving water from contamination and maintaining public health.

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THE DISTRIBUTION OF THE MASS CONCENTRATIONS OF POTASSIUM, THORIUM AND RADIUM IN THE SOILS OF THE TEKIJA REGION, THE NP ĐERDAP

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Abstract

Soil samples (24) were collected in June 2018, on the territory of NP Đerdap (from region the Tekija, 4 management units). In this study, the mass concentrations of potassium, radium and thorium, were calculated based on specific activities of these radionuclides measured by gamma-ray spectrometry. The mean values of elemental mass concentrations in analyzed soil samples were found to be 1.75% for potassium, 2.54 mg kg^{-1} for radium and 8.88 mg kg^{-1} for thorium. The strength of the absorbed gamma radiation dose originating from the activity of radionuclides in the soil and the yearly effective dose were determined. Values of the strength of the absorbed gamma radiation dose and the yearly effective dose from external exposure to gamma radiation based on the content of natural radionuclides in soil were in the range of the expected values and close to the average values in the world.

Keywords: NP Đerdap, mass concentration, potassium, thorium, radium

INTRODUCTION

National parks (NP) are large areas incorporating a number of diverse natural ecosystems of national interest from the view point of preservation, complexity and biographical characteristics with different forms of original flora and fauna, representative physico-geographical objects and events, and cultural-historical values, representing exceptional natural entities of national significance [1]. There are five natural parks (NP) in Serbia, and the Đerdap is one of them since 1974, with an area of 63,350 ha. It is located in the Northeast of Serbia on the boundary with Romania and occupies 100 km of the right bank of the middle course of the river Danube. The complex relief in this NP, specific gorge mesoclimate, large number of relic species and phytocenosis, and exceptional diversity in view of lithological rock compositions, genetic origin and geological age [2], lead to the formation of a number of different types of soil with different properties and production potential [3]. All organisms of planet Earth are exposed to radiation that is classified by place of origin into earth and cosmic. Sources of ionization radiation by their genesis and occurrence in the environment are classified as: natural, anthropogene and radioactive waste. Natural radionuclides in soil (^{40}K, ^{232}Th, ^{226}Ra, ^{238}U…) give the highest contribution to gamma radiation (96%) in the environment. They are formed during the nucleosynthesis process and have a long half-life and different physical, geochemical properties, half-life types, radiation intensities, isotropic prolific quantities, occurrence method and geochemical cycles [4]. The activity levels of radionuclides in soil depend on: the mineral composition and physicochemical properties of soil, meteorological conditions and possible translocations and migrations of radionuclides. Natural radioactivity is part of the environment and is changed from place to place and acts on the population over a long time period. According to the UNSCEAR report the average mass concentrations (concentration span) of uranium, radium, thorium and potassium in soil in the world are: 2.82 (1.29–8.87) mg kg^{-1}; 3.18 (1.53–5.45) mg kg^{-1}; 7.32 (2.68–15.61) mg kg^{-1} and 1.54 (0.54–3.28) (%), respectively [5]. Research has shown that average mass concentrations in brown woodland soil in Serbia were: potassium 1.74 %; thorium 7.88 mg kg^{-1} and uranium 1.78 mg kg^{-1} [6]. Our research of soil in the Tekija region (NP Đerdap) in the period 2015 and 2016 has shown that the mean values of mass concentrations of potassium, radium and thorium were in the range: from 1.41 to 2.11% (mean 1.67%); from 0.37 to 3.02 mg kg^{-1} (mean 1.91 mg kg^{-1}) and from 1.27 to 11.22 mg kg^{-1} (mean 6.98 mg kg^{-1}) that is within the range of measurements made in the world [7,8].

In order to obtain a real picture of the radioactivity state of the soil, the most important and vulnerable component of the environment in the Tekija region (NP Đerdap), samples of soil were collected in 2018 and the obtained results are presented in this work.

MATERIALS AND METHODS

Soil samples (24) were collected in the Tekija region NP Đerdap from 4 management units (GJ) (Tekija, Crni vrh, Manastirički gaj and Prapezišće), to the depth of 10 cm, in June 2018. The management units for soil sampling were carefully selected based on radioactivity bioindicator from previous years. Samples were transported to the laboratory and cleaned from visible dirt, dried, homogenized and packed into 0.5 L Marinelli vessels that were hermetically closed, sealed with wax and left for at least 40 days to establish radioactive equilibrium of post-radon series members ^{238}U, prior to gammaspectrometric analysis. Sample mass was up to 600 g. A high purity semiconducting germanium detector ORTEC–AMETEK, USA with 8192 channels, resolution 1.65 keV and relative efficiency of 34% at 1.33 MeV for ^{60}Co was used for determining radionuclide activity levels. Spectra were analyzed using the Gamma Vision 32 software package.

Specific activity of ^{40}K, ^{228}Ra and^{232}Th were converted into mass concentrations of elemental potassium, radium and thorium [9], respectively, using equation (1):

$$F_E = \frac{M_E \times C}{\lambda_{E,i} \times N_A \times f_{E,i} \times A_{E,i}} \tag{1}$$

where: F_E - participation of element E in the sample, M_E - atomic mass (kg mol^{-1}), $\lambda_{E,i}$ - constant of radioactive isotope i half-life of element E (1/s), $f_{E,i}$ - isotope i representation in nature, $A_{E,i}$ - measured specific activity (Bq kg^{-1}) of radionuclides (^{40}K, ^{226}Ra, ^{232}Th), N_A - Avogadro number (6.023×10^{23} atom mol^{-1}) and C - constant with values of 10^6 for Ra and Th (mass concentration mg kg^{-1}) or 100 for K (mass concentration in %).

According to the recommendation of UNSCEAR [5], based on measured activity levels ($A_{Ra,}A_{Th,}A_K$) (Bq kg^{-1}) of natural radionuclides in investigated soil samples calculation of the strength of the absorbed gamma radiation dose (D) 1m above soil level can be performed according to equation (2) assuming that all descendants are in equilibrium with their precursors and that radionuclides contribute only slightly to the total dose due to external exposure, using the conversion factor for ^{226}Ra, ^{232}Th and ^{40}K 0.462; 0.604 and 0.042 (nGyh^{-1}/(Bq kg^{-1}) respectively:

$$\mathrm{D\ (nGyh^{-1}) = 0.462A_{Ra}+0.604A_{Th}+0.042A_K} \tag{2}$$

Knowing the total strength of the gamma absorbed radiation dose (D) equation (3) can be used to calculate the yearly effective dose for an adult H (mSv):

$$\mathrm{H\ (mSv) = D\times0.7\times0.2\times8760} \tag{3}$$

where: 0.7 (SvGy^{-1}) conversion coefficient (relation between the yearly effective dose received by the pollution and absorbed dose in air); 0.2 – exposure factor for external radiation (it is assumed that the population spends on average 20% time in the open); 8760 – number of hours in one year [5].

RESULTS AND DISCUSSION

Natural radioactivity of soil depends on the radiation type and geological structure of the area. Table 1 shows mass concentrations of potassium (%), radium and thorium (mg kg^{-1}) in soil collected in 2018 in the Tekija region (NP Đerdap), the total strength of the gamma absorbed radiation dose and the yearly effective radiation dose.

The average content of potassium in the lithosphere is 2.59% and its content in soil depends on the geological base, the base substrate whose decomposition creates the soil and on pedogenetic processes. Taking into account the data in Table 1 it follows that the mean mass concentration of potassium in soil samples collected in 2018 in the Tekija region (NP Đerdap) is 1.75% that is somewhat higher than the mean mass concentration in the world [5]. The minimal mass concentration of potassium was measured in the soil sample from GJ Manastirički gaj, division 8a (0.65%), while the maximum value was measured in the soil sample from Tekija, division 41a (2.83%) that is within the measurement range in the world [5]. Mean values of mass concentrations of potassium (%) in GJ increase in the following order: Manastirički gaj (0.68) < Crni vrh (1.62) < Tekija (1.9) < Propezešće (2.27).

In nature radium is found in uranium ores in the form of oxides and hydroxides. It is a descendant of uranium and member of the radioactive series ^{228}U. From Table 1 it follows that the mean mass concentration of radium in soil from the Tekija region is 2.54 (mg kg^{-1}) and it is lower than the world average (3.18 mg kg^{-1}) [5]. The minimal mass concentration of radium was measured in the soil sample collected in GJ Manastirički gaj, division 8a (1.20 mg kg^{-1}), and the maximum in the sample from GJ Propezešće, division 25a (3.79 mg kg^{-1}). The values of mass concentrations of radium in the Tekija region are in the range of values determined during research in the world [5]. Mean values of mass concentration of radium (mg kg^{-1}) in GJ increase according to the following order: Manastirički gaj (1.36) < Crni vrh (2.54) < Tekija (2.69) < Propezešće (3.04).

Table 1 *Mass concentrations of potassium (K), radium (Ra) and thorium (Th) in soil collected in 2018 in the Tekija region (NP Đerdap), the total strength of the gamma absorbed dose (D) and effective yearly radiation dose (H)*

No.	Management unit, division	K	Ra	Th	D	H
		(%)	(mg kg^{-1})		nGyh^{-1}	mSv
1.	Tekija, 41a	2.83	2.93	6.98	71.3	0.087
2.	Tekija, 41a	2.42	2.27	7.32	62.9	0.077
3.	Tekija, 67	2.31	2.74	8.17	66.3	0.081
4.	Faca Tekija, 48b	1.72	3.10	9.98	65.0	0.080
5.	Faca Tekija, 48b	1.91	3.00	9.85	66.6	0.082
6.	Tekija, 78	1.89	2.62	9.02	62.1	0.076
7.	Tekija, 78	1.94	2.32	9.95	63.4	0.078
8.	Tekija, Kosovica	1.63	2.29	8.24	54.9	0.067
9.	Tekija, Kosovica	1.58	2.48	9.20	57.7	0.071
10.	Tekija, Dafin	1.67	3.11	10.59	65.9	0.081
11.	Crni vrh, 1	0.83	1.88	5.95	36.3	0.045
12.	Crni vrh, 3	1.70	2.64	9.22	60.2	0.074
13.	Crni vrh, 4	1.16	3.23	10.95	60.8	0.075
14.	Crni vrh, 13	1.65	2.91	10.71	64.9	0.080
15.	Crni vrh, 17	1.89	3.29	10.56	69.8	0.086
16.	Crni vrh, 45	1.60	3.07	10.71	65.1	0.080
17.	Crni vrh, 47	1.49	2.88	11.20	63.7	0.078
18.	Crni vrh, 57	2.02	1.51	9.73	59.3	0.073
19.	Crni vrh, 59	2.11	1.73	9.07	60.0	0.074
20.	Crni vrh, 59	1.70	2.26	7.98	55.0	0.067
21.	Manastirički gaj, 8a	0.65	1.20	3.20	23.2	0.028
22.	Manastirički gaj, 8a	0.71	1.52	3.98	27.8	0.034
23.	Propezešće, 25a	2.58	3.79	13.78	89.7	0.110
24.	Propezešće, 25a	1.95	2.28	6.71	55.3	0.068

Thorium is obtained from uranium treatment. Thorite and alanite are the most significant thorium minerals found in granite. From Table 1 it follows that the mean mass concentration of thorium in soil in the Đerdap region is 8.88 (mg kg^{-1}) and it is higher than the world average (7.39 mg kg^{-1}) [5]. The minimal mass concentration of thorium was measured in the soil sample collected in GJ Manastirički gaj, division 8a (3.59 mg kg^{-1}), while the maximum was measured in GJ Propezešće, division 25a (10.25 mg kg^{-1}). The obtained values of mass concentrations of thorium are in the range of world values [5]. Mean mass concentrations of thorium (mg kg^{-1}) in GJ increase according to the following order: Manastirički gaj (3.59) < Tekija (8.93) < Crni vrh (9.61) < Propezešće (10.25).

High values of the Pearson coefficient among radionuclides Ra-Th (0.777) in soil indicate their common origin and strong linear bond. The values of the Pearson coefficient for K-Ra (0.433) and K-Th (0.437) indicate their medium connectivity.

The total strength of the absorbed gamma radiation dose (D (nGyh^{-1})) can be calculated based on equation (2). From Table 1 it follows that in the Tekija region D values (nGyh^{-1}) originating from potassium are from 8.48 to 37.25 (mean 23.00); originating from radium from 6.84 to 21.6 (mean 14.51) and originating from thorium from 7.91 to 34.13 (mean 21.98). The total absorbed gamma radiation dose (nGyh^{-1}) in the Tekija region was from 23.0 to 89.7 (mean 59.47) and is in the range of world values (32–107, mean 57.6) [5]. Mean values of the total strength of gamma radiation dose (Gyh^{-1}) in management units increase in the following order: Manastirički gaj (25.50) < Crni vrh (59.52) < Tekija (63.59) < Propezešće (72.51). From the results presented in Table 1 it follows that mean values of D (nGyh^{-1}) in all GJ, except Manastirički gaj, are somewhat higher than average world values.

Knowing D (nGyh^{-1}), and based on equation (3) the calculated yearly effective radiation dose H (mSv) in the Tekija region was from 0.028 to 0.110. Mean values of H (mSv) in all GJ increase in the following order: Manastirički gaj (0.031) < Crni vrh (0.075) < Tekija (0.078) < Propezešće (0.089). The yearly effective doses originating from terrestrial gamma radiation in GJ Crni vrh, Tekija and Propezešće are higher than the mean world values (0.070 mSv), but in the measuring range in the world. This research is in agreement with the research of other scientists [10,11]. The mean value of H in the Đerdap region is 0.073 mSv and in accordance with the mean world value 0.070 mSv. Based on the Rule book [12] the yearly effective dose for the population is increased if it is higher than 1 mSv for a year. In the territory of the Tekija region the mean value of the yearly effective radiation dose is 0.073 mSv for a year and is significantly lower than 1mSv.

CONCLUSION

The mean values of the mass concentration of potassium (%), radium and thorium (mg kg^{-1}) are the lowest in GJ Manastirički gaj and the highest in GJ Propezešće.

High values of Pearson coefficients for radionuclides Ra-Th (0.777) in soil indicate their common origin and strong linear bond. The values of Pearson coefficients for K-Ra (0.433) and K-Th (0.437) indicate their medium connectivity.

Mean values of the total strength of absorbed gamma radiation doses (nGyh^{-1}) are the lowest in GJ Manastirički gaj and the highest in GJ Propezešće. Mean values of the yearly effective dose (mSv) are the lowest in GJ Manastirički gaj and the highest in GJ Propezešće. The mean value of H in the Đerdap region is 0.073 mSv and is in accordance with the mean value on the world level of 0.070 mSv.

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EXPERIMENTAL DETERMINATION THE PARAMETERS OF ROCK MASS OSCILLATION EQUATION AT COPPER ORE USING SIMPSON'S RULE

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Abstract

In mining practice, as a way of the hard rock exploitation, massive blasting has an increasing application. During exploitation, the use of explosives increases the quantity of the blasted rock mass and decreases the production costs. However, the use of great quantities of explosive brings about increase of negative blasting effects. By negative blasting effects we understand seismic effect of blasting, the effect of the air blast wave, sound effect, scattering of blasted rock mass, etc. To estimate, to control and plan seismic effects of blasting it is necessary to determine rock mass oscillation equation. One of the most frequently used is the equation of M.A. Sadovskii, which defines the change of rock mass oscillation velocity depending on the distance from blasting point, quantity of explosive, conditions for performing blasting and geological characteristics of the rock mass. In this paper, analysis of the methods for the determination the parameters of the rock mass oscillation equation have performed, for the equal reduced distances at experimental blastings. To determine parameters in the Sadovskii equation, besides the usual model – Method of Least Squares, one more model has been presented applying Simpson's rule.

Keywords: working environment, negative effects of blasting, oscillation velocity, rock mass oscillation equation, Simpson's rule

INTRODUCTION

Dynamic characteristics of the oscillation, in the elastic deformations zone of the rock mass, is the most defined by the oscillation velocity. As the relation between the rock mass oscillation velocity and basic parameters affecting its magnitude, such as: the amount of explosive, the distance from the blast site, characteristics of the rock material and the type of blasting, the equation of M.A. Sadovskii.

By applying the equation of rock mass oscillation while blasting, the determination of the rock mass oscillation velocity is enabled for each blast operation in advance, thus blasting is, as regards seismic effect, under control, and that gives an opportunity to plan the magnitude of shock waves for each future blast operation. In this way adverse blasting effects are reduced [1].

ROCK MASS OSCILLATION EQUATION

In the equation of Sadovskii, rock mass oscillation velocity is given in the following form [2]:

$$v = K \cdot R^{-n} \tag{1}$$

where there are:

v – velocity of rock mass oscillation [cm/s],
K – coefficient conditioned by rock mass characteristics and blasting conditions, where the amount of explosive is given by way of the volume. K is determined by terrain surveying,
n – exponent, conditioned by rock mass properties and mining conditions and determined by field measurements as well,
r – distance from the blast site to the monitoring point [m],
Q – amount of explosive [kg],
R – reduced distance, expressed as $R = \frac{r}{\sqrt[3]{Q}}$.

The Sadovskii equation is determined based on test blasting for the concrete working environment.

MODELS OF DETERMINING THE PARAMETERS OF EQUATION OF ROCK MASS OSCILLATION VELOCITY

In the equation (1) two parameters appear, K and n, which need to be determined for a specific work environment and specific blasting conditions.

Model 1 - determining the parameters by applying the Least Square Method

The Least Square Method is mainly used to obtain the parameters K and n which represents the most commonly model [3].

Model 2 – determining parameters by applying Simpson’s rule

In this paper, as model 2, we will use Simpson’s formula to approximate the values of the definite interval functions [3,4].

Let the values for the negative function $y = y(x)$ be known as $y = y_0, y_1, y_2, \ldots, y_{2m}$ for $x = x_0 + ih$, $i = 0,1,2, \ldots, 2m$; $h = \frac{x_{2m} - x_0}{2m}$. Then

$$\int_{x_n}^{x_{2m}} y(x)dx \approx \frac{h}{3}\left[y_0 + y_{2m} + 4(y_1 + y_3 + \cdots y_{2m-1}) + 2(y_2 + y_4 + \cdots + y_{2m-2})\right] \quad (2)$$

Formula (2) is Simpson’s formula for the finding approximative values of the definite integral function $y = y(x)$ in the given interval $[x_0, x_{2m}]$.

In order to verify this model, experimental blasting is performed. Ten explosions are registered during the blasting operation, with corresponding reduced distances and oscillation velocities.

For $R = R_i$ we have $v = v_i$; $i = 0, 1, 2, \ldots, 9$; which means that according to Equation (1) we have:

$$v_i = K \cdot R_i^{-n}, i = 0, 1, 2, \ldots, 9. \quad (3)$$

Equation (3) is written in the following form:

$$R_i^n = \frac{K}{v_i}, \quad (4)$$

from where we have:

$$\left(\frac{R_0 \cdot R_1 \cdot \ldots \cdot R_4}{R_5 \cdot R_6 \cdot \ldots \cdot R_9}\right)^n = \frac{v_5 \cdot v_6 \cdot \ldots \cdot v_9}{v_0 \cdot v_1 \cdot \ldots \cdot v_4}. \quad (5)$$

By logarithm operation of Equation (5) we get

$$n log \left(\frac{R_0 \cdot R_1 \cdot \ldots \cdot R_4}{R_5 \cdot R_6 \cdot \ldots \cdot R_9}\right)^n = log \left(\frac{v_5 \cdot v_6 \cdot \ldots \cdot v_9}{v_0 \cdot v_1 \cdot \ldots \cdot v_4}\right), \tag{6}$$

from where we find:

$$n = \frac{log \left(\frac{v_5 \cdot v_6 \cdot \ldots \cdot v_9}{v_0 \cdot v_1 \cdot \ldots \cdot v_4}\right)}{log \left(\frac{R_0 \cdot R_1 \cdot \ldots \cdot R_4}{R_5 \cdot R_6 \cdot \ldots \cdot R_9}\right)}. \tag{7}$$

According to Simpson’s formula (2) we have:

$$\int_{R_n}^{R_9} v dR \approx \int_{R_n}^{R_9} K R^{-n} dR \approx S_s, \tag{8}$$

where S_s represents the right side in formula (2).

$$S_s = \frac{h}{3}[y_0 + y_{2m} + 4(y_1 + y_3 + \cdots y_{2m-1}) + 2(y_2 + y_4 + \cdots + y_{2m-2})]. \tag{9}$$

How it is:

$$\int_{R_0}^{R_9} K R^{-n} dR = \frac{K}{n-1}\left(\frac{1}{R_0^{n-1}} - \frac{1}{R_9^{n-1}}\right) = \frac{K}{n-1}\left[\frac{R_9^{n-1} - R_0^{n-1}}{(R_0 R_9)^{n-1}}\right] \approx S_s, \tag{10}$$

from Equation (10) we find:

$$K = \frac{(n-1) \cdot (R_0 R_9)^{n-1}}{R_9^{n-1} - R_0^{n-1}} \cdot S_s. \tag{11}$$

By substituting K from Equation (11) into Equation (1) we get the following formula:

$$v = \frac{(n-1)(R_0 R_9)^{n-1}}{R_9^{n-1} - R_0^{n-1}} \cdot S_s \cdot R^{-n}, n \neq 1. \tag{12}$$

For $n = 1$ Equation (1) is reduced to:

$$v = \frac{S_s}{log R_9 - log R_n} \cdot R^{-1}, n = 1. \tag{13}$$

DEFINING STATISTICAL CRITERIA

For the above-mentioned models 1 and 2, based on experimental data, we have obtained equations, which make possible to determine the oscillation velocities of the rock mass v depending on the reduced distance R.

In order to assess the degree of connection between the reduced distance R and rock mass oscillation velocity v, we have used the curved line dependency index ρ [5,6].

METHODOLOGY OF RESEARCH

General characteristics of the work environment in Majdanpek open pit

Experimental researches were performed on copper ore at open pit Majdanpek, eastern Serbia [7]. By examining the physical and mechanical properties of the work environment, the following values were obtained: compressive strength $\sigma_p = 109\ [MPa]$; bending strength $\sigma_s = 19\ [MPa]$; tensile strength $\sigma_I = 13\ [MPa]$; cohesion $C = 19\ [MPa]$; strength coefficient $f = 11$; volume density $\gamma = 26\ [kN/m^3]$; angle of internal friction $\varphi = 50\ [°]$; porosity $p = 3.6\ [\%]$.

Method of blasting in Majdanpek open pit

The measurements of shocks resulting from blasting in Majdanpek open pit were performed during blasting using half-second electric detonators. Blasting of 10 boreholes with a depth of 0.5 m was performed. Delay time of initiation between boreholes was 0.5 s. It led to ten explosions and appropriate rock mass oscillation velocities.

The boreholes were arranged in a single line at the distance of 1 m. One cartridge of explosive amonex 1, with a weight of 0.1 kg, was placed in each borehole. The distance between measuring point and the first borehole was 5 m.

Seismographs are instruments used for seismic parameters observation. From seismographs maximum values for three oscillation velocity components can be recorded:

v_t – rock mass oscillation velocity horizontal transversal component,

v_v – rock mass oscillation velocity vertical component,

v_l – rock mass oscillation velocity horizontal longitudinal component.

Maximum, i.e. resulting rock mass oscillation velocity v_r was determined with the following formula:

$$v_r = \sqrt{v_t^2 + v_v^2 + v_l^2} \tag{14}$$

CALCULATION FOR PARAMETERS OF ROCK MASS OSCILLATION EQUATION IN THE OPEN PIT MAJDANPEK

The values of distance from the blasting point to the point of observation r, amount of explosive Q, calculated values of reduced distances R, registered values of rock mass oscillation velocities by components v_t, v_v, v_l and resulting rock mass oscillation velocities v_r for a total of ten explosions, are given in Table 1.

Table 1 *Review of blasting parameters and measurement results*

No	r [m]	Q [kg]	R	$v_t[{}^{cm}/_{s}]$	$v_v[{}^{cm}/_{s}]$	$v_l[{}^{cm}/_{s}]$	$v_r[{}^{cm}/_{s}]$
1	5.0	0.1	10.7722	0.700	0.900	1.150	1.6194
2	6.0	0.1	12.9266	0.300	0.925	1.150	1.5060
3	7.0	0.1	15.0810	0.255	0.540	0.850	1.0388
4	8.0	0.1	17.2355	0.260	0.350	0.650	0.7827
5	9.0	0.1	19.3899	0.245	0.325	0.550	0.6842
6	10.0	0.1	21.5443	0.155	0.240	0.405	0.4956
7	11.0	0.1	23.6988	0.205	0.275	0.440	0.5579
8	12.0	0.1	25.8532	0.110	0.200	0.285	0.3651
9	13.0	0.1	28.0077	0.085	0.190	0.230	0.3102
10	14.0	0.1	30.1621	0.090	0.130	0.200	0.2550

Based on data given in Table 1, the rock mass oscillation equation is calculated by the formula (1) – by the models 1 and 2. The calculation of the curve was carried out for values of reduced distances from $R = 10.7722$ to $R = 30.1621$. Thus, curve parameters were calculated enabling us to determine the equation of rock mass oscillation in the form of:

- Model 1

$$v_1 = 146.7047 \cdot R^{-1.8326} \tag{15}$$

Graphic review of the rock mass oscillation equation is shown in figure 1.

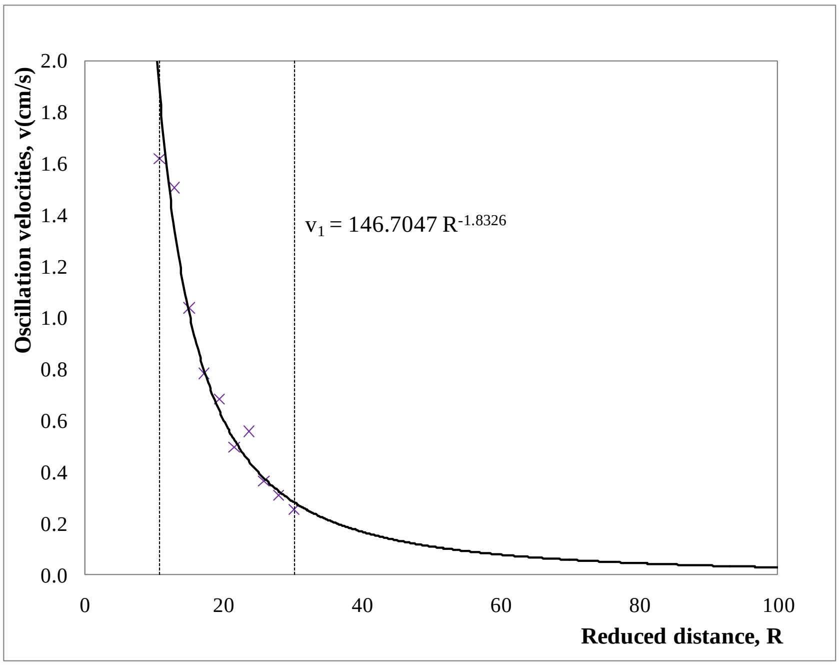

Figure 1 *Graphic review of oscillation velocity and reduced distance in the open pit Majdanpek*

- Model 2

$$v_2 = 166.3503 \cdot R^{-1.8568} \tag{16}$$

Based on the obtained equations for rock mass oscillation (15) and (16), it is possible to calculate values of rock mass oscillation velocities for the corresponding reduced distances for models 1 and 2.

Review of reduced distances R, registered rock mass oscillation velocities v_r, calculated rock mass oscillation velocities v_{i1}, v_{i2}, as well as the difference between registered and calculated oscillation velocities for models 1 and 2 are given in Table 2.

Table 2 *Review of recorded and calculated rock mass oscillation velocities for models 1 and 2*

No	R	$v_r[{}^{cm}/_{s}]$	$v_{i1}[{}^{cm}/_{s}]$	$v_{i2}[{}^{cm}/_{s}]$	$v_r - v_{i1}$	$v_r - v_{i2}$
1	10.7722	1.6194	1.8821	2.0148	-0.2627	-0.3954
2	12.9266	1.5060	1.3475	1.4361	0.1585	0.0698
3	15.0810	1.0388	1.0159	1.0787	0.0229	-0.0399
4	17.2355	0.7827	0.7954	0.8418	-0.0127	-0.0591
5	19.3899	0.6842	0.6410	0.6764	0.0432	0.0078
6	21.5443	0.4956	0.5284	0.5563	-0.0328	-0.0607
7	23.6988	0.5579	0.4437	0.4660	0.1142	0.0919
8	25.8532	0.3651	0.3783	0.3965	-0.0132	-0.0314
9	28.0077	0.3102	0.3267	0.3417	-0.0165	-0.0315
10	30.1621	0.2550	0.2852	0.2978	-0.0302	-0.0428

Based on the data in Table 2, a statistical analysis i.e. between the reduced distance R and rock mass oscillation velocity v:

- **for model 1**: $\rho_1 = 0.9730$ (there is a strong correlation between R and v, given in the formula (15)).
- **for model 2**: $\rho_2 = 0.9557$ (there is a strong correlation between R and v, given in the formula (16)).

CONCLUSION

In this paper, parameters K and n in the Sadovskii equation have been determined by way of two models in the given working environment. First model represents the usual method of the Least Squares, and the second model has been derived by applying Simpson’s rule. Thus, we obtained the adequate functions which represent rock mass oscillation velocity depending on reduced distance.

Comparing values of the recorded oscillation velocities of the rock mass with the corresponding calculated ones, it is visible that they are approximately the same. Calculated corresponding indices of curvilinear correlation show that between the reduced distance and the rock mass oscillation velocity there is a significant and very strong curvilinear relationship expressed by the functions obtained.

Based on the values obtained by statistical analysis we conclude that this new model can be used for equal reduces distances with application of Simpson’s rule, at experimental blastings.

ACKNOWLEDGEMENT

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COMPARISON OF THE INFLUENCE OF TEMPERATURE AND ULTRASOUND ON DEHP MIGRATION FROM PLASTIC PACKAGING INTO FOOD RECIPIENTS

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Abstract

Aim of this research was to determine the amount of migrated di-(2-ethylhexyl) phthalate (DEHP) from plastic packaging materials into food recipients with different fat content under the influence of increased temperature and ultrasound as a type of agitation. Investigated food products were infant formula, milk powder and water. The results were obtained using liquid-liquid extraction (LLE) followed by gas chromatography-mass spectrometry (GC/MS). The base peak ion of DEHP (m/z 149) was selected for further research and recording was performed in the selected ion monitoring mode (SIM). The response of the mass-selective detector (MSD) was linear for the considered range of DEHP concentrations, 0.25 – 2.50 µg mL^{-1}*. Obtained results showed that the amount of migrated DEHP from plastic packaging materials into dairy products was higher for dairy products with higher percentage of fatboth in the case of influence of temperature and in the case of combined effect of increased temperature and ultrasound agitation. The largest amount of DEHP migrated to infant formula, followed by milk powder and water. Since phthalates being just incorporated into plastics and not chemically bound to plastics, migration of DEHP was increased when ultrasound as type of agitation was applied.*

Keywords: DEHP, plastic packaging materials, migration, LLE, GC/MS

INTRODUCTION

Phthalates are compounds that are widely used for plasticizing polymers to produce suitable plastic material with specific properties – soft, flexible, resistant. As such, plastic can be used in production of toys, medical equipment and many household products, including plastic wrap, plastic containers, and other things made of vinyl or PVC.The most commonly used phthalate is di-(2-ethylhexyl) phthalate (DEHP) and plastics can contain from 1 to 40% of this phthalate [1]. Since phthalates are not chemically bound to the plastics they are continuously released into the air, food or liquid. Human are exposed to the effects of phthalates in various ways: through ingestion, absorption and inhalation. Animal studies show a harmful effect of phthalates, phthalates represent endocrine disruptors and affect reproduction, induce cancer, cause liver disorders [2,3]. Due to easy release of phthalates in the environment and because of their negative effects, it is of great importance to constantly analyse the food and drink on the phthalate content. It is also important to determine the conditions under which phthalates migration takes place.

In this paper, the effect of temperature and ultrasound on the migration of DEHP from plastic packaging into food recipients with different fat content were investigated.

MATERIALS AND METHODS

Reagents and materials

HPLC grade *n*-hexane was purchased from Sigma–Aldrich (St. Louis, MO, USA). Di(2-ethylhexyl) phthalate (DEHP) was purchased, in the highest available purity, from Sigma–Aldrich (St. Louis, MO, USA). Dibutyladipate (DBA) was purchased from Fluka (Buchs, Switzerland) and used as an internal standard.

Water from a Milli-Q system (Millipore, Bedford, MA, USA) was used. Dialysis bag (Baxter, USA) was used. Milk powder and infant formula were purchased from commercial manufacturers offered at the Serbian market.

Calibration standard series with DEHP concentration range 0.25, 0.50, 1.00, 1.50 and 2.50 µg mL^{-1} with DBA, as the internal standard, at a concentration of 1 µg mL^{-1}, was obtained by dilution of working solutions of DEHP in *n*-hexane.

GC-MS analysis

Gas chromatograph 6890 (Hewlett-Packard) equipped with a mass selective detector (MSD) 5973 (Agilent, USA) and a DB-5 MS capillary column (30 m × 250 mm × 0.25 mm) (Agilent, USA) was used forDEHP determination. The gas chromatograph was operated in the split less injection mode. The oven temperature was programmed from 60 °C (1 min) to 220 °C (1 min) at a rate of 20 °C min^{-1} and then to 280 °C (4 min) at a rate of 5 °C min^{-1}. Helium was the carrier gas (1.0 mL min^{-1}) and the inlet temperature was 250 °C. The operating temperature of the MSD was 280 °C with the electronic impact of 70 eV. The MSD was used in the single ion-monitoring mode (SIM) at *m/z* 149 for DEHP and ion *m/z* 185 for DBA. The identification and quantification of DEHP was based on the relative retention time, the presence of target ion and its relative abundance.

Sample preparation

The following dairy products with different fat content were used as food recipients: infant formula (fat content 22.8 %) and powdered milk (fat content 20 %). Also, phthalate migration was carried out in water as food without fat. Milk powder (45 g) and infant formula (45 g) were dissolved in 1 L of water from a Milli-Q system, respectively, following to the producer instruction. The dialysis bag was used as plastic packaging material with the high content of DEHP. This reliable source of phthalate contains about 35.8 % of DEHP compared to the total weight [4].

Dairy samples (35 mL) and the exact weight of the dialysis bag (1 cm^2) were set in the vessel and heated to a temperature up to 60 °C, for 60 min. In parallel, the set of samples were exposed to temperature up to 60 °C, for 60 min but with agitation in ultrasonic bath. Pieces of dialysis bag, were subjected to repeated migration tests into dairy products, providing total heating time of 60 hours. The experiment was performed until the plateau was reached on the curve $m = f(t)$, where m is mass of the migrated DEHP and t exposure time.

After each heating, cooling and filtering, liquid-liquid extraction (LLE) with *n*-hexane (20 mL) as extraction agent was done. LLE conditions were: 15 minutes of manually shaking and 30 minutes of extraction agitation on the ultrasonic bath. After clarification and separation of two layers, the *n*-hexane layer concentrated to the volume of 1 mL. Addition of DBA was performed so that the concentration of DBA was 1 µg mL^{-1}. Thus, prepared samples were immediately analysed by GC-MS. All analyses were performed in triplicate and quantification on GC-MS was repeated twice.

RESULTS AND DISCUSSION

GC/MS acquisition

The obtained GC/MS chromatogram shows good separation of DEHP and DBA with retention times for DBA and DEHP 9.990 and 18.426 min, respectively.Figure 1 shows the linear analytical curve obtained for DEHP within concentration range 0.25 – 2.5 µg mL^{-1} with correlation coefficient of $R^2 = 0.990$ and linear equation $y = (505228 \pm 9612)\,x - (8473 \pm 13465)$. The limit of determination (LOD) and the limit of quantification (LOQ) values, calculated from the signal/noise ratios which were multiplied with the factor 3 and 10 respectively [5], for DEHP are 0.04 µg mL^{-1} and 0.12 µg mL^{-1} with relative standard deviation (RSD) value 3.6 % (n = 3).

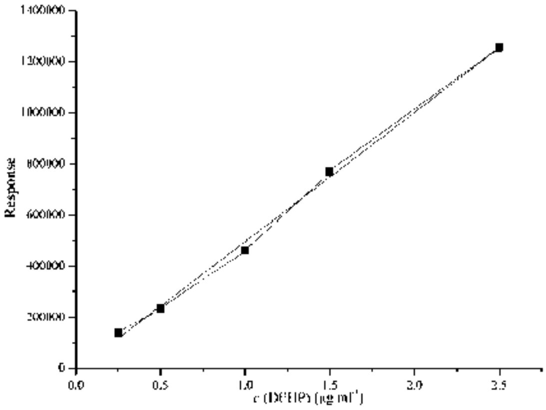

***Figure 1** The analytical curve for DEHP within concentration range 0.25 – 2.5 µg mL^{-1}*

Comparison of influence of temperature and ultrasound on the migration of DEHP

The aim of this study was to compare the effect of temperature and ultrasound on the repeated migration of DEHP from plastic packaging material into food recipients with different fat content. Obtained results, mass of migrated DEHP and percentage of migrated DEHP, were given in Table 1. By comparing the various food receiving matrices, the food with the highest fat content was the best recipient for the migrated DEHP, because DEHP is a non-polar molecule and has a greater tendency to dissolve in a non-polar medium. For this reason, the best recipient for migrated DEHP was the infant formula (fat content 22.8%), followed by milk powder (fat content 20%) and water (fat content 0%). The same trend of DEHP migration was observed in cases when the migration was carried with increasedtemperature, as well as by influence of temperature assisted with ultrasound agitation. The maximal amount of migrated DEHP under the influence of increased temperature was 601.29 µg, 384.66 µg and 135.67 µg for the following food recipients, infant formula, milk powder and water in the order. The amount of migrated DEHP under the influence of ultrasound-assisted migration, followed the same trend, only the maximum amount of migrated DEHP was higher for all food recipients, due to the additional influence, as shown in Figure 2. The obtained data show that ultrasound-assisted migration had greater effect on the migration of DEHP then effect of temperature alone.

Table 1 *Migration of DEHP into different food recipient influenced by (1) temperature and (2) temperature assisted with ultrasound agitation*

	Food receiving matrix	Mass of dialysis bag (g)	Mass of DEHP in dialysis bag (g)[4]	Maximal amount of migrated DEHP (µg)	Percentage of migrated DEHP (%)
(1)	Water	1.7410	0.6233	135.67±1.23	0.02
	Milk powder	1.6200	0.5800	384.66±3.61	0.07
	Infant formula	1.4560	0.5212	601.29±2.73	0.12
(2)	Water	1.4709	0.5266	292.16±1.37	0.06
	Milk powder	1.6049	0.5745	1170.33±1.96	0.20
	Infant formula	1.4502	0.5192	1323.36±1.87	0.25

a) *b)*

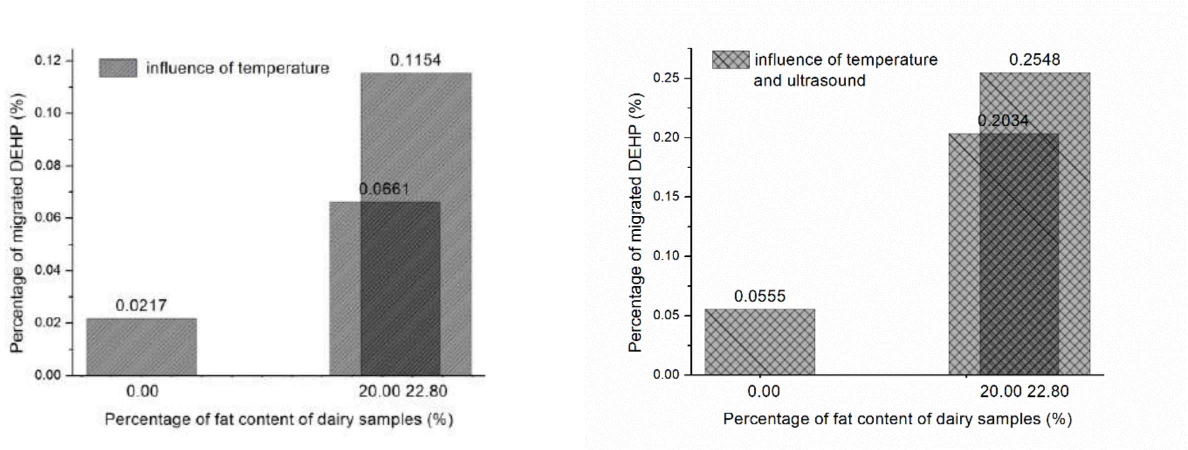

Figure 2 *The effect of temperature and ultrasound on DEHP migration into food recipient with different fat content*

When it comes to the exposure time of a given plastic packaging material to a certain effect, it was observed that with increasing of exposure time, the mass of migrated DEHP also increases. The mass increases linearly to a certain point, after which saturation was reached. A saturation indicated a plateau on the curve *m=f(t)* where *m* is mass of migrated DEHP and *t* is exposure time, and this plateau showed that the migration no longer occurred due to the application of the corresponding effect (Figure 3). Maximal amount of migrated DEHP was reached faster due to the combined effect of increased temperature and ultrasound compared with applied increased temperature alone. When water was a recipient, ultrasound application reduced exposure time from 2500 min to 1450 min, plateau was reached almost 1000 min faster (Table 1). The time to achieve saturation, when the ultrasound was applied was shorter than when only temperature was applied for about 200 minutes for milk powder and infant formula, as recipients. Expected reason was that water, as polar molecule, only "washed" molecules of DEHP from plastic surface. On the other hand, non-polar milk samples can dissolve DEHP from all plastic material and for this is necessary longer period.

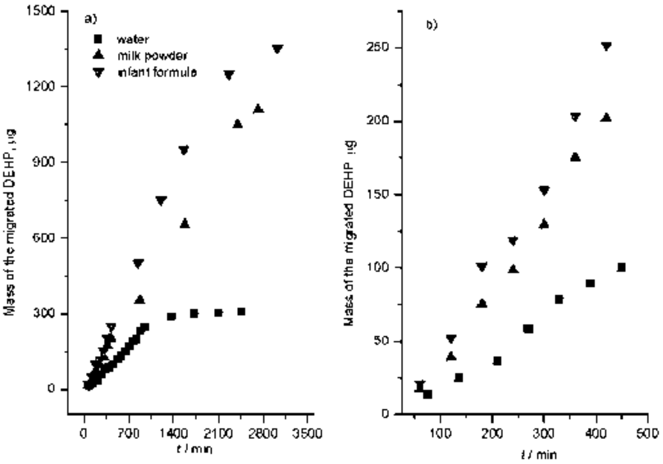

***Figure 3** Mass of the migrated DEHP under the influence of ultrasound a) in time period of 3500 min and b) in time period of 450 min*

In a first time period (450 min) correlation between mass of migrated DEHP and exposure time was almost linear and in this period about 30 % of the total migration was taken place under the both influences. But, taking any time period during the DEHP migration under both influences, a higher mass of DEHP was always obtained, under the influence of ultrasound. This increased efficiency of DEHP migration was a consequence of the power and energy provided by oscillations produced by ultrasound. In this way, the plastic pieces of the dialysis bag came in better contact with the sample, the sample under the influence of the energy of the ultrasound infiltrates deeper into the plastic, and soils DEHP in a larger quantity.

CONCLUSION

Obtained data shows that DEHP migration from plastic packaging materials into food products depends on fat content of these products, increased temperature and applied ultrasound as an adjunct to increased temperature. In both cases, when temperature alone was applied and when effects of temperature and ultrasound was combined, amount of migrated DEHP decreases by following order: infant formula, powdered milk, water, indicating the effect of fat content of dairy products. The highest DEHP migration occurred into dairy product with highest fat content. The influence of combined increased temperature and ultrasound on the DEHP migration from plastic packaging materials into dairy products is higher than the influence of temperature, for all dairy products. By comparing these effects, conclusion is that ultrasound disrupts structure of plastic material and accelerates diffusion and release of phthalate from plastic packaging materials into different recipient medium.

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DETERMINATION OF PHTHALATES IN PVC MEDICAL DEVICES BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

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Abstract

The aim of this work was to determine phthalates in PVC medical devices using the FTIR spectroscopy, as a rapid pre-screening test. Phthalates were isolated from the PVC samples by tetrahydrofuran and then plastic is precipitated by the addition of an excess of methanol. The FTIR spectrum of PVC samples were recorded and on the basis of specific absorbance bands occurring in the spectra, the existence of phthalates in the PVC samples was checked. The characteristic adsorbance bands for phthalates in FTIR spectrum were at 743 cm^{-1}, 1579 cm^{-1} and 1599 cm^{-1}. Based on the intensity of absorption for three investigated PVC samples, it could be concluded that tubing for infusion set contains the most phthalates, following by tubing for dialysis set and dialysis bag, respectively. The absence of these characteristic peaks in the FTIR spectra obtained by the precipitation method demonstrated the effectiveness of this method in the removal of phthalates. Comparison of obtained amount of phthalates in tetrahydrofuran/methanol solution, PVC precipitate and in PVC sample showed that FTIR method can be used as a rapid pre-screening test for qualitative determination of phthalates.

Keywords: phthalates, PVC, FTIR, precipitation

INTRODUCTION

Phthalates are the esters of 1,2-benzene dicarboxylic acid that are formed by the addition of an aliphatic or aromatic alcohols to phthalic anhydride in the presence of a catalyst. The resulting ester groups are in the *ortho-* position. Phthalates are a family of chemicals used to make plastics (primarily polyvinyl chloride - PVC) more flexible, elastic and soft, and for this reason phthalates are also called plasticizers. Because of that, phthalates are used in hundreds of products in households, hospitals and other spheres. Since phthalates are not chemically bonded to PVC, they can leach out of plastic under appropriate conditions. The consequences of phthalate migration from PVC are: the plastic becomes rigid and brittleand the phthalates reaches the environment. Due to their properties (non-polar molecules, easily soluble in fats), they are easily dissolved in food, dairy products, beverages, blood, urine, *etc*. This way human are exposed to the harmful effects of phthalates. Research has shown that phthalates cause infertility in men, cause testicular cancer, and affect the secretion of glands, thereby classifying phthalates as endocrine disruptors [1–3].

In order to determine phthalates in various media due to their harmful effects, different methods have been developed, among which gas chromatography-mass spectrometry (GC/MS) is the most common used method for this analyse [4]. Phthalate structure with the ester groups in the *ortho-* position has great importance for the further phthalates determination by Fourier Transform Infrared Spectroscopy (FTIR). FTIR method as non-destructive, reliable, rapid, not expensive, without the need of special sample preparation, can be considered as significant in the pre-screening for phthalate determination in PVC [5].

The aim of this work was the qualitative determination of phthalates in medical devices, made of PVC. By removing phthalates from the plastic packaging materials by the dissolution/precipitation method, the phthalate content qualitatively checked in phthalates free – plastic and phthalate plastic by FTIR technique, while phthalate content in THF/methanol system was checked by GC/MS technique.

Comparison of obtained amount of phthalates in tetrahydrofuran/methanol solution, PVC precipitate and in PVC sample showed that FTIR method can be used as a rapid pre-screening test for qualitative determination of phthalates.

MATERIALS AND METHODS

Chemicals and reagents

The tetrahydrofuran (THF) with HPLC purity was purchased from Fischer scientific (USA). The methanol with HPLC purity was purchased from Carlo Erba (France).

Medical devices made of PVC was taken from local Clinical Center Niš, Serbia. Dialysis bag with coupled dialysis tubing which constitute a set for peritoneal dialysis (Baxter, USA) and tubing for infusion set (Mediaset, Spain) were used for analysis.

FTIR technique

FTIR spectra were scanned on a laser Fourier Transform Infrared Spectroscope (BOMEM Hartman & Braun — Michelson MB series 100).

The manual hydraulic press (Graseby Specac) was used to create pellet samples for further analytical determination by analytical equipment such as FTIR.

Amalgamator (Wig-L-Bug) was used for mixing precipitates from this analysis with appropriate substance.

Gravimetric technique

Methanol was used to produce the PVC precipitate from THF solution. The centrifuge (Jouan C4I Benchtop, Termo Fisher) was used to separate precipitates from the aliquot. Mass of PVC precipitate after drying was measured on the analytical balance with accuracy of ±0.00001 g.

Sample preparation

Dissolving PVC sample in THF

Accurately weighed mass of PVC medical equipment (0.01 g) was dissolved in 4 ml of THF. This was the first step in qualitative phthalates determination using the FTIR instrument. Dissolution of PVC was accelerated by heating, with caution not to evaporate THF. The next step was to evaporate THF solution in order to form a polymer film of PVC. The formed Phthalate-PVC polymer (PPVC) filmon the evaporating dish was mounted on an IR cell holder on FTIR instrument and FTIR spectrum was scanned. Each analysis was repeated three times.

Precipitation of PVC by methanol

The same mass of the sample (0.01 g) as in the previous experiment was dissolved in 4 ml of THF. After dissolution, 10 ml of methanol was added to form PVC precipitate without phthalates (P-free PVC), leaving dissolved phthalates in the supernatant above the precipitate. The P-free PVC precipitate was separated by centrifugation (3500 rpm). In order to confirm the complete release of phthalates from PVC samples by THF/methanol, the analysis was conducted in three directions:

(1) P-free PVC precipitate (pre-dried at 80°C in the oven) was mixed with KBr to form pellets using manual hydraulic press and amalgamator and scanned on FTIR instrument.

(2) P-free PVC precipitate was dissolved in THF. After evaporation of THF, the obtained polymer film was scanned on FTIR instrument.

(3) Evaporation of the dissolved phthalates supernatant into evaporating dish was done. Obtained disk was gravimetrically measured. The weight of the disk represented mass of the phthalates in PVC. In this way the mass percentage of phthalates in PVC samples was calculated.

Safety precautions and reduction of sample contamination by phthalates

Due to the volatility and flammability of the used solvents, care must be taken. Evaporation of THF must be done in the digester due to the toxicity of THF. Only glassware equipment was used, because THF dissolves PVC and in order to reduce laboratory phthalates contamination. All glassware was washed with soap, tap water and ultrapure water, then washed with acetone and *n*-hexane and dried at 200 °C in the oven for 4 hours [6].

RESULTS AND DISCUSSION

Characterization of FTIR spectra of PVC samples

Given that the phthalates aromatic ring was substituted in the *ortho*- position, the expected absorbance band at 743 cm^{-1}, characteristic of that group appeared on the FTIR spectrum. This strong absorbance band at 743 cm^{-1} identifies the phthalates. On the FTIR spectrum doublet bands at 1599 cm^{-1} and 1579 cm^{-1} appeared as a result of the aromatic ring quadrant stretching vibration and also were useful for infrared analysis of phthalates. Frequency and intensity of these bands depends on the aromatic ring substitution. Other useful and characteristic FTIR spectra absorption bands for PVC are: 2960 cm^{-1} (for -C-H bond), 1718 cm^{-1} (for the phthalate ester), 1450 cm^{-1} (for $-CH_2-$ and $-CH_3$), 1278 cm^{-1} (for $-CH_2-$), 1073 cm^{-1} (for $-CH_3$). In Figure 1 FTIR absorption spectrum of dialysis bag was given.

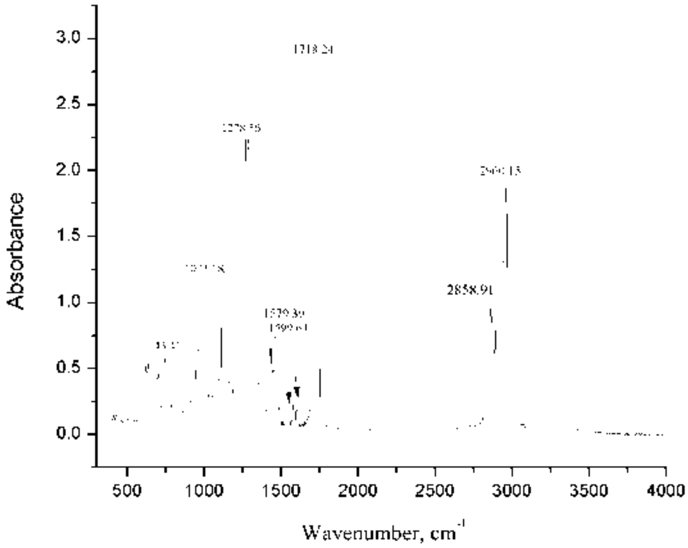

Figure 1 *The FTIR spectrum of dialysis bag with qualitative bands identified*

In Figure 2 two regions of the FTIR spectra of the investigated medical devices were given, region from 730 to 760 cm^{-1} and region from 1590 to 1610 cm^{-1}. Based on the graphs *Absorbance=f (Wavelength)*, it can be concluded which PVC sample contains the most phthalates. The tubing for infusion set contains the most phthalates, followed by tubing for dialysis set and dialysis bag, respectively.

a) *b)*

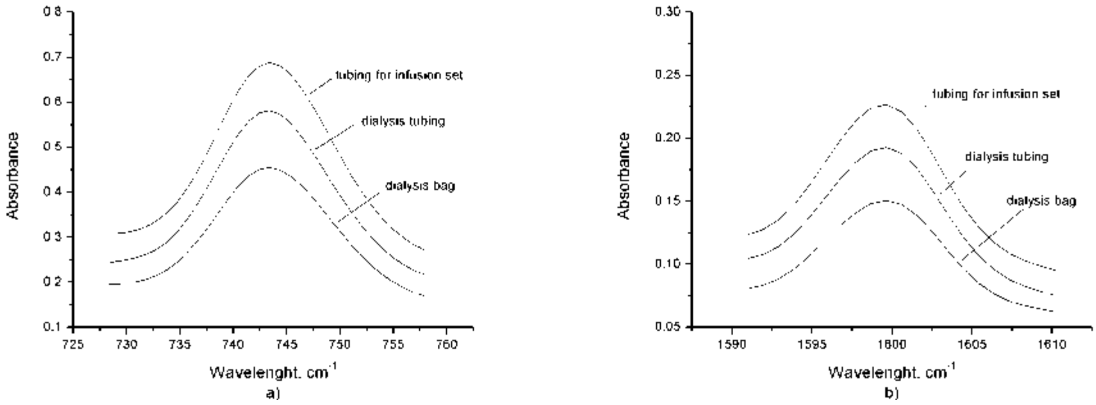

Figure 2 *The FTIR spectrum of PVC samples: a) region 730-760 cm^{-1} b) region 1590-1610 cm^{-1}*

Characterization of FTIR spectra of P-free PVC sample

Prepared the KBr pellets, were scanned on FTIR instrument to confirm complete release of the phthalates into methanol-THF aliquot and given spectra show absence of characteristic absorbance bands for phthalates at 743 cm^{-1}, 1579 cm^{-1} and 1599 cm^{-1}. In Figure 3 FTIR spectrum of KBr pellet was given. The absence of these absorbance bands showed that the precipitation method by methanol completely released phthalate from PVC samples. The same FTIR spectrum was obtained by recording a polymer film obtained by evaporation of the dissolved P-free PVC precipitate in THF.

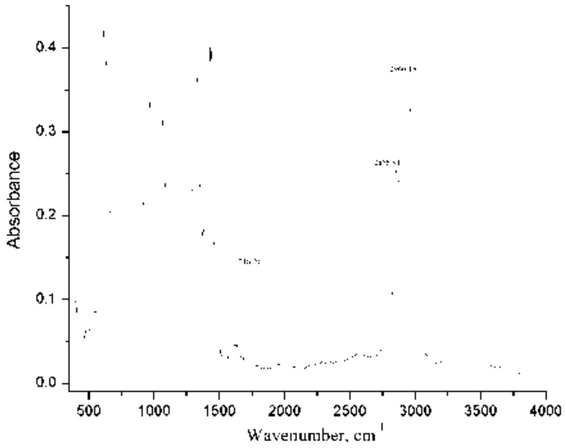

***Figure 3** The FTIR spectrum of dialysis bag without phthalates*

Determination of dissolved phthalates in methanol-THF supernatant

Analysis of methanol-THF supernatant given the following results. The weight of polymer film obtained after evaporation of THF/methanol was measured. The weight of this polymer film represented the total mass of phthalates in the sample. Obtained calculated mass percentage of phthalates in investigated PVC samples was given in Table 1.

***Table 1** Mass % of phthalates of PVC sample*

Sample	Mass % of phthalates
Tubing for infusion set	25.96±0.53
Tubing for dialysis set	20.95±0.41
Dialysis bag	19.2±0.36

Qualitative comparison of obtained polymer films

In this investigation two different polymer films were obtained. The PPVC polymer film with phthalates, obtained by evaporation of THF from the THF solution of PVC, was elastic and flexible, because phthalates have the function of plasticizers in PVC plastic. The P-free PVC polymer film, obtained by evaporation of THF-methanol, was rigid and brittle, which was a consequence of removal of phthalates from the PVC sample.

CONCLUSION

Considering the impact of phthalates on human health, determination of phthalates in various food, beverage, plastic packaging, medical equipment, etc. is of great importance. Given that determination methods generally are expensive and complicate, it is important to develop a method that is fast, reliable and inexpensive. Such a method uses FTIR technique described in this paper. The disadvantage of this method is that it is not specific method, because the obtained characteristic absorbance band at 743 cm^{-1} and absorbance doublet at 1579 cm^{-1} and 1599 cm^{-1} in FTIR spectra are characteristic of each phthalate. However, this method is useful, because it can be used in pre-screening, after which the GC/MS analysis can be performed.

Also, the precipitation method was used in this work to remove phthalates from plastic, and evidence of the removed phthalates was provided by the FTIR method. The free phthalates-plastic film was brittle and rigid, unlike the phthalate-containing plastic that was flexible and elastic. Comparison of obtained amount of phthalates in tetrahydrofuran/methanol solution, PVC precipitate and in PVC sample showed that FTIR method can be used as a rapid pre-screening test for qualitative determination of phthalates.

ACKNOWLEDGEMENT

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REDUCTION OF DRILLING DUST USING DRY DUST COLLECTION SYSTEMS IN SURFACE BLASTING OPERATIONS

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Abstract

Drilling and blasting are still the most effective and cheapest methods of the exploitation of solid mineral raw materials in surface mines. The quality of drilling process reduces the drilling costs and increases the productivity. However, drilling dust can be a serious health hazard, not only to operators, but also to worksites in general. Respirable dust generated by drilling operations can lead to high exposure levels for the drill operator, drill helper, and other personnel in the local vicinity during operation. This negative effect of every drilling process in surface mines cannot be avoided and should be controlled by the efficient dust suppression or collection systems. Reduction of dust during drilling operation is carried out to improve work conditions and to increase productivity. The paper mostly deals with dry dust collection systems.

Keywords: dust, drilling, collector, rock blasting, surface mine

INTRODUCTION

The drilling process is applied in surface mines for blasting operations which are conducted for the fragmentation of rock. The drilling methods that are mostly used in surface mines are rotary percussion drilling and rotary drilling with rolling tricone bits. Rotary percussion drilling is based upon the combination of the following [1]:

– *Percussion.* The impacts produced by repeated blows of the piston generate shock waves that are transmitted to the bit through the drill string (in top hammer) or directly upon it (down the hole).

– *Rotation*. With the movement, the bit is turned so that the impact is produced on the rock in different positions.

– *Feed or thrust load.* In order to maintain the contact of the drill bit with the rock, a thrust load or feed force is applied to the drill string.

– *Flushing*. Flushing removes the drill cuttings from the blasthole.

Rotary drilling with rolling tricone bits is the most widely used method for drilling large diameter blastholes in large surface mining operations [2]. This drilling method is applicable to a wide range of soft to hard rock materials. Rotary blasthole drill rigs have large size and high weight and their masts are sturdy enough to withstand high forces generated by the pulldown mechanism and stresses due to vibration that develop in the rotary head. Rotary rock drills essentially comprise a power source; a string of pipes which transmit the load; and rotation and flushing air supplied to a bit with steel teeth or tungsten carbide inserts, which in turn acts upon the rock [1,2]. The components in a rotary blasthole drill string are a tricone bit, stabilizers, drill pipes, shock absorbers and crossover subs [2,3].

Drilling dust poses a serious health hazard, not only to operators, but also to worksites in general [4]. Respirable dust from drilling operations can lead to high exposure levels for the drill operator, drill helper, and other personnel in the local vicinity during operation [5]. Silicosis can be caused by stone dust containing quartz particles with a granular size less than 0.005 mm. In view of this health risk, many countries have introduced stringent standards and measures concerning dust separation in rock drilling [4].

Operator cabs are increasingly becoming an acceptable method for protecting the drill operator from respirable dust generated by the drilling operation. However, the protection provided, is only available to the personnel inside the cab. Other personnel working in the vicinity of the drilling operations, the drill helper, shotfirer, mechanics, etc., cannot be protected in this manner [5].

The empirical formula for determining the dust emission in drilling of boreholes is presented in the form [6]:

$$E = i\, V_0\, d_0^2\, \rho\, f\, K_1\, K_2\, K_3,\ (mg/s) \qquad (1)$$

where:

E – dust emission in drilling (mg/s), i – coefficient taking the drilling and cleaning method of the borehole ($i = 155 \cdot 10^{-8}$ in normal drilling and borehole washing with water, $i = 90 \cdot 10^{-8}$ when the water softeners are added, $i = 16 \cdot 10^{-8}$ at optional drilling and borehole washing with water), V_o – drilling speed (mm/s), d_o – diameter of borehole (mm), ρ – rock density, f – strength coefficient according to Protodjakon, K_1 – coefficient of simultaneous operation for multiple drilling hammers ($K_1 =1$ for one drilling hammer, $K_1 =1.7$ for two drill hammers, $K_1 =2.7$ for three drilling hammers, for drillers in the open pit exploitation $K_1 =1$), K_2 is the coefficient of inclination angle of borehole ($K_2 =1$ for horizontal, $K_2 =1.3$ for inclined and vertical upwards, $K_2 =0.7$ for inclined and vertical downwards), K_3 – coefficient taking into account the impact of the type of hammer drill or drill ($K_3 =1.3$ for working with manual drilling hammer, $K_3 =1$ for drilling hammer or chisel on rack, $K_3 =0.5$ for pivot drill hammer or hydraulic pushing drilling accessories).

REDUCTION OF DRILLING DUST

The reduction of dust during drilling is carried out to improve work conditions and to increase productivity. Other technical and economic reasons that justify the elimination of dust during drilling are [1]:

– lower maintenance of the motor–compressor equipment, giving higher mechanical output. Uncontrolled drilling dust can clog motors and filters on adjacent machinery, promoting faster wear through abnormal friction and overheating. This can lead to more servicing and repairs, and a costly decline in production [4];

– higher drilling rate (about 2 to 10% more), due to the fact that the cuttings are removed from the blasthole, therefore avoiding their regrinding. Besides, the operator can be closer to the controls of the machine, increasing the efficiency and control of drilling;

– lower drilling costs because of higher output as well as less wear on the bits.

There are two basic methods for controlling dust on drills [5]:

– wet suppression system or,

– dry cyclone/filter type collector.

Wet systems operate by spraying water into the bailing air as it enters the drill stem. Dust particles are conglomerated as the drill cuttings are bailed out of the hole [5].

Dry collectors operate by withdrawing air from a shroud or enclosure surrounding the area where the drill stem enters the ground. The air is filtered and exhausted to the atmosphere. When dust controls are implemented effectively at drilling operations, both wet suppression and dry collection systems can achieve good dust control efficiency [5].

DRY DUST COLLECTION SYSTEMS

Dust collectors basically consist of:

– Suction head that is placed on the surface at the blasthole collar where the dust is aspirated and sent through the suction hose to the separation and filter unit [1];

– System of separation and filtering which is carried out in two stages: first with cyclone, where bigger particles and most of the dust is separated by means of centrifugal force, and secondly, the filtering is carried out that retains the dust particles under 5 µm;

– Depression or partial vacuum system, with a fan placed behind the filter unit that is operated by hydraulic or electrical energy, or pneumatically on occasions.

Medium– to large–diameter drill dust collection systems

Typical dry dust collection system on a medium– to large–diameter drill is shown in Figure 1. Drill dust is generated by the bailing air, which is compressed air that is forced through the drill steel out the end of the drill bit and used to flush the cuttings from the hole. In a properly operating collection system, these cuttings are contained by the drill deck and shroud located over the drilling area. This dusty air from underneath the shrouded drill deck is removed by the dust collector system [5]. The collector is composed of an exhaust fan and filters which filter the air from underneath the shroud area. It is generally self–cleaning, using compressed air to pulse through the filters at timed intervals to clean them and prevent clogging. The filtered fine–sized material then drops out the bottom of the collector to the collector dump [5].

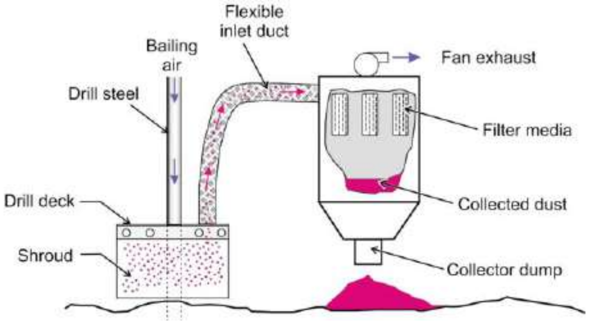

***Figure 1** Typical dry dust collection system on a medium– to large–diameter drill [5]*

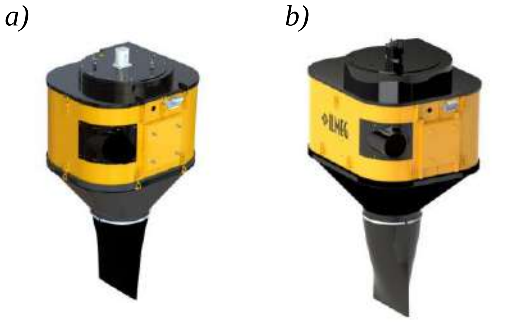

***Figure 2** Hydraulic ILMEG dust collectors a) ILMEG X–150; b) ILMEG X–200 [7]*

The ILMEG X–150 and X–200 hydraulic dust collectors (Figure 2) are used in rock drilling applications for improved productivity and working conditions with regards to dust [7]. A typical application is for blast hole drilling with top hammer rock drills or down the hole rock drills. The filter cleansing function is carried out with reversed air [7].

Table 1 *Technical specification of ILMEG hydraulic dust collectors [7]*

Specification	*ILMEG X–150*	*ILMEG X–200*
Max hole size (mm)	165	203
Filter area (m²)	16	24
Number of filters: 4	4	6
Oil flow requirement (l/min)	44	76
Oil pressure requirement (bar)	200	160
Width x depth x height (mm)	1078 x 897 x 1133	1263 x 1065 x 1133
Approx. weight (kg)	220	350
Filter cleansing i–clean:	Reversed air through filters in sequences while drilling	Reversed air through filters in sequences while drilling
Rec. working pressure (bar)	7	7

Dust collection system used for small– to medium–diameter drill rigs

A dust collection system used for small– to medium–diameter surface crawler drills is shown in Figure 3. The difference from the large diameter drill dust collection system is that this system collects all the drill cutting material, sends it to a large separation cyclone on the drill boom to drop out the large diameter material, and then sends the remainder to the dust collector at the back of the drill where the fine–sized material is discharged [5].

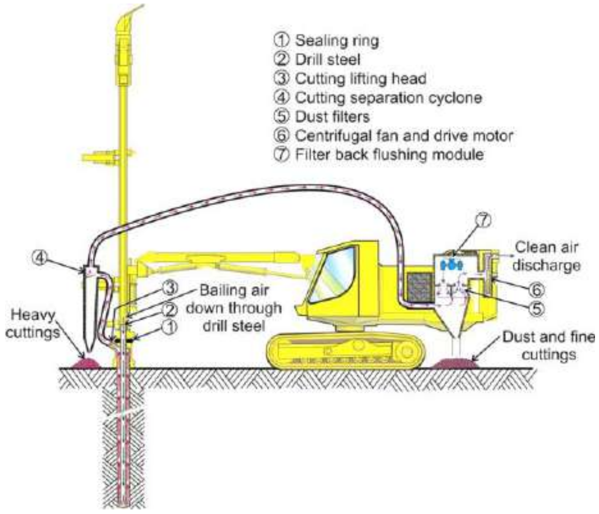

Figure 3 *Dust collection system used for small– to medium–diameter surface crawler drill rigs [5]*

Dust collection system on surface crawler drill rig FlexiROC T35

FlexiROC T35 (Figure 4) is flexible and versatile tophammer drill rig for hole diameter: 64–115 mm, developed and designed for high performance in demanding construction applications. It can also be applied in small and medium size quarries [8].

Figure 4 *Drill rig FlexiROC T35 [8]*

Figure 5 *Dust collection system on surface crawler drill rig FlexiROC T35 a) heavy cuttings; b) dust and fine cuttings*

DCT dust collectors (Figure 5) operate via a two–stage filtration process. A coarse separator isolates 90% of dust in the first stage, thus reducing the risk of overload of the filters. Then the remainder is separated in secondary filters to get rid of the highly injurious, microscopic stone dust of particle size less than 0.005 mm [4]. DCT dust collectors [4] have very few moving parts. The drive ejector has been positioned behind the filters, creating a partial vacuum in the entire system. As a result, there is no dust leakage, even in the event of a suction hose becoming damaged. The drive ejector operates continuously in clean, filtered air, eliminating risk of erosion by drill dust. Steady, high airflow speed in the suction hose counteracts blockage of the suction hose. Compressed air to the ejector does not pass by way of the filters, reducing their load [4].

Table 2 *Technical specification of drill rig FlexiROC T35 [8]*

Main Components		**Dust collector DCT 110**	
Track frames with single grouser pads and cleaning holes	Aluminium profile feed beam	Filter area	11 m^2
Hydraulic track oscillation and two speed traction	Hydraulic cylinder feed system	Suction capacity at 500 mm wg	560 l/s
Atlas Copco screw type compressor	Carousel type rod handling system, 1 + 7 rods	Suction hose diameter	127 mm
Operator’s cabin, ROPS and FOPS approved	Hydraulic rock drill	Cleaning air pressure, max	7.5 bar
LED work lights	Dust collection system	Cleaning air consumption	2–4 l/pulse
Folding boom system	Dust pre separator	Number of filter elements	11 pcs

Field experience has shown that, using DCT dust collectors, nett penetration rates can improve by 5–10%. This is partly because the drill cuttings are removed from the drill hole, reducing recrushing, and improving bit performance [4].

DCT dust collectors remove virtually 100% of all drilling dust, and, most important of all, separate the microscopic stone particles.

CONCLUSION

The drilling process is applied in surface mines for blasting operations which are conducted for the fragmentation of rock. The accuracy of drilling process according to design drill pattern reduces the drilling costs and increases the productivity.

However, drilling dust poses a serious health hazard, not only to operators, but also to worksites in general. Reduction of drilling dust can be done by wet suppression system or dry cyclone/filter type collector. Dust collectors offer effective, reliable dust separation with operational simplicity, while improving the working environment and increasing productivity.

ACKNOWLEDGEMENT

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DETERMINATION OF PARACETAMOL USING CARBON BASED SENSOR ELECTRODES

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Abstract

Paracetamol (acetaminophen, APAP) is commonly used analgesic and antipyretic medication. Hence, it is interesting to evaluate its amounts in commercial tablets and syrups, as well as in human body fluids. As a consequence of its widespread application it is found in the environment as well, where it presents a potential risk and also should be monitored. One of the possible approaches includes application of various electrochemical methods. It is presented within the paper that carbon based electrodes can be efficiently used for its determination. These methods can include expensive electrodes such as glassy carbon electrodes or modifications of other types of carbon electrodes and on the other side pencil graphite electrodes that are low cost variation, and equally adequate. Due to the facts that they are cheap and easy to work with the pencil graphite electrodes receive increasing attention.

Keywords: paracetamol, pencil graphite electrode, modified carbon electrodes, electrochemical techniques, voltammetry.

INTRODUCTION

Paracetamol (also known as acetaminophen and APAP), which structure is presented in Figure 1, is a pharmaceutical compound very often used as analgesic and antipyretic medication. Hence, there is interest to provide efficient techniques for its qualitative and quantitative determination, either to test the accuracy of the amounts present in pharmaceuticals or to monitor its presence in human fluid samples and in the environment.

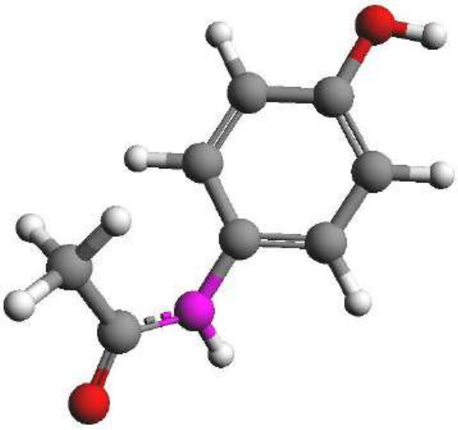

Figure 1 *Structure of paracetamol*

There are numerous studies [1–5] that distinguish pharmaceuticals, amongst which is paracetamol one of the most frequent ones, as environment pollutants and a potential risk to the ecosystem. The results like these bring out the question of monitoring of pharmaceutical compounds such as paracetamol in water systems. The application of some electroanalytical techniques can be one of the possible ways to do that. Electrochemical techniques can be very convenient since the measurements are fast so results are very quickly obtained and there is a possibility to make them cost effective by use of some low cost electrodes such as pencil graphite electrodes. This paper presents a summary of literature data on determination of paracetamol (PAR) using carbon-based electrodes, with special attention paid to pencil graphite electrodes.

RESULTS AND DISCUSSION

Pencil graphite electrode as the electrochemical sensor for paracetamol

There are numerous different approaches and electrochemical techniques used for paracetamol determination and different electrode pretreatments. For instance, Özcan and Şahin [6] used N-acetyl-p-benzoquinoneimine (NAPQI) reduction on the electrochemically treated pencil graphite electrode (ETPG) to determine paracetamol. The electrochemical treatment was potential cycling between −0.3V and +2.0V with a scan rate of 50mVs^{-1} for 5 scans in 0.1M H_3PO_4. NAPQI was formed by electrochemical oxidation of paracetamol on ETPG. Mechanism of paracetamol oxidation to NAPQI and its reduction is presented in Figure 2. Since paracetamol can adsorb on ETPG the method adsorptive transfer stripping differential pulse voltammetry (ATSDPV) can be used for its determination in body fluids in the presence of uric acid. Values of limit of detection and linear range are shown in Table 1.

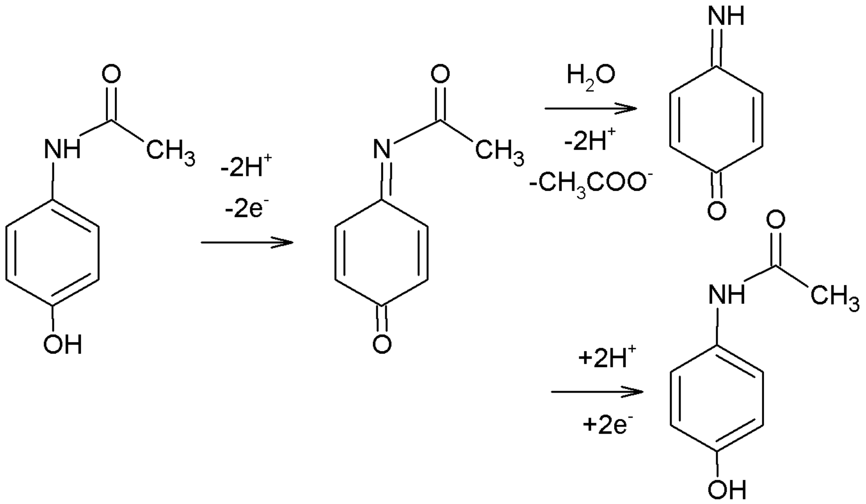

Figure 2 *Mechanism of paracetamol oxidation/reduction according to Özcan and Şahin [6]*

The same authors [7] previously prepared and tested molecularly imprinted polypyrrole modified pencil graphite electrode (MIP) as paracetamol sensor using differential pulse voltammetry (DPV). The MIP was obtained by the process of electrodeposition on the surface of the PGE using cyclic voltammetry in aqueous solution containing 0.1M $LiClO_4$, 0.05M pyrrole and 0.02M paracetamol. The embedded paracetamol were afterwards extracted to give a surface complimentary in shape and functionality to the original template paracetamol. The best results are obtained in phosphate buffer medium at pH 7.0, with 0.05M phosphate and 0.1M KCl. This electrode can be used to determine paracetamol even if commonly known interferences such as phenol, glucose, phenacetin, dopamine and ascorbic acid are present.

Recently, Keskin and Ertürk [8] investigated electrochemical behavior of paracetamol on the oxidative pretreated pencil graphite electrode (OP-PGE) using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). It is found that acetate buffer solution (0.1M, pH4.8) provided optimal conditions for determination of paracetamol. It is proposed that the electrochemical improvement of OP-PGE occurs due to the increase in oxygenated functional groups, microporosity and surface area on the electrode surface. The focus of the research was also on the effect of the interferences commonly present in real samples on determination of paracetamol under the optimized experimental conditions. The results indicated that molecules such as glucose, fructose, sucrose, saccharin and cations such as Na^+, K^+, Ba^{2+}, Ca^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+} did not affect the peak current of PAR up to 1000-fold-excess. Acetylsalicylic acid did not interfere up to 11-fold-excess and at higher concentration interference occurred and decreased peaks of PAR. Oxidation peaks of PAR and dopamine merged and disabled the determination of PAR when dopamine concentration was higher than 1.23 times of PAR concentration. In their research Mondal *et al.* [9] constructed nickel ferrite-modified pencil graphite electrode (NF-PGE) that showed good sensor characteristics, shown in Table 1, for determination of paracetamol alone and in the presence of ascorbic acid in phosphate buffer solution (pH 7.4).

Table 1 *Limit of paracetamol detection and linear range for pencil graphite electrodes*

Electrode	Limit of detection	Linear range	Reference
ETPG	2.5×10^{-9}M	0.05-2.5μM	[6]
MIP	7.9×10^{-7}M	5-500μM	[7]
OP-PGE	14.8×10^{-9}M	0.052-2.85μM	[8]
NF-PGE	0.106×10^{-6}M	0.8-55.5μM	[9]
AuNPs−PA−PGE	5.0×10^{-8}M	0.2-6.0μM	[10]

In order to improve usual approach based on the laboratory experiments, Güzel *et al.* [10] applied the experimental design and optimization (EDO) methodology for finding the optimal electrochemical conditions for paracetamol determination. This methodology have several advantages such as diminishing of the duration of analysis and use of reagents for experiments and the opportunity to obtain the exact optimal electrochemical conditions for the best determination results. They developed gold nanoparticles–polyaniline modified pencil graphite electrode (AuNPs−PA−PGE) and used it for the quantitation of paracetamol in commercial syrup and tablet. Satisfactory results were obtained for the determination of paracetamol using differential pulse voltammetry (DPV) method under the optimal electrochemical conditions provided by EDO technique which were: the optimal values for the accumulation potential –524 mV, 294 s accumulation time and 0.1 M phosphate buffer solution medium at pH 8.69. The results obtained by all the above-mentioned studies are summarized in Table 1.

Glassy carbon electrode and other carbon electrodes as the electrochemical sensors for paracetamol

Even bare glassy carbon electrode can be efficiently used for paracetamol determination as Engin *et al.* [11] demonstrated using glassy carbon electrode for the electroanalytical study of paracetamol by cyclic voltammetry and differential pulse voltammetry (DPV) techniques. Optimal results were obtained in 0.2M acetate buffer (pH 4.51). The proposed technique can be applied for paracetamol determination in commercial medicaments. The obtained results can be seen in Table 2.

However, there are numerous possibilities to improve characteristics of the electrodes by various modifications. Graphene and graphene oxide gave good results for modifications of the electrode surfaces. For example, Kang *et al.* [12] modified glassy carbon electrode (GCE) with ethanol suspension of graphene that was cast on electrode surface and dried in air. The conclusion was that the modified electrode shows superior characteristics as paracetamol sensor and exhibits very well defined redox peaks in cyclic voltammetry (CV) graph in pH 9.3 buffer ($NH_3 \times H_2O$-NH_4Cl, 0.1M, scan rate $50mVs^{-1}$). In order to provide high sensitivity accumulation potential of 0.0 V was applied for 240 s when square-wave voltammetry (SWV) was used. This method can be used in the presence of ascorbic acid or dopamine. On the other hand, Li *et al.* [13] successfully applied electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and differential pulse voltammetry (DPV) for paracetamol determination on glassy carbon electrode modified with Pd/graphene oxide (Pd/GO/GCE) in 0.1M phosphate buffer solution (pH 6.8). The effect of commonly present interferences is also evaluated and it was found that this method has an excellent selectivity towards paracetamol since the response of paracetamol is not distinctly affected in the presence of 10-folds of ascorbic acid, dopamine, uric acid and 4-aminophenol, 20-folds of tyrosine, tryptophan and guanine, 30-folds of adenine and vitamin B_1, and 50-folds of glucose, and 100-folds of K^+, Ca^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}, SO_4^{2-} and Cl^-. The presented method was also successfully applied to the determination of paracetamol in practical analysis of commercial tablets and human urines. Summary of the experimental results is presented in Table 2. Fan *et al.* [14] developed the Nafion/TiO_2–graphene (TiO_2-GR) composite film modified glassy carbon electrode (GCE) and tested the possibility of its application as paracetamol sensor. Electrochemical behaviour of paracetamol was studied in 0.1M phosphate buffer solution (pH 7) by application of cyclic voltammetry and for determination differential pulse voltammetry was applied with good results presented in the Table 2. Whereas, Santos *et al.* [15] succeeded in the simultaneous determination of paracetamol and ciprofloxacin using glassy carbon electrode modified with graphene oxide and nickel oxide nanoparticles (NiONPs-GO-CTS: EPH/GCE). Square wave adsorptive anodic stripping voltammetry (SWAdASV) was the method of choice developed firstly in 0.2M phosphate buffer solution (pH 6) and afterwards applied with success in synthetic biological fluids. Parameters are presented in Table 2.

Cheemalapati *et al.* [16] used glassy carbon electrode (GCE) modified with multiwalled carbon nanotubes (MWCNT)/ graphene oxide (GO) nanocomposite for the simultaneous determination of paracetamol and dopamine. They use cyclic voltammetry and amperometric i–t technique and successfully determined studied compounds in pharmaceuticals and human urine samples. Similar modified electrode MWCNTs-graphene nanosheet nanocomposite modified glassy carbon electrode (MWCNTs-GNS/GCE) was used by Arvand and Gholizadeh [17] for the simultaneous determination of paracetamol and tyrosine in phosphate buffer solution (pH 7) using differential pulse voltammetry (DPV). The established method was also successfully applied for their determination in human blood serum and pharmaceutical samples.

***Table 2** Limit of paracetamol detection and linear range for glassy carbon and other carbon electrodes*

Electrode	Limit of detection	Linear range	Reference
graphene modified GCE	3.2×10^{-8}M		[12]
Nafion/TiO_2–GR/GCE	2.1×10^{-7}M	1-100μM	[14]
Pd/GO/GCE	2.2×10^{-9}M	0.005–0.5μM and 0.5–80μM	[13]
NiONPs-GO-CTS: EPH/GCE	6.7×10^{-9}M	0.1-2.9μM	[15]
MWCNT/GO/GCE	0.05×10^{-6}M	0.5-400μM	[16]
MWCNTs-GNS/GCE	0.1×10^{-6}M	0.80–110μM	[17]
GCE	3.69×10^{-7}M	4-100μM	[11]
iron oxides/G	13×10^{-6}M	13-320ppm	[18]
CNP/CPE	0.015×10^{-6}M	0.1-1000μM	[19]
PyC	1.4×10^{-6}M	15 - 225μM	[20]

According to Benchettara *et al.* [18] graphite electrode modified with iron oxides can be used to successfully determine paracetamol in an alkaline solution of pH 12. Amiri *et al.* [19] studied the possibility to simultaneously determine paracetamol, phenylephrine and dextromethorphan since they are commonly found in pharmaceutical used against the common cold. The authors applied electrochemical techniques such as: cyclic voltammetry and differential pulse voltammetry using tosyl carbon nanoparticles (CNP) for modifying carbon paste electrode (CNP/CPE). Solution used for experiments was 0.1 M phosphate buffer of pH 7.0, human serum and solutions of different pharmaceuticals. The modified electrode was able to separate overlapping voltammetric peaks of PHE and DX into two well-defined voltammetric peaks. Keeley *et al.* [20] studied the electroanalytical properties of thin pyrolytic carbon (PyC) films prepared by chemical vapor deposition (CVD) on Si/SiO_2. They were found to be competitive with the best commercial carbon electrodes and have the advantage of being inexpensive, disposable, high-performance nanostructured electrodes for sensors, fuel cells and energy conversion. They also demonstrated the simultaneous detection of dopamine and paracetamol using these pyrolytic carbon electrodes. Values of obtained limit of detection and linear range are shown in Table 2.

CONCLUSION

The survey of the literature dealing with the topic of paracetamol detection and determination in various media on carbon-based electrodes is presented. It can be concluded that different electrochemical techniques can be efficiently employed, however, differential pulse voltammetry is the dominantly used one. Different types of carbon-based electrodes are tested and showed good sensor characteristics, but in the view of cost and the simplicity of work pencil graphite electrodes stand out. They are much cheaper and the limit of detection for paracetamol is in the range of other tested electrodes, also there are numerous ways to improve their properties by different modifications.

ACKNOWLEDGEMENT

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2020-14/ 200131.

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THE ROLE OF SUSTAINABLE DEVELOPMENT IN THE CEMENT INDUSTRY IN SERBIA

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Abstract

The cement industry is one of the largest carbon emitting industrial sectors in the world. The carbon dioxide emissions in this sector should be significantly reduced due to their high environmental impact and climate change. Accordingly, the cement industry in Serbia is taking all the measures necessary to reduce the impact of incineration of fossil fuels and to reduce their use. Cement plants in Serbia are increasingly turning to the use of alternative fuels and waste as a raw material for thermal energy. This paper presents the results of the use of alternative fuels in Serbian cement industry and their positive environmental impact.

Keywords: cement plants, alternaive fuels, cement production

INTRODUCTION

Sustainable development has been defined in many ways, but the most frequently quoted definition is from Our Common Future, also known as the Brundtland Report:

"Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs" [1].

Social development in modern conditions is linked to the model of sustainable development. The concept of sustainable development itself was adopted as a global concept of the development at the Rio de Janeiro Conference in order to overcome the problems related to the development of modern civilization and to find a possible path for industrial and economic development, as well as for the environmental protection.

One of the first industries to apply the concept of sustainable development is the cement industry. Cement is certainly one of the most important building materials today. World cement production in 2017 was estimated at approximately 4.1 billion tonnes. China produces 57% of the world's cement, with EU28 representing 4.2% and CEMBUREAU members representing 6.3% of the world's production [2]. According to the IMF World Economic Outlook, the 2018 global growth was estimated at 3.7%, and projected to grow at 3.5% in 2019 and 3.6% in 2020 [2].

The increasing use of cement enabled rapid development of construction, especially of concrete structures, but on the other hand, the progress of construction was set before the cement industry had increasingly demanding tasks, and nowadays it is gradually overcome [3]. Cement is the building material of our future, making it sustainable. Cement companies that have integrated sustainable development into their global goals are industry leaders and innovators in reducing CO_2 emissions.

As the environment is polluted in the cement production process, the cement industry has set the principle of sustainable business and aims to produce as much cement as possible with as little waste and pollution per ton of material produced. The cement industry accepted the challenges of sustainable development very early and with full responsibility. The guidelines developed by the Cement Sustainability Initiative (CSI) are supported and applied by the Cement Industry of Serbia (CIS), whose representatives are LafargeHolcim group Serbia and TITAN Cement Plant Kosjeric. In 2011, they signed a Sustainable Development Statement and thus supported the Cement Sustainability Initaitive [4].

SUSTAINABLE DEVELOPMENT IN CEMENT PRODUCTION

Lafarge Serbia has a tradition in cement production for more than a century. The annual capacity of the cement plant is 1,350,000 tonnes of cement and binder [5]. On the other hand, Titan cement plant produces about 750,000 tonnes of cement annually [6]. These factories initially met with environmental problems. However, they also showed a high level of readiness in this field. In order to improve their environmental performance, they focused on the following areas: energy efficiency, use of alternative fuels, climate change, and waste management.

Energetic efficiency

Cement production is one of the industries with the highest specific consumption of electricity and heat per unit of product. In the dry portland cement clinker production process, 3.3 to 3.6 GJ of heat is consumed to produce 1 ton of clinker with approximately 100 kWh/t of cement consumed [5]. For this reason, the cement industry is particularly interested in the use of cheaper (alternative) fuels. The following alternative fuels are used [7]:

-Waste tires

-Waste oil

-Municipal industrial waste

-Oil sludges

-Biomass

-Meat bone flour

In the past year, TITAN Cement Plant Kosjeric has used thermal energy from the combustion of fossil fuels and biomass, and electricity. Compared to 2017, the consumption of thermal energy and electricity in 2018 was higher (thermal energy by 2.6% and electricity by 8.2%) resulting from an increase in production volume. However, energy efficiency was actually improved, as indicated by a decrease in specific energy consumption (by -0.2% and -5.0%, respectively) [8].

Use of alternative fuels

Tires have a high caloric value, which makes them suitable for the clinker production process. Based on the 2018 Environmental Impact Assessment Study, Lafarge used waste tires with a share of heat substitution up to 30% of total needs. The waste oil content was at most 12%, of the total heat demand energy [9]. Municipal, industrial waste and biomass could replace 30% of the heat generated from fossil fuels. Meat bone flour was also used as alternative fuel which replaced conventional fuel consumption by 13% per year [9]. The use of alternative fuel in the Lafarge cement group and CRH cement plant is shown in Figures 1 and 2, respectively.

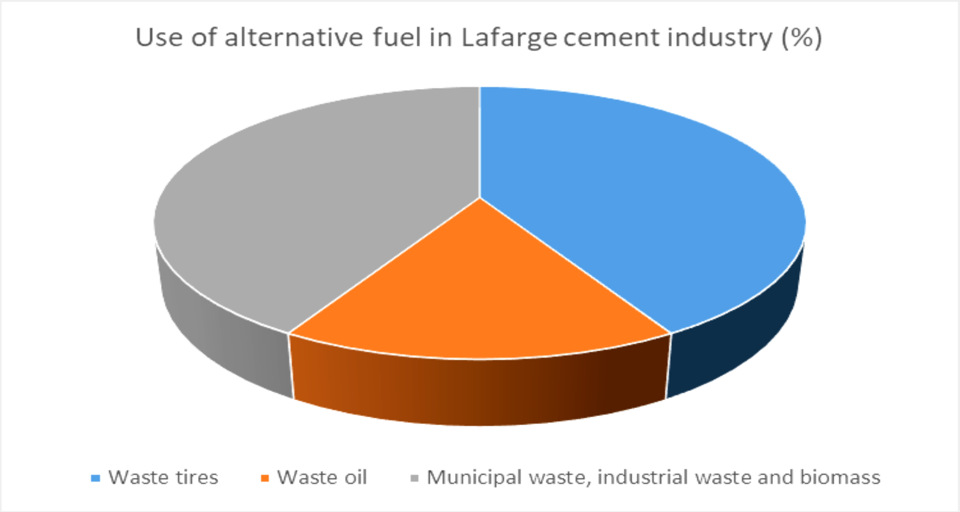

Figure 1 *Percentage share of alternative fuels in Lafarge cement group [9]*

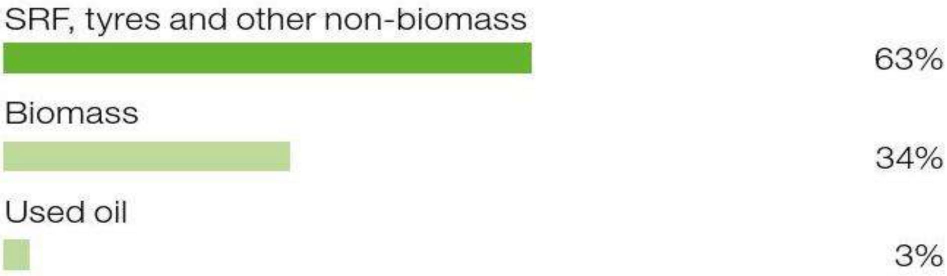

Figure 2 *Percentage share of alternative fuels in CRH cement plant [10]*

Due to the positive effects in the EU countries, a high percentage of alternative fuels is represented (Figure 3) [8].

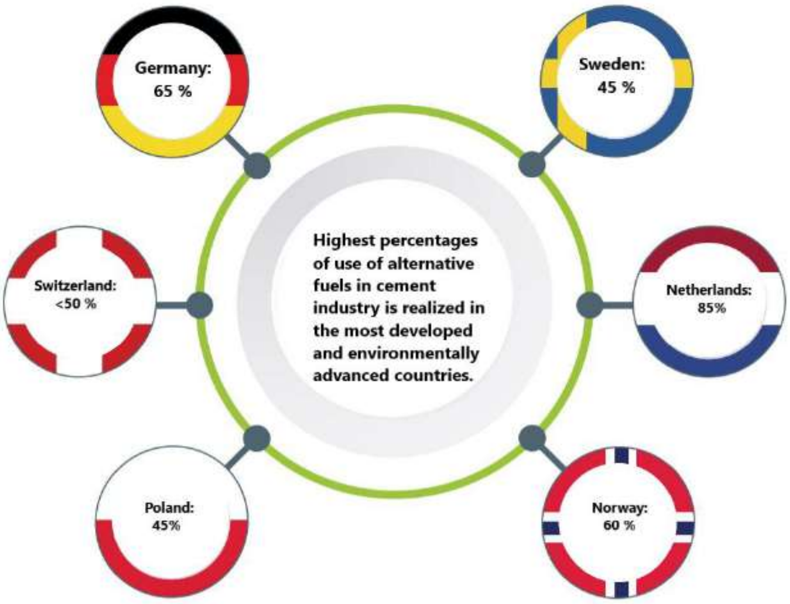

***Figure 3** Percentage share of alternative fuels in EU countries [8]*

Reduction of carbon dioxide emissions

The cement industry has faced problems of environmental pollution. The negative environmental impacts that characterize the production of all building materials occur in the expensive cement production process. The use of non-renewable natural resources to obtain raw materials, the emission of harmful gases (CO_2, NO_x and SO_x) and energy consumption are the most important aspects of the sustainability of the cement industry. The cement industry must be actively involved in implementing the Kyoto Protocol to reduce CO_2 emissions. In cement production, CO_2 emissions are caused by the decarbonisation reaction from the feedstock and the combustion of fuel [5].

Lafarge aims to reduce by 2030 CO_2 emissions by 40% per ton of cement compared to 1990, or an additional 19% reduction when compared to 2014 [11]. On the other hand, CRH Popovac aims to reduce carbon dioxide emissions by 25% in 2020 [10]. In Titan cement plant total direct carbon dioxide emissions in 2018 were about 1.4% higher than in 2017, due to increased production volumes. In the same period, total biogenic CO_2 emissions from wood pellet combustion were 553 tonnes. Specific direct carbon dioxide emissions per tonne of product were 3.5% lower than in 2017 [12].

Waste management

In accordance with its waste management in innovative ways, with a focus on alternative energy sources, some of these factories have a platform for pre-treatment of non-hazardous waste. Table 1 shows the total quantities of waste generated at the cement plant [9].

Today, a large amount of non-hazardous waste at the Lafarge Serbia cement plant is recycled, where some of it is used as an alternative fuel and the rest is landfilled.

Table 1 *Total amount of waste*

Types of waste	Amount of waste (t)
Hazardous waste	466.78
Non-hazardous waste	1,055.74

CONCLUSION

In line with the EU commitment to fighting climate change, the cement industry, as one of the largest carbon emitting industrial sector, needs a more sustainable future. The use of alternative raw materials in the process of clinker production or as a substitute for clinker in cement has a significant positive contribution to the environment. The use of alternative raw materials reduces the consumption of natural, non-renewable raw materials and CO_2 emissions (caused by the decarbonisation reaction from the raw material and the combustion of fuel). Cement plants in Serbia are implementing all necessary arrangements in accordance with the EU law to reduce the emission of carbon dioxide into the atmosphere. They also have a long-term plan for protecting the environment and reducing the impact of production and the emission of harmful gases into the atmosphere.

ACKNOWLEDGMENT

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2020-14/ 200131.

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ANALYSIS OF Al, Cr AND Mn IN THE ROOT ZONE SOIL AND PLANT PARTS OF WILD ROSE (*Rosa* spp.) IN THE BOR AREA

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Abstract

Concentrations of Al, Cr and Mn in the root zone soil and plant parts of wild rose (Rosa spp., predominantly Rosa canina L.) were determined by ICP-AES in order to assess their origin. The sampling of soil and plant material was performed in the city of Bor and its surroundings which is known for mining and smelting of copper ores. According to the concentrations of Al, Cr and Mn in the soil, as well as the Enrichment factor, it can be considered that these elements were naturally present in soil from the study area. However, the origin of Al in the plant material was from resuspended particles from the soil, while the concentrations of Cr and Mn in plants from the sites around the open pits and rural area were influenced by mining and smelting activities.

Keywords: Al, Cr, Mn, wild rose, *Rosa* spp.

INTRODUCTION

The usage of herbs is widespread all over the world due to their mild features and low side effects [1]. The fruits of wild rose (*Rosa* spp.) are used for strengthening of the body and protection from infections and cold, as well as like a supplement in the treatment of some diseases [2]. The rosehips are great source of vitamin A, B3, D, E, and especially vitamin C [3]. Herbs may be contaminated with toxic elements (Pb, Cd, Al, Hg and other elements like Cr), and their usage in human consumption could cause some health problems [1,4].

Mining and smelting activities represent one of the main anthropogenic sources of the environmental pollution in the study area (the city of Bor and its surroundings). Particulate matter which contains large quantities of toxic elements, as well as the waste gases emitted from industrial activities pose a great risk for living organisms and plants. In our earlier study performed in the selected area, results indicated that the origin of As, Cd, Cu, Pb, Mo and Zn in the soil and plant parts of wild rose was anthropogenic [5].

The aim of this study was to determinate the concentrations of Al, Cr and Mn in the root zone soil and parts of wild rose sampled in Bor area in order to assess their origin. Also, the obtained results were compared with some relevant literature data.

MATERIALS AND METHODS

The sampling of plant material and root zone soil was performed in the city of Bor and its surroundings. The sampling site B was characterized as background due to its distance of 17 km from Bor. The sampling site TR was located along the traffic road 20 km from the city of Bor (traffic pollution). The sites T1 and T2 were in Brestovac spa and Bor lake, respectively. These sites were located in the direction of the dominant winds that transmit the pollution from the mining-metallurgical complex (MMC) in Bor. The sampling site UI was in the center of Bor, while the site U was located on the broader area of Bor (pollution from MMC). The settlement Brezonik was denoted as the sampling site SU, while Oštrelj and Slatina were the sites R1 and R2, respectively (pollution from MMC and flotation tailing ponds). Sampling site I1 was located close to the quarry, I2 and I3 were in the surroundings of the copper mine Cerovo, I4 was in the surroundings of the copper mine Veliki Krivelj and I5 was in the vicinity of the flotation tailing ponds of the copper mine Veliki Krivelj. Position of the sampling sites and pollution sources are given in Figure 1.

Leaves (washed and unwashed), branches, fruits and roots of wild rose (*Rosa* spp., predominantly *Rosa canina* L.) as well as root zone soil were sampled and prepared as described in Kalinovic *et al*. [5] and afterwards digested according to the U.S. EPA method 3050B [6]. Concentrations of Al, Cr and Mn were determined by ICP-AES at the Mining and Metallurgy Institute Bor.

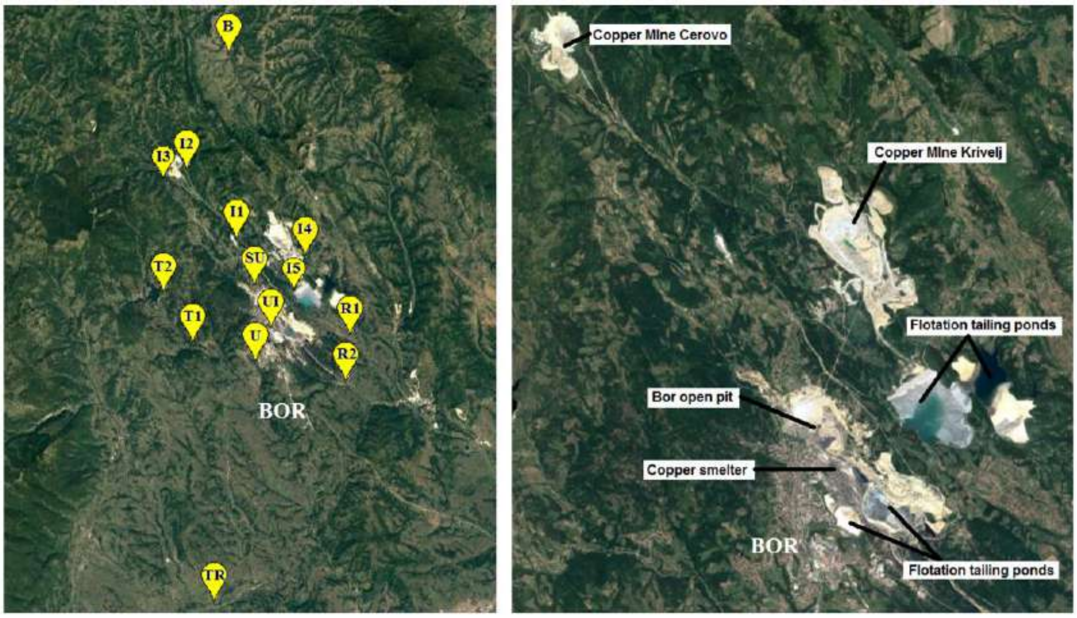

Figure 1 *Position of the sampling sites of the root zone soil and plants in regard to the pollution sources*

RESULTS AND DISCUSSION

The concentrations of Al, Cr and Mn in the root zone soil of the wild rose from the sampling area are shown in Figure 2. The concentrations of Al in root zone soil were within world average level [7]. The lowest concentration was at the I1 site and the highest at the T1 site. The concentrations of Cr in root zone soil were below the limit value (100 mg/kg) according to the Serbian Regulation [8], except at the sampling site UI (100.4 mg/kg). The lowest concentration of Cr in root zone soil was found at the sampling site I1. The concentrations of Mn in root zone soil were above the world average level (411-550 mg/kg)

[7]. The highest concentration of Mn was detected in the soil from the site I4, while the lowest concentration was found in the soil from the site R2. The highest concentrations of the examined elements were not observed in the areas affected by the pollution from the mining-metallurgical copper production (except for Cr at the UI site), as well as the lowest concentrations were not recorded at the B site which was characterized as unpolluted. This observation could indicate natural presence of Al, Cr and Mn in the soil.

The ratio of element concentration in the soil sample and the corresponding element concentration from the background site represents the Enrichment factor (EF) [9]. Figure 3 shows the EF values for Al, Cr and Mn in soil from the study area. The soil samples from all the 14 sites were not enriched with Al and Cr (EF<2), while the moderate enrichment with Mn was noticed only at the sites I4, U and T2 (2≤EF<5). Considering the EF values, which were used to assess the origin of the elements in the soil, it could be noticed that Al, Cr and Mn were naturally present in soil of the study area.

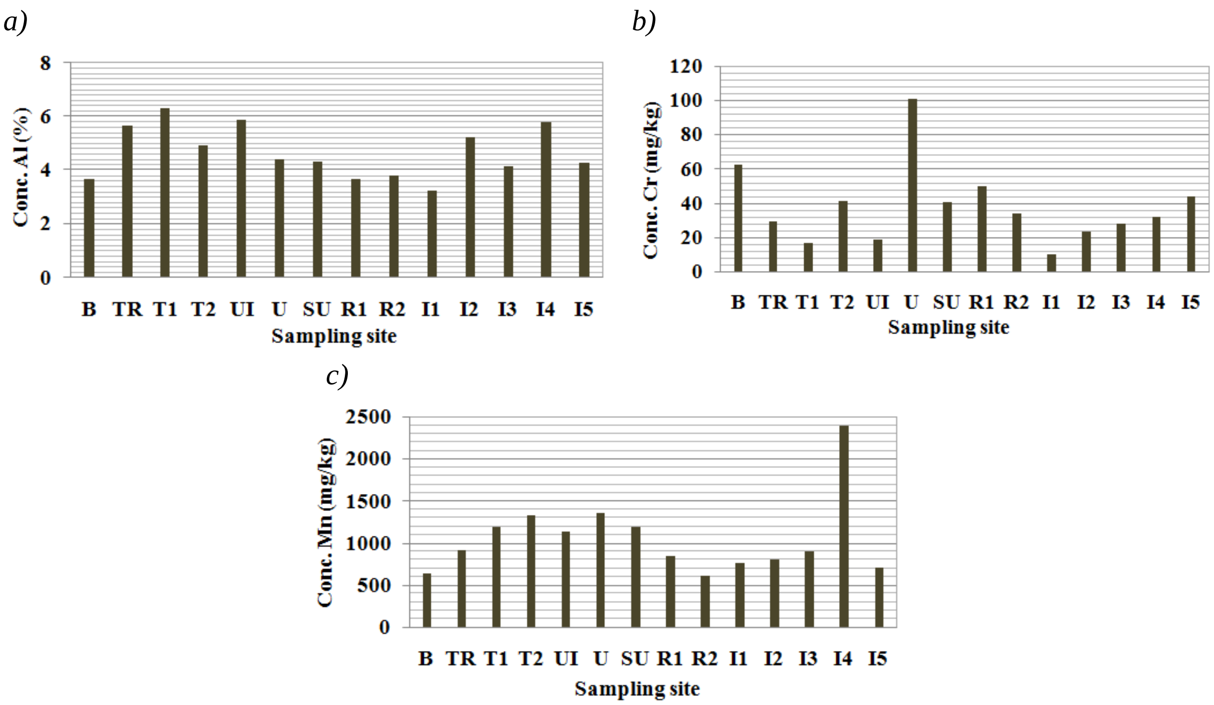

Figure 2 *Concentrations of a) Al b) Cr and c) Mn in root zone soil of wild rose from the sampling sites in the study area*

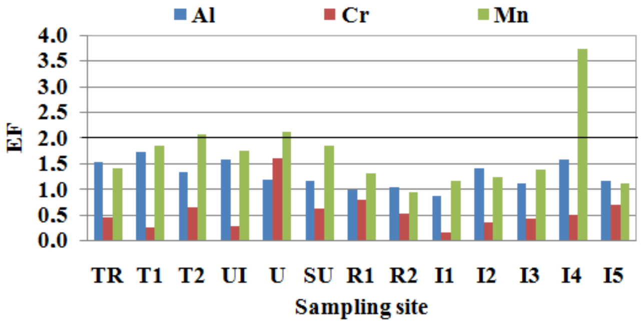

Figure 3 *Root zone soil Enrichment factor for Al, Cr and Mn in the study area*

The concentrations of Al, Cr and Mn in plant material of wild rose (*Rosa* spp., predominantly *Rosa canina* L.) from the sampling area are shown in Figure 4. Among the analyzed plant parts, branch was characterized with the lowest content of analyzed elements at all sampling sites. The highest concentration of Al in root was at the UI site, while the highest concentrations in leaves and fruits were at the sites I2, I4 and I5. Site I2 was located in the vicinity of the copper mine Cerovo, while the sites I4 and I5 were located in the vicinity of the copper mine Veliki Krivelj and flotation tailing ponds, respectively. Based on this, it could be considered that the origin of Al in the plant material was from resuspended particles of soil. The highest concentration of Cr in root of wild rose was at the T2 site, while in leaves the highest concentrations were at the I3 and I4 sites. The concentration of Cr in fruit was detected only in samples from R2 and I4 sites. In the root of wild rose, the highest concentration of Mn was in the sample from I3 site, while the concentrations of Mn in leaves were higher in the samples from the SU, R2 and sites located in the industrial zone (I) and in the vicinity of open pits and flotation tailing ponds, compared to the other sites. The highest concentration of Mn in fruit samples was found at the I3 site. According to the obtained concentrations of Cr and Mn in parts of wild rose, it can be considered that mining and smelting activities influenced higher concentrations of these elements in samples from the sites in the vicinity of open pits Cerovo and Veliki Krivelj and in the rural zone.

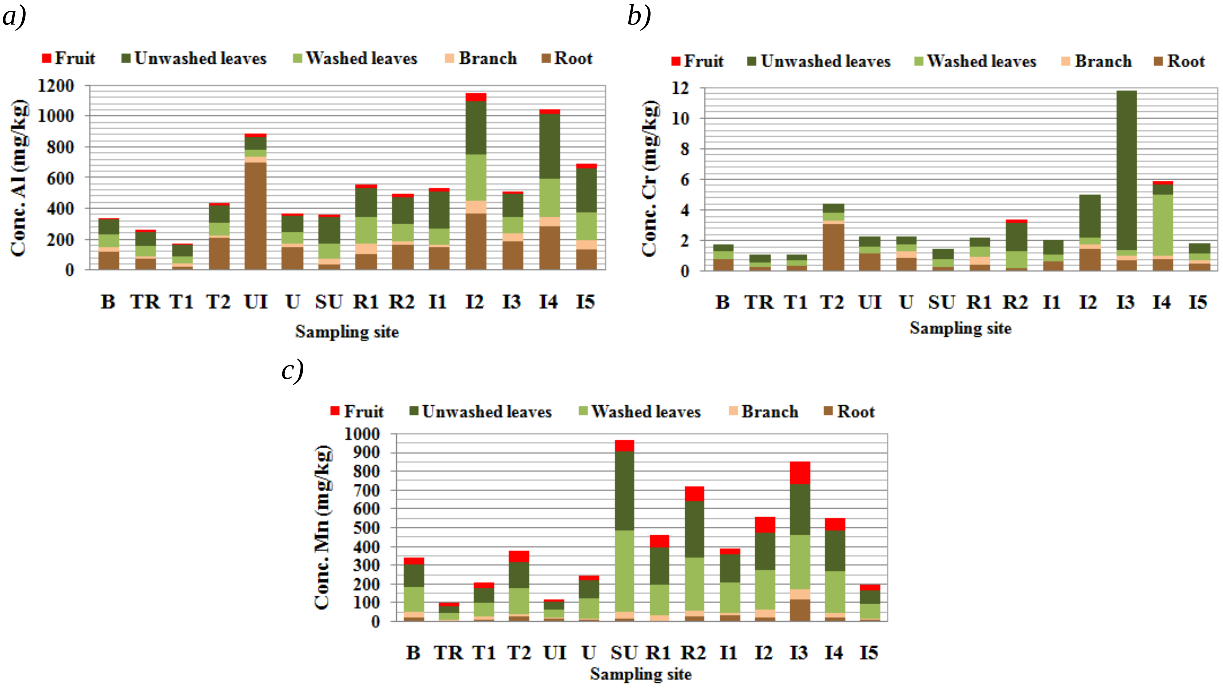

***Figure 4** Concentrations (mg/kg) of a) Al; b) Cr and c) Mn in plant parts of wild rose*

Comparing the content of Al, Cr and Mn in washed leaves and fruits of wild rose obtained in this research with the data from the literature (Table 1) it can be seen that concentrations of Al and Cr in the leaves were approximate, while the concentration of Mn was higher in the samples from the study area in Bor and the surroundings. Concentrations of Al, Cr and Mn in fruit samples analysed by Başgel and Erdemoğlu [1] were several times higher than the concentrations in this study.

Table 1 *Literature data for the element concentrations (mg/kg dw) in the parts of wild rose*

Al	Cr	Mn	References
Washed leaves			
0.022±0.005*	2.441±0.16	110 ±10.97	[10]
Fruit			
Al	**Cr**	**Mn**	**References**
157±12	0.92±0.07	244.0±13.8	[1]
13.70±11.24	1.33±1.14	13.93±11.71	[11]
/	0.79±0.02	35.8±0.7	[4]

dw - dry weigh basis; *concentrations are given in %; / not determined.

CONCLUSION

Concentrations of Al, Cr and Mn in the root zone soil and parts of wild rose sampled in Bor area were determined in order to assess the origin of these elements. Based on the obtained concentrations of the examined elements in root zone soil of wild rose and values of Enrichment factor it can be noticed that Al, Cr and Mn were naturally present in soil. Regarding the concentration of elements in the plant material it was observed that Al originated from resuspended particles of soil, because this element is surely present in soil. Higher concentrations of Cr and Mn in the plant material were influenced by mining and smelting activities especially at the sites around the open pits and rural area.

ACKNOWLEDGEMENT

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THE DISTRIBUTION OF Al, Fe, Cu, Zn, Pb, Ni, As AND Cd WITHIN THE PINE TREES FROM THE CHEMICALLY IMBALANCED ENVIRONMENT

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Abstract

Estimation of Al, Fe, Cu, Zn, Pb, Ni, As and Cd distribution among the roots, branches and needles of the pine trees from the zones in the chemically imbalanced environment due to the soil and air pollution from the copper production processes and unpolluted zone, was presented. Distribution of Al throughout the pine tree in the most cases was characteristic for the natural environmental conditions probably due to the absence of a nonpoint source of Al pollution in the examined area. Higher Fe concentrations in the pine branches than in the needles could be attributed to rougher branches surfaces, which contributed to higher ability for retaining Fe from the atmospheric deposition. Differences in the distribution of Cu, Zn, Pb, As and Cd among parts of pine from the extremely polluted urban-industrial relative to the background zone, point out the different ways of plant adaptations in the environmentally stressed habitats. Cu was predominantly accumulated in the branches, while the roots had the lowest Zn, Pb and Ni content.

Keywords: pine, distribution, environmental pollution, copper production

INTRODUCTION

Plants respond to chemical stress caused by both deficiencies and excesses of nutrients in ecosystems. During evolution and course of life, plants have developed several biochemical mechanisms that have resulted in the adaptation to and the tolerance of new or chemically imbalanced environments. Therefore, this relations should always be investigated for the particular soil–plant, as well as the air–plant systems [1]. Contents of certain elements in the plant parts can be indicative of (1) atmospheric pollution via incorporation through the stomata or (2) soil pollution taken up via roots and transported to the leaves [2,3]. The transfer and accumulation of heavy metals into the plant organs is usually substantially influenced by the various factors: primarily by soil heavy metal content and soil characteristics, by soil reaction, by cation exchange capacity, or by Ca/Mg content ratio [4]. However, the ability to transfer metals from the soil/air to the plant organs makes some tree species suitable for the colonization and vegetation restoration of the contaminated areas [5].

Chemically imbalanced environments due to the soil and air pollution are the most attractive for the investigations of the interactions in the soil–plant and air–plant systems. However, little attention was given to the distribution of the essential elements, as well as heavy metals and metalloids within the parts of trees. The aim of this research was to estimate distribution of Al, Fe, Cu, Zn, Pb, Ni, As and Cd among the roots, branches and needles of pine trees from the different zones located in the area affected by the polluting substances from the copper production processes relative to the unpolluted background zone.

MATERIALS AND METHODS

Plant material was sampled from 10 sampling sites distributed in 7 zones. The urban-industrial (UI) zone/sampling site was located in the city of Bor (Serbia). This zone was characterized by decades of the extreeme air pollution from the copper smelter, flotation tailing ponds, heating plant and traffic [6]. The urban (U) zone/sampling site characterized with the periodical impact of the polluting substances from the copper production proceses was situated in the most populous part of the city. The suburban (SU) zone/sampling site was polluted predominantly with the pollution from the copper smelter. The I1 and I2 sampling sites within the industrial (I) zone represented area in the vicinity of the Copper mines Veliki Krivelj and Cerovo, respectively. Polluting substances at these sampling sites predominantly originated from the flotation tailing ponds and overburden dumps, as well as from the acid mine drainage waters. Two sampling sites, T1 (Brestovac spa) and T2 (Bor lake), represented the tourist zone (T). The rural (R) zone (R1 and R2 sampling sites) under the pollution from the copper smelter, flotation tailing ponds and acid mine drainage was the most vulnerabled area, due to the ussage of agricultural land for food production. The background (B) zone/sampling site represented the unpolluted area, about 17 km from the facilities for the copper production.

Plant material was sampled during September and the first half of October. Samples were collected under the stable weather conditions, after prolonged periods without rain, and during days without winds. Three to five healthy individuals were sampled from the each sampling site. Needles and branches (about 2 cm thick) were sampled at the high of 1.5 to 2 m, from the outer of the canopy, on the east, west, north and south sides. Needles and branches remained unwashed. Roots (up to 4 cm thick) were sampled at a depth of 10–20 cm, with several sides of the canopy depending on the availability. The composite root samples were repeatedly washed in distilled water with brushing. Plant samples were air dried at the room temperature and then milled. Microwave digestion of the plant material was performed according to the US EPA method [7]. The concentrations of Al, Fe, Cu, Zn, Pb, Ni, As, and Cd in the needles, branches and roots were determined on the atomic emission coupled plasma–induced spectrometer, with radial and axial plasma observations, (Atomic Emission Spectrometer with dual view simultaneous Inductively coupled plasma, ICP–AES) manufactured by SPECTRO model Blue.

RESULTS AND DISCUSSION

Pine roots from 6 sampling sites had higher Al concentrations, compared to the rest analyzed pine parts (Figure 1a). This was in accordance with the results by Zhang *et al.* [8] and Wang *et al.* [9] who found that Al mainly accumulates in the pine roots. Pine branches contained higher Al concentrations than the needles at the most sampling sites. Distribution of Al in the pine parts from the most polluted (UI) and unpolluted (B) sampling sites differed, althouth nonpoint source of Al pollution in the examined area did not existed [3].

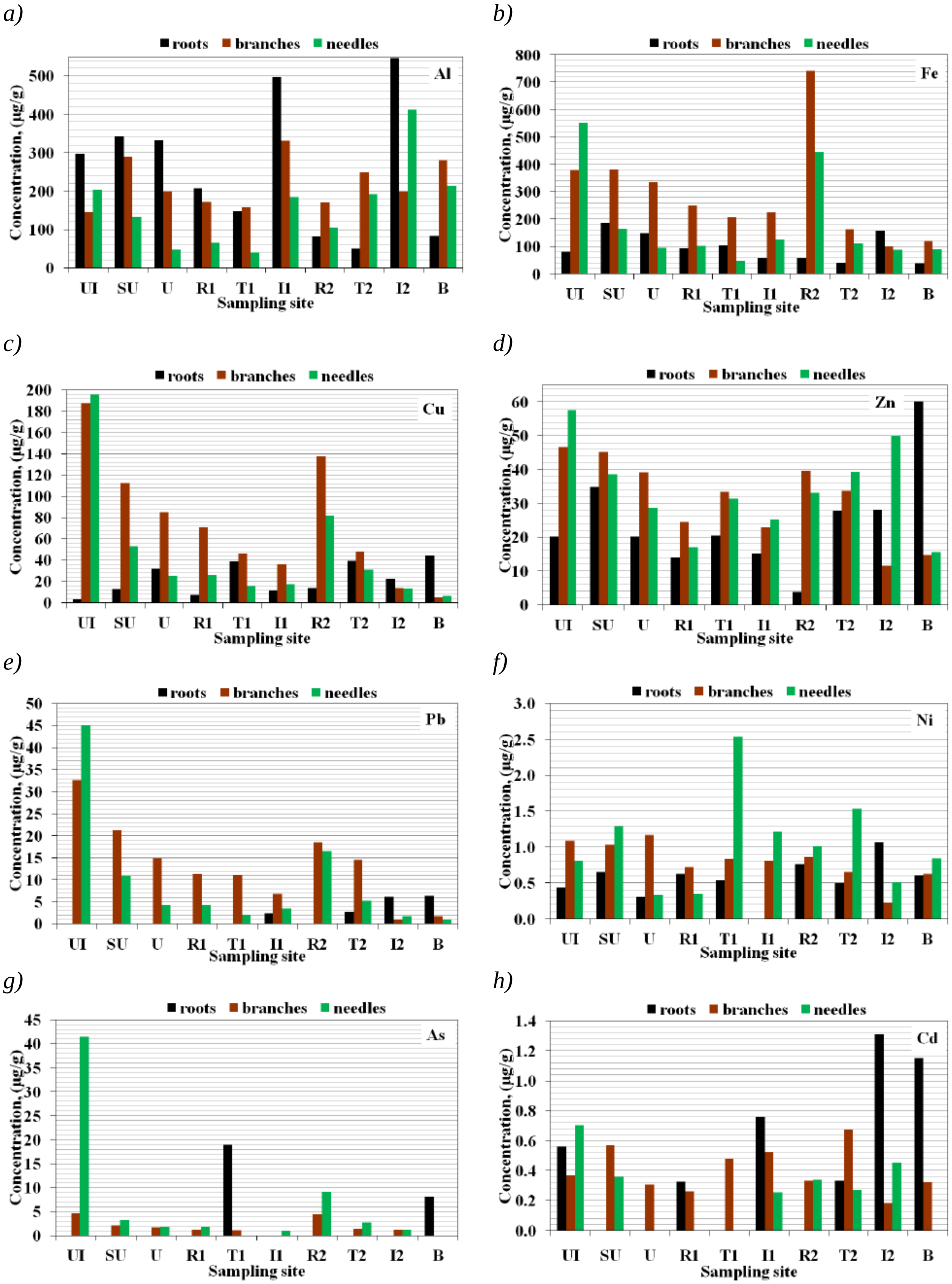

Figure 1 Distribution of: a) Al, b) Fe, c) Cu, d) Zn, e) Pb, f) Ni, g) As and h) Cd in the roots, branches and needles of pine

Pine branches (except from the UI and I2 sites) retained higher Fe concentrations relative to the roots and needles (Figure 1b). Branches have rugher surface than the needles which could be the cause of higher Fe concentrations in the pine branches. Kalinovic *et al.* [3] noticed significant decrease of Fe concentrations resulting from the washing of tree leaves which indicated the presence of Fe in the atmospheric deposition.

Pine branches contained more Cu, compared to the rest examined plant parts, except at the sampling sites UI, I2 and B (Figure 1c). Skonieczna *et al.* [10] detected the highest Cu concentrations in the branches of pine growing in the environmentally stable area. Pine from the sampling sites I2 and B, had the highest Cu concentrations in the roots, while branches and needles had similar Cu contents. Cu has low mobility relative to other elements in plants and most of this metal appears to remain in the root and leaf tissues until they senesce [11]. Such behaviour in this investigation was observed only for the sampling sites with the lowest environmental pollution, esspecially for the sampling site B with natural environmental conditions. Differences in Cu distribution depending on the plant part and sampling site, point out the different ways of adaptation which plants develop to survive in the habitats with high Cu contents. This observation was based on the data from the most polluted zone (UI sampling site) and the background zone. Kalinovic *et al.* [3] found that soil from the vicinity of the copper smelter was the most polluted with Cu, while soil from the background zone had the lowest Cu content. Also, the washing procedure resulted in the significant reduction of the Cu content in the needles from the examined area [3], which indicated environmental pollution with Cu.

The determined Zn concentrations were the lowest in the pine roots compared to the other parts, at 6 out of 10 sampling sites (Figure 1d). From this regularity deviated Zn concentrations in the plant material from the suburban, industrial and background zone. Pine roots from the unpolluted area (B zone) had higher Zn content compared to the branches and needles, which was contrary to the results from the UI zone. That indicated the specific behavior of the pine tree under different environmental conditions, similarly to the results for Cu. Kalinovic *et al.* [3] detected the highest Zn contents in the pine soil from the UI zone, while statistically significant Zn content was washed from the pine needles. In the conditions of hight levels of Zn in soil, this element may be translocated from the roots and accumulated in the tops of the plant [11], which was in agreement with the results of this study.

The lowest Pb content was detected predominantly in the pine roots, except for the sampling sites I2 and B, where Pb content in the roots was higher compared to the other parts (Figure 1e). According to Kabata–Pendias and Mukherjee [12] a great proportion of Pb was accumulated in the pine roots, which was the case only at the sampling sites with the lowest environmental pollution (i.e. I2 and B). Pine branches contained the highest Pb levels, except at the sampling sites UI, I2 and B. The variations in the Pb distribution among the roots, branches and needles from the urban–industrial and background zone, point to the different mechanisms of Pb accumulation and translocation in the pine tree, under the specific environmental conditions, similar as in the case of Cu and Zn.

The lowest Ni concentrations were observed in the pine roots from 7 out of 10 sampling sites, including the sampling site B which represented the unpolluted zone (Figure 1f). The aerial pine parts contained the highest Ni concentrations. Distribution of Ni among the pine parts from the UI and B zone did not differ greatly.

Branches and needles had higher As contents than the roots, except from the sites T1 and B (Figure 1g). These results indicated that pine tree used the same mechanisms for accumulation and translocation of this nonessential element, in almost the entire study locations. The differences in the distribution between UI and B zones, as in the case of Cu, Zn and Pb, were observed. The copper smelter had enormously influence on the pollution of soil and air with As in the entire study area [6]. Jana *et al.* [13] concluded that the pine roots retained more As than the trunk, branches and needles. These results were contrary to the our findings, probably because of the different source and level of pollution.

The distribution of Cd in the pine parts very greatly in all the investigated zones (Figure 1h). It is important to point out that the needles from the urban–industrial zone contained the highest Cd concentrations, while the roots had the highest concentrations in the background zone. The results from the background zone were in agreement with the statement by Kabata-Pendias and Mukherjee [12] who reported that Cd concentrations are ussually the highest in the roots and decreases towards the top of plants. These results indicated specific mechanisms of pine adaptation depending on the degree of the environmental pollution by Cd. The trend of the environmental pollution with Cd was similar as in the case of Cu and As reported by Kalinovic *et al.* [3].

CONCLUSION

The contents of Al, Fe, Cu, Zn, Pb, Ni, As and Cd in the pine roots, branches and needles from 9 sampling sites under the pollution from the copper production processes, and one unpolluted site were determined and compared in order to evaluate the elements distribution through the pine tree. Aluminum accumulated predominantly in the roots (at 6 out of 10 sampling sites). The distribution of Al throughout the pine tree in the most cases was in a compliance with the results from the literature data, probably due to the absence of a nonpoint Al pollution source in the examined area. Pine branches contained higher Fe concentrations than the needles, which could be effect of the rougher surface which captured more Fe from the atmospheric deposition. The differences in Cu, Zn, Pb, As and Cd distribution among the parts of pine from the extremely polluted urban-industrial and unpolluted background zone, point out different ways of adaptation which plants develop to survive on the chemically imbalanced habitats. Cu was accumulated predominantly in the branches, while the roots had the lowest Zn and Pb content (at 8 out of 10 sampling sites), and Ni content (at 7 out of 10 sampling sites).

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THE RELATIONS BETWEEN SOIL PHYSICO-CHEMICAL PROPERTIES AND SOIL ENZYME ACTIVITIES IN LONG-TERM CONTAMINATED AREA

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Abstract

This study aims to evaluate the influence of selected soil properties on soil enzyme activities in the area characterized with long-term contamination originating from the mining-metallurgical processes. Sampling of Plantago spp. root zone soil was performed at five sites. Selected soil properties, such as soil pH, soil organic carbon and soil moisture were determined. The activities of five hydrolases (i.e. ß-glucosidase, urease, arylsulphatase, acid and alkaline phosphatase) with essential roles in soil nutrient cycling were assessed. Calculated total enzyme activity index (TEI) inhibition rate denoted soil enzyme activities inhibition at the site Brezonik, while the other sites were characterized with higher soil enzyme activities in comparison to the control site. Spearman's correlation coefficients between soil properties, soil enzyme activities and TEI were also calculated. Among the five studied enzymes, Arl activity was found to be sensitive to distance from the main pollution source. Assessed soil properties (pH, organic carbon and moisture) did not significantly influence soil enzyme activities. On the other hand, soil properties determination along with soil enzyme activities is necessary considering the complexity of interrelations between these variables.

Keywords: soil enzyme activities, hydrolases, soil properties, TEI, copper smelter, *Plantago* spp.

INTRODUCTION

Contaminants emitted during different anthropogenic activities are primarily accumulated in the upper soil horizons where most organic matter is found and microbial processes are occurring [1]. Different soil properties are affected by contamination, such as the amount and quality of potential organic inputs, as well as soil microbial processes [2]. Unlike soil physico-chemical properties, soil biological properties (i.e. soil enzyme activities) are sensitive indicators responding rapidly to the environmental disturbances of both natural and anthropogenic origin [3,4]. Soil processes mediated by enzymes are regarded as integrators of soil physical, chemical and biological characteristics, and represent excellent candidates to reflect changes in soil properties [5]. The methods for determination of soil enzyme activities are considered to be relatively easy and fast, thus soil enzyme activities represent cost-effecting monitoring tools [2,6]. Soil enzymes are catalysts of different reactions, and have crucial roles in the stabilization of soil structure, organic matter formation and nutrient cycling [4]. Nutrient cycling is one of the most important soil functions, whereby the processes catalyzed by enzymes provide the basis of fundamental elements cycling in soil [2,5].

Soil properties including pH, organic carbon content and soil moisture level, beside the presence of soil contaminants (i.e. heavy metals), highly influence soil enzyme activities [2,4,5,7]. The investigations based on the identification of the relations between soil physico-chemical properties and soil enzyme activities can improve current knowledge of soil biogeochemical dynamics and cycles [7]. The evaluation of soil hydrolytic enzymes activities provides the measure of the effects of soil alteration on the biological processes related to C, N, S and P cycling [3]. Special emphasis is given to the assessment of the soil enzyme activities in long-term contamination areas with the specific environmental conditions [2]. Taking into account aforementioned, this study aims to evaluate the influence of selected soil properties on the soil enzyme activities with crucial roles in essential element cycling, namely ß-glucosidase, urease, arylsulphatase, acid and alkaline phosphatase, in the long-term contaminated area.

MATERIALS AND METHODS

Soil sampling

Soil sampling was performed at the 5 sites in the Bor area previously described with the highest amount of heavy metals in air and soil: Town park, Brezonik, Oštrelj and Slatina, while site Gornjane was used as control [8–10]. At each selected site, root zone soil of *Plantago* spp. (predominantly *Plantago lanceolata*) from 5-10 individual plants was sampled, and combined into one composite sample. Sampled soil was further air dried in the laboratory and physico-chemical properties were determined. One part of the soil was sieved (<2mm), kept at 4°C and used for the analyses of soil enzyme activities.

Soil physico-chemical properties

Air dried soil samples were sieved (<2 mm), grinded and further analyzed. Soil pH was determined in 1M KCl solution [2,4,11]. Standard pH meter (Model MU 6100L) was used to determine pH of soil:KCl suspension. The ratio used for pH determination was 1:5 mass/volume [12]. Soil water content (moisture) was determined from the loss of weight after drying of field moist soil samples (<2 mm) at 105°C until constant mass. In order to calculate soil organic carbon content, soil organic matter was first determined from the loss-on-ignition method (550°C for 2 h) [13]. Soil organic carbon (OC) was calculated by using the conversion factor of 2, based on the assumption that organic matter is 50% carbon [14].

Soil enzyme activities determination

The activities of ß-glucosidase (Glu), urease (Ure), arylsulphatase (Arl), acid and alkaline phosphatase were determined on the basis of product released after the specific reaction between the enzymes and substrates [15]. The specific substrates were salicin (for Glu determination), urea (Ure), p-nitrophenylsulfate (Arl) and p-nitrophenyl phosphate (AcP and AlP). The enzyme activities are expressed as released products per unit of dry soil mass (dm).

Total enzyme activity index (TEI) was calculated according to expression: $TEI = \Sigma X_i / \overline{X}_i$, where X_i represents the measured activity of the soil enzyme *i*, while $\overline{X}_i$ represents the average activity of the soil enzyme *i* in all samples [3,16]. TEI inhibition rate proposed by Fang *et al*. [16]: [1–($TEI_{polluted}$/$TEI_{unpolluted}$)]*100 was also calculated.

Data analysis

All statistical analyses were conducted and graphs were created using R programming language, v 3.5.2, R core team 2018 [17]. Non-parametric correlation analysis (Spearman's coefficients) was used to assess the relationships between soil enzyme activities, soil physico-chemical properties and TEI. The correlation matrix of data was plotted by the R package corrplot [18].

RESULTS AND DISCUSSIONS

Soil properties

The results of analyzed soil physico-chemical properties are given in Table 1. Soil pH values were in the range of 4.22 to 7.20, whereby the sampling site Slatina was characterized with the lowest and site Gornjane with the highest pH. Moisture content in the soil samples was in the range from 9.22% (at the site Gornjane) to 20.24% (at the site Town park). The lowest organic carbon content was determined in the soil samples from the site Gornjane (1.88%), while the highest was in the samples from the site Slatina (5.52%).

Table 1 *Physico-chemical properties of the sampled soils*

Sampling site	Distance (km)*	pH (KCl)	Moisture (%)	OC (%)
Town park	0.5	6.81	20.24	5.52
Brezonik	2.5	6.26	14.31	3.30
Oštrelj	4.5	7.19	18.79	4.67
Slatina	6.5	4.22	18.32	5.53
Gornjane	17	7.20	9.22	1.88

* From the copper smelter

Total enzyme activity index (TEI) and TEI inhibition rate

Soil enzyme activities across the study area were: 309.83 μg saligenin g^{-1} dm (Glu); 96.04 μg N g^{-1} dm (Ure); 75.10 μg p-nitrophenol g^{-1} dm (AlP); 548.71 μg p-nitrophenol g^{-1} dm (AcP) and 442.18 μg p-nitrophenol g^{-1} dm (AlP). The lowest TEI value was calculated for the sampling site Brezonik, while the highest for the site Oštrelj (Table 2). Contrary to our results, Fang *et al.* [16] found the highest TEI for the unpolluted area.

Table 2 *Calculated TEI and TEI inhibition rate*

Sampling site	TEI	TEI inhibition rate (%)*
Town park	4.24	-0.33
Brezonik	3.73	11.67
Oštrelj	7.85	-85.66
Slatina	4.95	-17.08
Gornjane	4.23	/

* calculated in comparison to the control site

TEI inhibition rate for the site Brezonik amounted to 11.67% indicating inhibition of soil enzyme activities compared to the control site (Table 2). TEI inhibition rate calculated for the other sampling sites amounted to -0.33, -85.66 and -17.08% for the sites Town park, Oštrelj and Slatina, respectively. Negative TEI inhibition rate indicated the enhancement of the soil enzyme activities in comparison to the control site.

The influence of soil properties on the soil enzyme activities

Correlation matrix between soil enzyme activities, soil properties and TEI is given in Figure 1. The positive correlation found between Arl activity and distance from the main pollution source ($r=0.900$, $p<0.05$) was in accordance with the previous studies [4,11,19]. Statistically significant positive correlation was found between TEI and Ure activity ($r=1.000$, $p<0.001$) (Figure 1), which was in accordance with the study by Tan *et al.* [3]. Soil properties did not exhibit significant influence on TEI. However, Tan *et al.* [3] found that TEI was strongly influenced by soil OM and pH levels (OM content had positive, while pH had negative effect on TEI) in comparison to the individual soil enzyme activities. Also, Fang *et al.* [16] found that soil properties (i.e. electrical conductivity) negatively influenced TEI.

Soil pH value was in positive relation with the activities of AcP and Glu and in negative relation with the activities of AlP and Arl, although relations were not significant. This finding was supported with statistically significant negative correlations ($r=-0.900$, $p<0.05$) between AcP and AlP activities, as well as between Glu and Arl (Figure 1). Our results are in accordance with the previous studies which indicated that AlP activity was predominant in neutral or alkaline soils, whereas AcP activity was predominant in acid soils [5].

The results from this study indicated that soil enzyme activities are poorly related to soil pH, in contrast with the previous studies highlighting influence of pH on the soil enzyme activities [4,5]. The changes in soil pH values influence soil enzyme activities through direct and indirect effects [5]. On the other hand, Garcia-Gil *et al.* [1] stated that it is very difficult to distinguish between the effects of pH changes on soil biological properties and the effects resulting from the presence of soil pollutants.

OC was negatively correlated with Glu, Ure and AcP activity, while positively with Arl and AlP, although not statistically significant (Figure 1). The absence of significant influence of organic C on the soil enzyme activities, Angelovičová and Fazekašová [6] attributed to the quality of the organic inputs into the soil. Niemeyer *et al.* [2] denoted positive relations between soil enzyme activities and soil organic carbon in the surrounding area of lead smelter plant in Brazil. According to the literature [2,4], organic matter acts like an energy and C source for microbes, as well as the substance-complexing heavy metals and thus protecting soil enzymes. Also, regarding the influences of organic matter on the soil capacity for water retention, soil enzyme activities are considered to be positively related to soil organic carbon.

Taking into account moisture level and soil enzyme activities, there were no significant correlation (Figure 1), which was in contrast to the previous study by Weintraub *et al.* [7] who denoted positive correlations between soil moisture level and enzyme activities. According to the study by Pereira *et al.* [20], low correlation coefficients indicated that the moisture level was not a limiting factor affecting soil enzyme activities in the mining area. Alvarenga *et al.* [21] stated that low enzymatic activities in soil sampled at the São Domingos mine, could be attributed to the specific climatic conditions resulting in the low soil moisture content. Soil moisture affects soil enzyme activities directly by influencing water availability to microbial activity, as well as by indirect effects related to changes in soil levels of oxygen and the flux of labile C and nutrients [7].

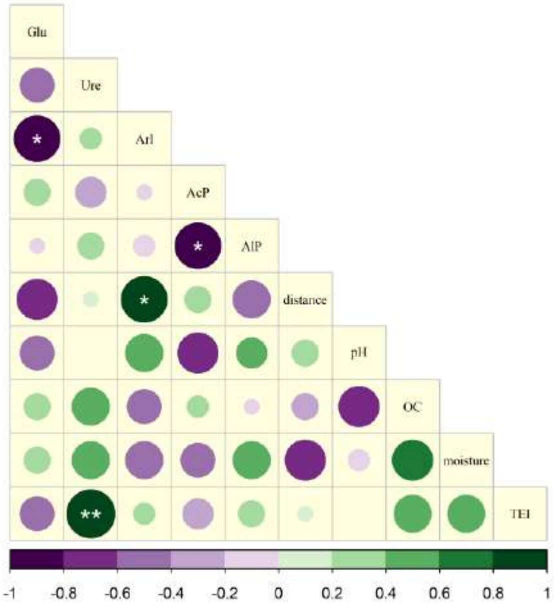

Figure 1 *Correlation matrix between soil enzyme activities, distance from the smelter, soil properties and TEI in the root zone soil of Plantago spp. based on Spearman's correlation coefficients. Purple and green colors indicate negative and positive correlations, respectively. The size of the circle is proportional to the correlation coefficients. Asterisks indicate statistical significance (*$^{*}p<0.05$*, *$^{**}p<0.001$*). Glu: ß-glucosidase, Ure: urease, Arl: arylsulphatase, AcP: acid phosphatase, AlP: alkaline phosphatase, OC: organic carbon content, TEI: total enzyme activity index.*

CONCLUSION

The influence of selected soil properties on the enzyme activities in soil sampled at five sites with distinct distance from the main pollution source was assessed. TEI inhibition rate denoted reduction of soil enzyme activities at the site Brezonik, while at the sites Town park, Oštrelj and Slatina soil enzyme activities were higher in comparison to the control site. Arylsulphatase activity was negatively correlated to the distance from the main pollution source, which indicated the reduction of the activity in the soil sampled in the close vicinity of the copper smelter. In general, soil enzyme activities were poorly related to soil pH, organic carbon and moisture content. Taking into account direct and indirect influences on the soil enzyme activities, the soil properties should be determined in the studies involving evaluation of soil enzyme activities as indicators.

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TOXICITY SCREENING AFTER DEGRADATION OF ORGANOPHOSPHORUS PESTICIDES WITH CHLORINE DIOXIDE

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Abstract

Effectiveness, mineralization and toxicity of four organophosphorus pesticides (OPPs) azamethiphos (AZA), dimethoate (DM), fenitrothion (FEN) and malathion (MAL) in water with chlorine dioxide (ClO_2) as degradation agent were investigated. Analyses included toxicity tests of parent pesticides and their degradation products (DPs), using Daphnia magna test organisms, and total organic carbon (TOC) analysis. Toxicity tests showed that all four pesticide DPs were less toxic than parent pesticides, but DM had higher toxic DPs compared to parent AZA, FEN and MAL. All DPs were classified as category III (on a scale from I to V) of toxicity as acutely toxic. TOC analysis showed that AZA has lowest (only 18%) and MAL has highest mineralization (56%). Considering the obtained results, it could be concluded that ClO_2 efficiently degrades AZA, DM, FEN and MAL and represents good solution for a safer environment.

Keywords: organophosphorus pesticides, chlorine dioxide, TOC, toxicity

INTRODUCTION

According to US EPA estimates, organophosphorus pesticides (OPPs) represent about 40% of the world market value [1]. They are the most popular and most used pesticides because of their low cost, wide spectrum of application and multi-pest control capability. The widespread application of the OPPs represents a great potential risk to environment and human life [2]. They could easily reach and contaminate the underground and surface water by leaching or runoff [3].

It has been found that OPPs could be very toxic to human health [2]. They can cause minor and major disruptive disorders, such as allergies, nausea, pancreatitis, spontaneous abortions and death [2,4]. It was reported that OPPs are neurotoxic and high doses of them involve inhibition of acetylcholinesterase [4]. Many researchers have suggested association between post natal exposure of children with OPPs and caused health disorders. Attention deficit hyperactivity disorder was noticed [5], also poorer short-term memory and attention [6], slower motor speed [7], and developmental delay [8]. Because of this and many other health disorders, significant number of OPPs has been restricted by Environmental Protection Agency (EPA) and European Union (EU) [9].

Among the oxidants, chlorine dioxide (ClO_2) has been increasingly employed as disinfectant in water treatment systems due to its antibacterial and antiviral properties [10]. As a powerful oxidant, ClO_2 can remove many organic and inorganic pollutants [11,12]. Previous studies reported oxidative degradation using ClO_2 of some pesticides and pharmaceuticals [3,13,14].

The aim of this study was to investigate effectiveness, mineralization and toxicity of four OPPs (AZA, DM, FEN and MAL (Figure 1)) and their DPs, in water using ClO_2 as degradation agent. Toxicity screening was examined with the test organisms *D. magna*. Also, the mineralization degree was obtained by total organic carbon (TOC) analysis.

MATERIALS AND METHODS

Chemicals

In this research AZA, DM (Makhteshim Agan, 98%, obtained from the Institute for Plant Protection, Belgrade), FEN and MAL (Sigma Aldrich, 97%) were used. Concentrations of pesticides in experiments were 10 mg/L for AZA and DM and 20 mg/L for FEN and MAL. Reason why we used 20 mg/L AZA and DM, not 10 mg/L like FEN and MAL, was the quantification limit on high performance liquid chromatography (HPLC) for these two pesticides which becomes important for trace monitoring in the final steps of degradation. For toxicity test pesticides were diluted in medium, prepared according to standard procedure OECD Guideline 202, 2004 [15, 16]. ClO_2 was prepared by dissolving sodium chlorite (TwinOxide®) and sodium bisulphate (TwinOxide®) in 1 L of deionized water and standardized with 0.1000 mol/dm^3 standard solution of sodium thiosulphate according to the Standard Method SRPS EN 12671:2009 [17].

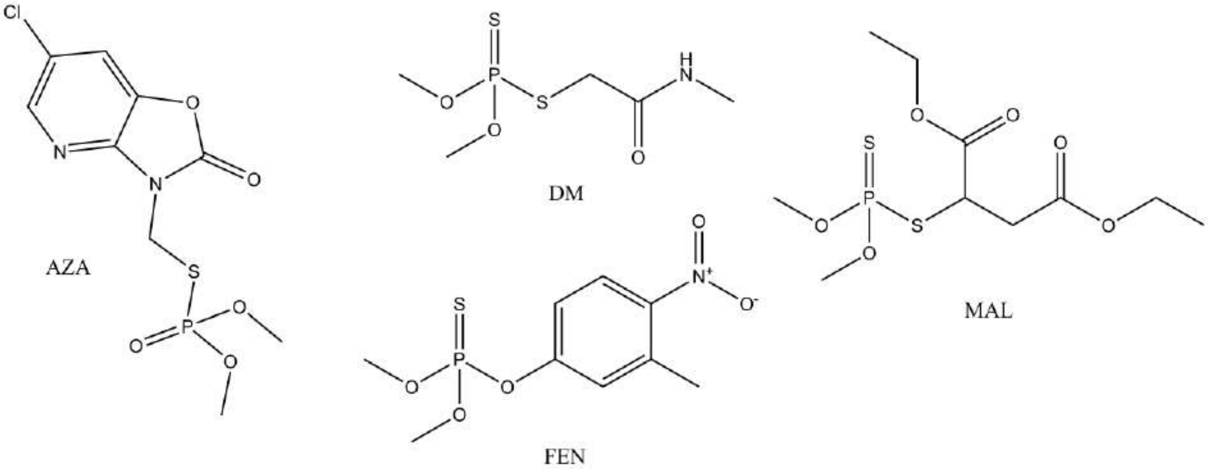

Figure 1 *Structures of organophosphorus pesticides*

Experimental

Optimization of pesticide degradation and preparation of samples for TOC analysis

The optimal conditions for degradation of OPPs with ClO_2 in deionized water had to be determined. Degradation using different concentrations of ClO_2 (5 and 10 mg/L), degradation time (0.5, 1, 2, 3, 6 and 24 h) and pH values (2, 3, 7, 9) was studied. The percentage of degradation was determined by HPLC analysis with photodiode array detection (DAD) as described previously by Pergal *et al.* [3]. Samples with the highest degree of degradation for each pesticide were analyzed by TOC analysis. TOC analysis was done on Zellweger LabTOC 2100 TOC Analyzer in accordance with method ISO 8245:2007 [3]. The optimal conditions for degradation of each pesticide were also applied to preparation of samples for toxicity tests.

Sample preparation for toxicity tests

All samples were diluted in medium prepared according to Klüttgen *et al.* [16]. One part of initial pesticide solution was taken for toxicity test and other part was set to optimal parameters and treated with optimal concentration of ClO_2 for obtaining of DPs. Test organisms *D. magna* were exposed to solution of pesticides and their DPs. A detailed examination using toxicity tests can be found in our paper Pergal *et al.* [3].

RESULTS AND DISCUSSION

Results of degradation efficiency

Optimization of OPPs degradation (AZA, DM, FEN and MAL) was performed in deionized water under sunlight conditions described previously by Pergal *et al.* [3]. In Table 1 are presented summarized optimal conditions for OPPs degradation (ranged from 81 to 100% in efficiency) and which were determined using HPLC-DAD analysis.

Table 1 *Optimized conditions for degradation of pesticides with ClO_2*

Sample name	Concentration of sample (mg/L)	Concentration of ClO_2 (mg/L)	pH value	Duration of degradation (h)	Degree of degradation (%)
Azamethiphos	10	10	9	0.5	100
Dimethoate	10	10	7	24	97
Fenitrothion	20	10	2	24	81
Malathion	20	5	7	24	98

Toxicity test results

Toxicity tests of the pesticide solutions and their DPs were evaluated using test organisms *D. magna*.

After a 48 h of test period number of live and dead neonates was determined, and LC_{50} (lethal concentration which causes 50% mortality in the daphnids) was calculated for each pesticide and its DP. Results of LC_{50} for parent pesticides and DPs are shown in Table 2. Solution of parent AZA has the highest mortality of neonates and FEN has the lowest mortality as compared to other parent pesticides, but it was still high. For DPs of pesticides, AZA has higher LC_{50} value, while DM has the lowest LC_{50} value compared to other pesticides. DM has the highest and AZA has the lowest mortality. The pesticides degradation products were less toxic than parent pesticides. When compared the toxicity results of pesticide solutions with their DPs, it could be concluded that ClO_2 degradation of AZA was successful. Also, there should be noted that in case of other tested pesticides toxicity of DPs was noticeable lower in comparison to starting pesticide solutions.

Table 2 *LC_{50} values of pesticides and their degradation products (DPs) after 48 h of ClO_2 treatment*

Sample name	LC_{50} (%, v/v) 48h	Sample name	LC_{50} (%, v/v) 48h
Azamethiphos	2.5	Fenitrothion	23.2
Azamethiphos DP	61.3	Fenitrothion DP	45.8
Dimethoate	12.2	Malathion	12.9
Dimethoate DP	35.4	Malathion DP	42.6

A toxicity unit (TU) was calculated for each sample using the LC_{50} results. On the scale from I to V [18] all DPs can be categorized in class III as acutely toxic.

Results of mineralization analysis

Mineralization percent was determined by TOC analysis for each pesticide and its DP. The results of mineralization are presented in Table 3. Results show that AZA and DM have low level of mineralization and MAL has the highest mineralization level as compared to other pesticides. But, low level of mineralization does not always mean that something is harmful or toxic. When all results have been compared (HPLC analysis, *D. magna* test and TOC analysis), we could see that AZA has a good degradation percent (100%) and its DP relatively high LC_{50} (61%). It means that ClO_2 degrades AZA very efficiently, with significantly less toxic DPs but they are still of organic origin. FEN and MAL both have good degree of degradation (81 and 98%, respectively) and mineralization (45 and 55%) and less toxic DPs. In case of DM, even ClO_2 degrades this OPP with degradation efficiency of 97%, ClO_2 creates relatively toxic DPs and they are mostly of organic origin (mineralization of only 23%).

Table 3 *Mineralization degree of degradation products (DPs) of pesticides*

Sample name	Degree of mineralization (%)
Azamethiphos DP	17.7
Dimethoate DP	22.5
Fenitrothion DP	45.2
Malathion DP	55.8

CONCLUSIONS

In this research, toxicity of AZA, DM, FEN and MAL pesticides and their DPs, after degradation with ClO_2 under optimal conditions for each pesticide, was studied. The toxicity test was done on *D. magna* neonates. Degree of mineralization was also obtained by TOC analysis for pesticides and DPs.

Results showed that AZA has a good degradation percent (100%) and relatively high LC_{50} (61%). It means that ClO_2 degrades AZA very well, with significant less toxic DPs but they are still of organic origin (18% of mineralization). FEN and MAL both have good degree of degradation (81 and 98% respectively) and mineralization (45 and 56%) and less toxic DP. In case of DM, ClO_2 degrades this OPP with degradation degree of 97%, ClO_2 creates relatively toxic DPs and they are mostly of organic origin (mineralisation of only 23%).

The results of toxicity tests showed that all DPs of pesticides belong to class III as acutely toxic. Further research should be directed towards obtaining less toxic products.

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Pistia stratiotes HEAVY METAL UPTAKE POTENTIAL: A STUDY OF MULTIPLY LEVEL CADMIUM POLLUTED WATER

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Abstract

Commonly found heavy metals in waters are As, Pb, Hg, Cd, Ni and Cr. The promising green technique for heavy metal removal from the environment is phytoremediation. Regarding polluted water, the best choice for phytoremediation are the free-floating macrophytes such as Pistia stratiotes. The aim of this study was to evaluate the time trend and sorption capacity of P. stratiotes with respect to increased cadmium concentration in aqueous cultivation medium. Sorption capacity of P. stratiotes towards cadmium with respect to the growth period, increases linearly in the first 4 day of growth; the linear correlation becomes weaker with the increasing pollution. Sorption capacity of P. stratiotes towards cadmium with respect to the level of pollution, increases linearly, up to 11th day, after which the adverse effect of prolonged plant exposure to cadmium was observed.

Keywords: water pollution, phytoremediation, *Pistia Stratiotes*

INTRODUCTION

Plants, animals and ultimately humans are negatively affected by heavy metal pollution of water supplies. Commonly found heavy metals in waters are As, Pb, Hg, Cd, Ni and Cr. One of the major consequences of this kind of pollution is bioaccumulation of heavy metals. There are many functional changes that can be observed in plants, after being exposed to heavy metals, such as plant membrane damage due to the formation of reactive oxygen species and radicals, disrupted metabolic activities or growth retardations. For example, the accumulation of cadmium in *P. stratiotes* stimulates malondialdehyde production, indicating that cadmium indirectly leads to production of superoxide radicals and increases lipid peroxidative products and oxidative stress [1]. However, toxicity degree of non-essential metals such as Cd, Pb, Hg depends on their concentration.

Techniques of phytoremediation arise as a cost-effective and ‘green’ solution for remediation of soils and water supplies contaminated by heavy metals. Many aquatic plants are currently under investigation to determine their phytoremediation potential, particularly high-growth rate plants *i.e.* macrophytes. *P. stratiotes* or water lettuce is a free-floating macrophyte from the family *Araceae*. The key properties of its potential phytoremediation effectiveness are high growth rate, high coverage of water surface and easy harvestability.

Mechanisms of phytoremediation varies between plant types. Metal uptake mechanisms may include accumulation, exclusion, translocation, osmoregulation and distribution. Among these accumulation, translocation and concentration of heavy metals in the aerial parts of hyper-accumulator plants are mostly suspected to occur [2]. Beside the plant type, an important factor of remediation capacity for a specific metal is the length of exposure, the metal itself, its concentration, environmental parameters (*e.g.* temperature, salinity and pH) and synergistic or antagonistic interactions with other metals in the environment [2].

P. stratiotes has been suggested for efficient removal of Cd and Pb from contaminated water since it has good rhizofiltration potential accompanied by a high tolerance to heavy metal stress, especially with respect to cadmium [3]. The aim of this study was to evaluate the sorption capacity of *P. stratiotes* with respect to increased cadmium concentration in aqueous cultivation medium.

MATERIALS AND METHODS

Reagents: the source of cadmium was the 72.958 µg mL^{-1} solution of cadmium-chloride [$CdCl_2$]. Nutrients for plant growth were not used.

Biosorbent: The samples of aquatic macrophyte *Pistia stratiotes* were handpicked from the natural freshwater habitat in Ostrovica, near Niš (Serbia), in the mid–June 2017.

Experimental setup

Collected plant samples were washed with tap water to eliminate the remains of pond sediments and particulate matter, placed in five different plastic tanks (labeled from I to V) and filled up to 35 L with tap water (Figure 1).

***Figure 1** Construction of P. stratiotes growth medium*

Each tank contained 15 specimens of *Pistia stratiotes* and different amount of Cd^{2+} ion (as $CdCl_2$), as given in Table 1. Plants were grown during 15 days in contaminated media. One plant per day was removed from each tank and analyzed.

Table 1 *Concentration of* $CdCl_2$ *and* Cd^{2+} *ion and amount of plant material in each tank*

Tank No.	I	II	III	IV	V
Cd^{2+} ion concentration, ppm	1	5	10	15	20
Cd^{2+} ion total amount in tank, mg	35	175	350	525	700
Total mass of plant material at start of experiment (fresh weight), g	490	480	528	426	522
Total mass of plant material at the end of experiment (fresh weight), g	402	355	388	292	349

Sample preparation

After removal from tanks, samples of *Pistia stratiotes* were washed out of excessive substrate solution with fresh water and left to dry indoor at ambient temperature until complete dryness. Afterwards, in order to remove possible residual humidity, plants were additionally dried in a laboratory oven, at 100 °C for 30 minutes, prior to weighing. Leaves and root of each plant specimen, were separated, weighted, cut in small pieces and pulverized. A weight of each specimen sample was then digested with 15 mL of a mixture (v/v 3:1) of concentrated 63% nitric acid and 30% hydrogen peroxide and solution was evaporated until dryness. The solid residue was re-dissolved in 13 mL of 0.1 mol/dm^3 nitric acid, filtered through filter paper, then through microfilter (0.45 µm), after which the mineralized plant material was ready for instrumental analysis.

Instrumental analysis

In order to determine the metal content in plant material, obtained extracts were analyzed by atomic absorption spectroscopy (AAS) using VARIAN Aanalyst 300 with acetylene/air flame.

RESULTS AND DISCUSSION

Effect of growth period in polluted water

Mass fraction of cadmium (mg kg^{-1}) in whole plant unit was calculated by summing up masses determined in roots and shoots, divided by mass of plant weighted prior to the separation of roots and shoots (dry weight).

Within tank No. I, cadmium amount in plant increases up from 66.47 to 307.25 mg kg^{-1} up to 4th day of growth (R_2=0.9989, linear fit). From 5th to 15th day it becomes practically uniform with average value of 303.90 mg kg^{-1} (RSD=25%). Similar was observed for tank No. III (Table 2). Linear increase in Cd amount up to 4th day (R_2=0.8876), after which it reaches 1944 mg kg^{-1} (RSD=35%). Within tank No. II increase in cadmium amount in plant is observed practically till 11th day of growth (R_2=0.8059, linear fit). 4th day linear correlation between Cd within-plant amount and growth period is weaker in tanks No. 4 and 5 (R_2=0.7552 and 0.7870, respectively). In this highly polluted water mediums, Cd amount through the period of 8 days (5th to 12th) reaches 3382 mg kg^{-1} in plants from tank IV (RSD=11%) and 3752 mg kg^{-1} in plants from tank V (RSD=25%). There is no correlation with measured amounts from 13th to 15th day of growth.

Table 2 *Cadmium amount in plant in mg kg^{-1} (dry weight) after exposure to cadmium polluted water*

	Tank No.				
Days	I	II	III	IV	V
	Amount mg kg^{-1} dry weight				
1	66.47	295.65	485.20	791.43	1550.72
2	139.36	592.57	1633.18	2592.75	2966.52
3	225.84	556.52	1843.56	3805.47	2689.64
4	307.25	698.89	2271.33	3374.47	3627.80
5	255.54	844.99	1475.13	2653.41	3218.94
6	288.62	779.36	1632.30	3835.65	2380.39
7	272.05	678.52	2479.26	3378.60	4200.69
8	282.18	898.74	3174.27	3685.47	3979.59
9	421.28	884.87	2447.61	3205.55	3618.25
10	280.10	897.68	1534.69	3273.23	5563.82
11	459.43	1138.03	2141.86	3302.57	4072.68
12	254.82	768.19	1158.27	3721.03	2983.39
13	236.68	355.09	797.40	661.14	678.83
14	360.15	995.28	2313.79	2828.99	1660.28
15	232.06	503.40	2230.63	2417.45	1852.88

Effect of increased cadmium pollution

The degree of linear correlation between the calculated fraction and cadmium concentration in aqueous solution is given in Table 3 for each day of the experiment and visualized in Figure 2 in five-days intervals. Strong correlation exists almost after each day of experiment, up to 11th day. Weaker correlation *i.e.* lesser mass fraction of cadmium at last days of experiment, especially after 12th day was probably due to the adverse effect of prolonged exposure to cadmium, since the destruction of plants was observed, mainly evidenced in root biomass reduction, as it was also elsewhere noticed [4]. Weight measurements showed that total mass of plant material measured from the beginning to the end of experiment (Table 1) was reduced for about 18.00, 26.00, 26.50, 31.00 and 33 % in tanks I, II, III, IV and V, respectively.

Table 3 *Coefficients of correlation between cadmium concentration in aqueous solution and in plant material (mg kg^{-1} dry weight) after each day during experiment*

Day	1st	2nd	3rd	4th	5th	6th	7th	
Correlation coefficient	0.918	0.979	0.756	0.951	0.987	0.666	0.974	
Day	8th	9th	10th	11th	12th	13th	14th	15th
Correlation coefficient	0.897	0.956	0.933	0.996	0.794	0.609	0.482	0.639

At the end the percentage of cadmium removal from experimental solutions by the total mass of plant can be pointed out. In the hypothetic case of a 100 % cadmium removal, the mass fraction of cadmium based on total plant mass from tank No. I would be 71.42 mg kg^{-1} of fresh weight. Experimentally determined fraction was 5.085 mg kg^{-1} of fresh weight; thus, the percentage of cadmium adoption/removal is 7.12%. The percentage for tanks No. II, III, IV and V was 3.75, 5.08, 5.25, 4.25%, respectively. However, it should be kept in mind that the removal percentage represent an uptake potential of 15 plant units, where each of them has been in contact with the polluted water for only 24 hours.

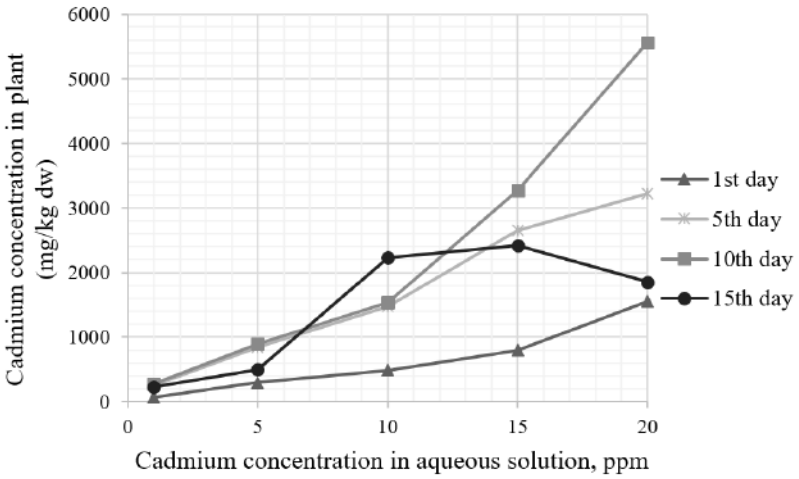

Figure 2 *Cd concentration in plants vs. concentration in tanks, for different exposure periods*

CONCLUSION

Sorption capacity of *P. Stratiotes* towards cadmium with respect to the growth period, increases linearly in 1, 10, 15 and 20 ppm cadmium polluted medium, but only in the first 4 day of growth. Furthermore, with increasing pollution linear correlation becomes weaker. The exception is water medium with 5 ppm of cadmium, where sorption capacity linearly increases up to 11th day.

Sorption capacity of *P. Stratiotes* towards cadmium with respect to the level of pollution, was reflected through strong correlation almost after each day of experiment, up to 11th day. Weaker correlation, especially after 12th day, was probably due to the adverse effect of prolonged exposure to cadmium, since the destruction of plants was observed, mainly evidenced in root biomass reduction.

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AGRICULTURAL SOIL POLLUTION BY HEAVY METALS IN THE MUNICIPALITY OF PLJEVLJA, MONTENEGRO

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Abstract

This paper aimed to investigate the agricultural soil pollution by heavy metals as a result of anthropological activities in the municipality of Pljevlja, north part of Montenegro. The soil samples contaminated by heavy metals (Zn, Cu, Cd, Cr, Pb, Hg and As) were taken from the settlement near the coal fired station Pljevlja and from open pit mine of lead and zinc "Šuplja Stijena". The soil pollution was evaluated using the ecological risk (RI) index and index of geo-accumulation (I_{geo}). The results have indicated the extremely polluted soils by Pb, Zn and Cr, unpolluted or unpolluted to moderately polluted soil by Cd, strongly to extremely polluted soil by As and unpolluted soil by Hg. The low ecological risk values were mainly obtained but three sampling sites indicated moderate, considerable and high ecological risk.

***Keywords**:* Heavy metals, agricultural soil, ecological risk index, index of geo-accumulation

INTRODUCTION

The problem of heavy metal contamination in the environment is widespread. Significant amount of pollutants from different sources can contaminate soil every year. Soil acts as natural buffer by controlling the transport of chemical elements and substances to the environment as well as a sink for the chemical pollutants. Toxic elements such as heavy metals contaminate agricultural soil that attracts the interest of people, because metals can be taken by plants and may enter the food chain, and therefore, humans can also be exposed to this kind of contamination [1]. Different kinds of industries can be generators of heavy metals and contribute their reaching in the soil through industrial effluent. The quality and concentration of the heavy metals varies from industry to industry and has a direct concern with nature of the product. Deficient environmental management have led to a large-scale pollution in the environment especially in developing countries, due to rapid industrialization, excessive application of metals and synthetic chemicals in the terrestrial environment. Although some of heavy metals are essential for a different metabolic process, the high intake of these elements lead to their accumulation in a human body and potential development of different diseases. The body burden of Cd and Pb have been well documented as toxic to the central nervous and renal systems while chronic exposure to Cu health problems such as: nausea, head-aches and diarrhea [2].

Environment pollution by heavy metals is a result of different anthropological activities. There are several sources of heavy metals pollution in the environment: 1) air sources from mining, smelting and refining of fossil fuels, production and use of metallic commercial products and vehicular exhaust, 2) water from domestic sewage, thermal power plants and atmospheric fallout, sewage and industrial effluents, and 3) soil - like agricultural and animal wastes, municipal and industrial sewage, coal ashes, fertilizers, discarded manufacture goods and atmospheric fallout [3]. The two main industrial pollution sources in Montenegro are located in the municipality of Pljevlja on the north part of Montenegro. The first one is a coal fired power station Pljevlja and second one is an open pit mine of lead and zinc "Šuplja Stijena". Since, both activity present a serious risk for a global community, this paper aimed to investigate the pollution of agricultural soils in the surrounding settlement of coal fired power station and mine. The sampling of agricultural soil at eleven locations was carried out and heavy metals concentrations (Zn, Cu, Cd, Cr, Pb, Hg and As) were determined.

MATERIALS AND METHODS

Materials and sampling

Soil samples were taken from maximum 20 cm depth, from agricultural fields near households in November 2019. The households are located near two sources of pollution, Thermal power plant (TE Pljevlja) and Zinc and lead mine (Gradir, Montenegro). Samples 1, 2, 3, 4, 6, 7 and 11 are located near Thermal power plant. Sample 5 is located between Thermal power plant and surface Coal mine. Samples 8, 9 and 10 are located near Zinc and lead mine. For metal analysis, wet soil was dried at 105°C and sieved through mesh 0.25 µm. 3 g of dried and sieved samples were digested with 25 ml of aqua regia, using reflux and heating source (EPA method 3050B). Samples were filtrated through Whatman No. 41 and flasks were washed with 5 ml of concentrated HCl and adjusted to final volume of 50 ml with distilled water. Concentrations of heavy metals were measured using inductively coupled plasma technique (ICP-OES), manufactured by Spectro Arcos with hydride technique for As determination.

Assessment of Soil Contamination

Ecological risk (RI) index and index of geo-accumulation (I_{geo}) defined by Müller [4] were used in order to define and determine soil contamination by arsenic by comparing current concentrations with pre-industrial levels. Based on the value of RI there are low, moderate, considerable and high risk contaminations while based on the value of I_{geo} there are seven classes of pollution (Table 1) [2].

Table 1 *Terminologies for the assessment of agricultural soil contamination by arsenic and terminologies for contamination classes on pollution indices*

Ecological risk index (RI) : $RI = \Sigma E_r$; $E_r = T_i \cdot C_f$;	$C f = \frac{Ci}{Cri}$
Low risk	$RI < 150$
Moderate risk	$150 \leq RI < 300$
Considerable risk	$300 \leq RI < 600$
High contamination	$RI \geq 600$
Index of geo-accumulation (I_{geo})	$I_{geo} = \log_2 \left[\frac{C_i}{1.5 \cdot C_{ri}} \right]$
CLAS 0, unpolluted	$I_{geo} \leq 0$
CLASS 1, from unpolluted to moderately polluted	$0 < I_{geo} \leq 1$
CLASS 2, moderately polluted	$1 < I_{geo} \leq 2$
CLASS 3, from moderately to strongly polluted	$2 < I_{geo} \leq 3$
CLASS 4, strongly polluted	$3 < I_{geo} \leq 4$
CLASS 5, from strongly to extremely polluted	$4 < I_{geo} \leq 5$
CLASS 6, extremely polluted	$I_{geo} > 5$

C_i is the total metal content in soil, C_r is background level (reference threshold for sensitive soil [5]) and Ti is the toxic-response factor for a given substance by Håkanson [6] (Table 2), C_f is contamination factor and E_r is ecological risk factor.

Table 2 *Toxic-response factor (T_i) by Håkanson Elements [6]*

Elements	Cu	Cd	Zn	Cr	Pb	Hg	As
Toxic-response factor	5	30	1	2	5	10	40

RESULTS AND DISCUSSION

Total contents and descriptive statistics for the heavy metals measured in this study are given in Table 3. The order of the total element content was Zn>Pb>Cu>Cr>As>Cd>Hg. The results have shown that the mean content of Pb exceeds the maximum allowed concentration of metals prescribed by National regulation [7] while the values of mean contents of other metals are below the prescribed limits.

Table 3 *Total contents and descriptive statistics of elements in agricultural soil samples*

Site	**Element (mg kg^{-1})**						
	Pb	**Cd**	**Cu**	**Zn**	**Cr**	**Hg**	**As**
1	11.73	0.92	15.78	43.3	6.14	0.06	4.06
2	21.07	0.99	52.35	96.54	16.35	0.425	10.52
3	20.00	1.26	59.43	129.85	13.8	0.08	8.11
4	17.43	0.24	22.32	30.73	13.76	0.11	4.33
5	35.76	1.78	49.67	92.55	17.47	0.12	7.12
6	23.97	0.63	52.92	117.98	18.86	0.17	9.54
7	37.65	3.08	56.79	140.27	28.24	0.93	12.7
8	37.82	0.52	37.82	81.57	15.7	0.07	8.24
9	837.4	2.8	18.85	1150.3	18.95	0.62	57.71
10	27.37	0.51	51.76	55.28	13.28	0.18	9.42
11	39.97	0.75	52.35	80.87	28.53	0.18	2.00
MAC*	**50**	**2**	**100**	**300**	**50**	**1.5**	**20**
Min	11.73	0.24	15.78	30.73	6.14	0.06	4.06
Max	837.4	3.08	59.43	1150.3	28.24	0.93	57.71
Mean	100.9	1.23	42.73	183.6	17.37	0.268	12.16
SD**	244.4	0.945	16.2	322.5	6.48	0.279	15.4

MAC* maximum allowed concentration.
SD** Standard deviation.

Geo-accumulation index (I_{geo}) and ecological Risk Index (RI)

According to geo-accumulation index (I_{geo}) (Figure 1) values for Pb, Zn, Cu and Cr the agricultural soil in the municipality of Pljevlja belong to Class 6 i.e. extremely polluted soils. The values for I_{geo} for Cd indicated the unpolluted (Class 0) or unpolluted to moderately polluted soil (Class 1). The soil belongs to the extremely polluted (Class 6) and the Class 5 i.e. strongly to extremely polluted soil with respect to the value of I_{geo} for As while there is no contamination by Hg since the values of I_{geo} indicated unpolluted soil.

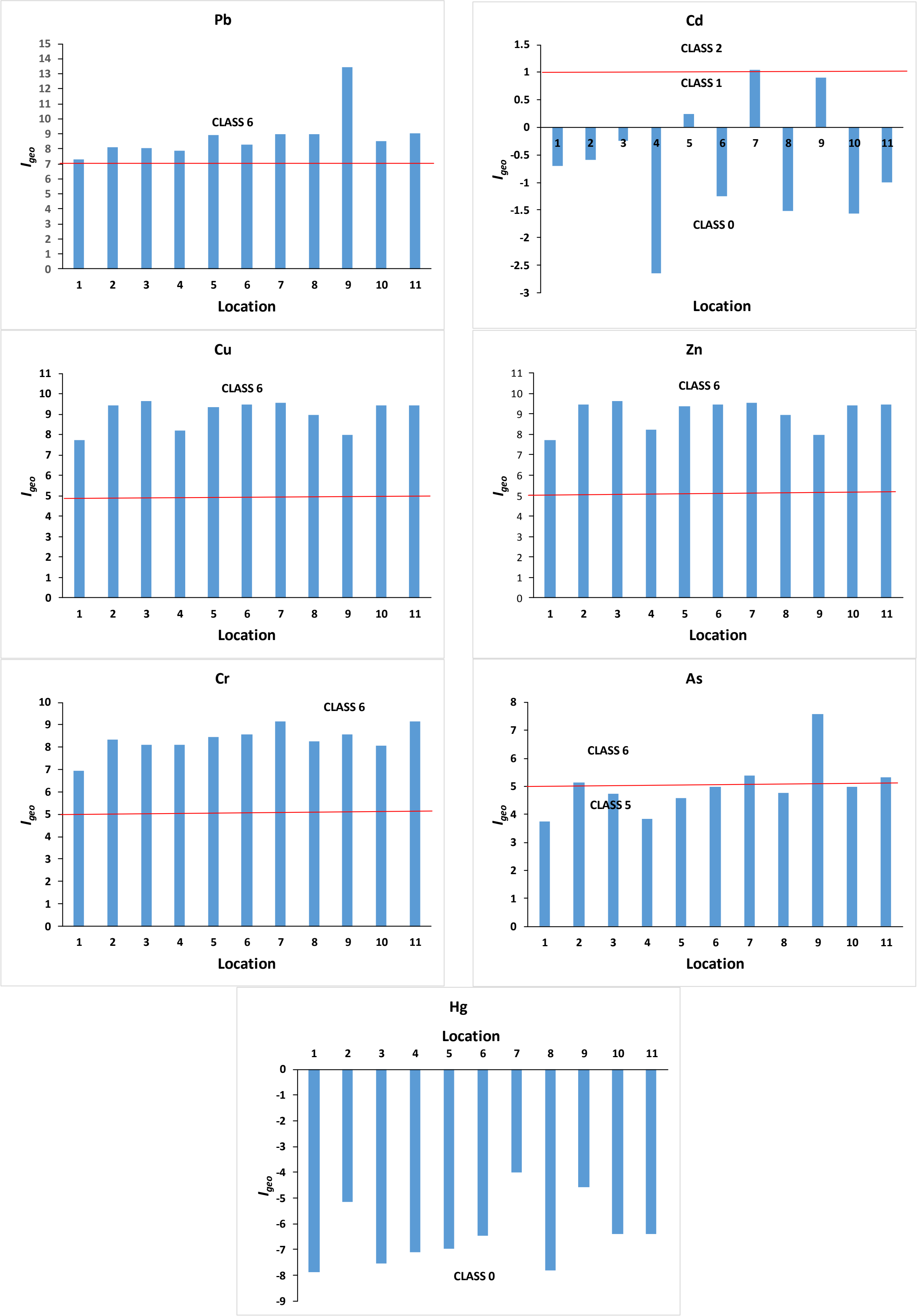

Figure 1 *Geo-accumulation index (I_{geo}) values of heavy metals in agricultural soil samples in the municipality of Pljevlja (Montenegro)*

The results obtained for ecological risk assessment (Figure 2) showed that *RI* values were mainly lower than 150 indicating the low ecological risk. However, the *RI* values at location 2, 7 and 9 indicated moderate, considerable and high ecological risk, respectively. Zinc, lead, copper and arsenic are the main contributors to *RI* values.

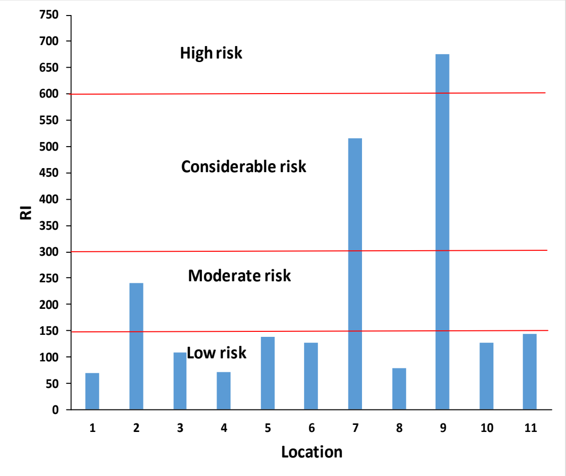

Figure 2 *Ecological risk index (RI) values of heavy metals in agricultural soil samples in the municipality of Pljevlja (Montenegro)*

CONCLUSION

The results of investigation have shown that the values of I_{geo} indicated the agricultural soil is extremely polluted by Pb, Zn, Cu and Cr, extremely polluted or strongly to extremely polluted by As, unpolluted or unpolluted to moderately polluted by Cd while pollution by Hg was not registered. With respect to the values of *RI* agricultural soil in the municipality of Pljevlja in Montenegro are characterized mainly by low ecological risk. However, the results obtained at three locations indicated moderate, considerable and high ecological risk.

ACKNOWLEDGEMENT

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THE INFLUENCE OF THE PROCESS OF WASHING ORE OF BORON MINERALS FROM THE "POBRDJE" DEPOSIT ON THE ENVIRONMENT

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Abstract

Pine ore deposits in Pobrdje and Piskanja, Baljevac - Serbia, are unique in this part of Europe so far. Trial excavation of trench ore by underground mineral extraction methods was organized at the „Pobrdje“ ore deposit. After excavation, the trench ore is transported by truck to the disposal site at the location of the Piskanja site. The hand-picked ore is taken to the customers and the tailings go to the landfill. There are small classes of ore in the tailings that could not be separated by hand, so the use of trench ore is about 20 to 30%, depending on geological conditions. The low utilization in the manual extraction of ore deposit "Pobrdje" indicates that for the future exploitation of ore from the "Piskanja" deposit, technical and technological solutions must be provided that will improve the utilization. Some of the possible solutions are: magnetic separation, optical separation, electrostatic separation, decryption, etc. To determine the optimal solution researchs and industrial tests must be performed. Each of these methods require the removal of impurities from the trench ore, that is, the trench ore washing, which will produce a certain amount of waste water. This paper will present the results of the analysis of wastewater used in the process of washing the primary trench ore in order to define the environmental impact.

Keywords: boron ore, trench ore washing, wastewater, environmental impact

INTRODUCTION

Since boric acid is widely used in many fields of industry, pharmacy, agriculture, etc., there is a real need for its production. One of the production possibilities is a technological process that uses a mixture of colemanite and haulite minerals, enriched with B_2O_3 at least 42%, for the feedstock. Boron oxides are present everywhere in nature, but boron minerals are very rare. Such deposit in which the boron minerals haulite and colemanite are represented is in the Jarandol basin.

The Jarandol Tertiary Basin is located in the valley of the Ibar river, territorially belonging to the Raska Municipality, about 14 km away. The basin is elongated in the W-NW-E-SE direction. The Ibar river is divided into two parts: the eastern, the Piskanjski which contains the deposit of the Piskanja boric minerals and the western, wich contains the Jarandol coal horizons, the mineral deposit of the "Pobrdje" in the Pobrdje stream and the boron mineralization in Raspopovic. The deposit of the boric minerals "Pobrdje" is located west of

Baljevac, about 1.6 km away. Traffic communications with „Pobrdje“ deposit are very convenient [1].

An ore body consisting of cholemanite and haulite is genetically related to younger volcanism, that is, volcanic gas fumaroles and hydrothermal solutions containing significant concentrations of boron. The accompanying rocks of the ore layers are: volcanogenic breccias and conglomerates of marls, tuff-sandstones, sandstones and clays, which often form larger and smaller layers in the ore layer, which negatively affects the depletion of the trench ore [2].

Balance ore reserves as of 31.12.2019. amounted to 124.701 t. Taking into account mining and geological conditions, the excavation of pine ore in the "Pobrdje" deposit is done by underground exploitation, and the trench ore in the pit "Pobrdje" is obtained by the process of drilling and mining operations. The mined ore from the pit is transported to the surface by a conveyor system, ie by chain conveyors and belt conveyors, from where it is transported by truck to a location in the area of Piskanja. The hand-picked ore is taken to the customers and tailings go to the landfill. Due to the presence of a lot of fine particles of both ore and tailings and the presence of moisture and bitumen, the very fractions of ore and tailings occur in the process of exploitation and transportation. They adhere to both the tailings surface and the ore surface, so it is difficult to visually distinguish the ore from the tailings. Ore itself is often very similar to tailings, especially sandstones that have a greyish color. The exception is haulite, which has a snow-white color and is no problem to spot and separate from the tailings. During the manual extraction of ore, the effects are very small due to the difficult distinction between ore and tailings. Better results are achieved when washing the ore, ie, by washing with water, it is easier to distinguish between ore pieces and tailings pieces.

Although much better results have been shown in practice when the ore was previously washed, manual ore selection due to low utilization is not an option and is unlikely to apply in the future. The methods used in the world to obtain boron ore concentrates, that is, colemanite concentrates, which in commercial form should contain from 35 to 43% of useful component B_2O_3, are magnetic separation as a very cheap form of separation, decryption, electrostatic separation, for optical separation or separation on optical sorters. For each of these types of separation, it is necessary to separate the ore and tailings grains from tiny micro particles in order to distinguish them. For example, in the case of magnetic separation, this is necessary because if the tailings were not removed from the ore, which, due to the content of the iron, were magnetic, the magnetic separator would attract them altogether. No matter which method of concentrate production is adopted, the need to wash ore is inevitable.

The purpose of this paper is to determine whether water can be discharged into watercourses after the process of washing trench ore, or whether a treatment facility or a wastewater treatment plant is required. To determine the correctness of such water, we took one quantity of trench ore and washed it with a certain amount of water.

MATERIALS AND METHODS

The trench ore from the pit, previously ground on a crusher with a hammer to a particle size of -16.0 + 0.00 mm, was used for the experiment. Thereafter, a measured amount of 1 kg of ore of such a granulometric composition was inserted into a plastic balloon. Then the water was poured into the balloon, shaken and cast. On this occasion, 9 liters of water was consumed to wash 1 kg of trench ore. The used washing water was taken from the city water supply system, for which the competent institution daily analyzes the water quality. Such water was poured into special balloons and collected. The process itself was repeated several times until a water of barely noticeable slight turbidity was obtained. The water was collected in two balloons, which were sent for testing to the Institute MOL d.o.o. During the test, the water was filtered and on this occasion sludge was obtained as a solid residue and a clearer liquid residue.

RESULTS AND DISCUSSION

According to the analyzes done earlier, the content of B_2O_3 in water after the first ore washing is 0.0856 mg/l, which indicates that boron ore can be washed because it is insoluble in water, more precisely it is poorly soluble [3]. During the ore washing, the water removes the dirt, dust and micro particles from the ore and tailings that are generated during the exploitation and transportation of the ore.

A balloon containing a sample of shredded trench ore was used in the experiment, and the appearance of such a sample before washing is shown in Figure 1a. As we emphasized, the water from the city water supply system was poured into a balloon containing trench ore. The balloon was shaken several times to make contact between water and all fractions of trench ore more intense. Afterwards, such water is drained and a new amount of water is poured into the balloon. When the first quantity was drained, the water was extremely turbid and parts of the wooden pit support that were floating on the water were present. The appearance of such turbid water is shown in Figure 1b.

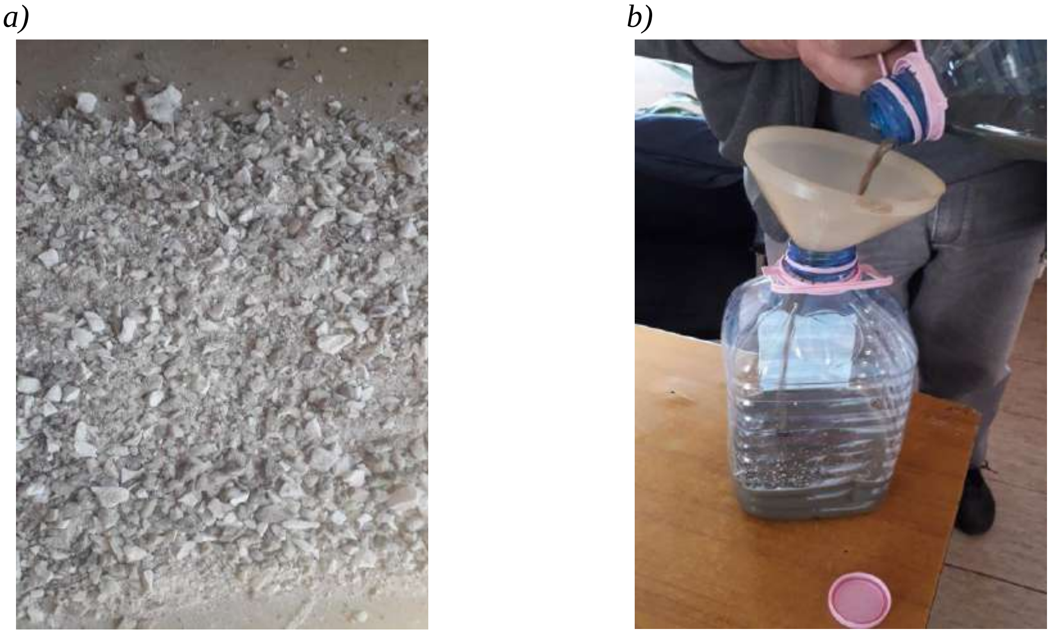

Figure 1 *Initial phase of trench ore washing a) the appearance of shredded trench ore before washing; b) the appearance of turbid water during washing when the first quantity is outflow*

This process was repeated several times until the watered water became almost clear, that is, until it had a slight turbidity. The appearance of such slightly turbid water is shown in Figure 2a, and the appearance of the sample of shredded trench after washing in Figure 2b. Visual differences between tailings and ore were noticeable, confirming the conclusion that trench washing would be of great benefit in the preparation phase for the selected separation method.

Figure 2 *Final stage of trench ore washing a) the appearance of slightly turbid water after removal at the end of washing; b) the appearance of shredded trench ore after washing*

In order for water to be allowed to enter the watercourses after washing, it must meet a certain ecological status according to the classification given in the ordinance, which prescribes ecological and chemical status parameters for surface waters. Decree on limit values of pollutants in surface and groundwater and sediment and deadlines for their attainment (Official Gazette RS No. 50/2012) defines limit values for parameters for a certain ecological status, ie class of surface waters [4].

After submitting the wastewater sample for testing, the MOL Institute d.o.o. did the analysis and produced the test report. The parameter concentrations were determined from the clear portion of sample I.b. 803, and the results of these analyzes are shown in Table 1. Methods which used to find parameter values are also shown in Table 1.

Comparing the limit values of the parameters for good ecological status, that is, for the II class of surface waters with the obtained results, it was found that the pH and ammonium ion values were increased [5]. Namely, the pH limit for the mentioned surface water class is 6.5-8.5, while the found value is 8.86. Also, the limit value for ammonium ions for the mentioned surface water class is 0.10 mg N/l, while the value of 0.28 mg N/l was found. The values found for other parameters were within the allowed values.

Table 1 *Test results for the clear portion of the sample I.b. 803, Mol Institute d.o.o. [5]*

Parameter	Method	Measurement unit	Found value
pH	SRPS H.Z1.111:1987		8.86
Specific conductivity	ASTM D 1125A:1999	µS/cm	335
Total residue after evaporation	Manual $^{2)}$ met. 2540 B:98	mg/l	318.0
Suspended matter	Manual $^{2)}$ met. 2540 D:98	mg/l	<15.0
Sedimentary matter	VM 068	ml/l	<0,1
Chemical oxygen demand (COD)	EPA M 410.2:1978	mg O_2/l	9.77
Biochemical oxygen demand (BOD)	SRPS EN 1899-1:2009	mg O_2/l	<3.0
Consumption of potassium permanganate	SRPS EN ISO 8467:2007	mg/l	5.69
Chlorides	VM 057-2	mg/l	4.51
Sulfates	VM 057-2	mg/l	38.12
Phosphates	VM 057-2	mg P/l	<0.1
Nitrates	VM 057-2	mg N/l	0,98
Nitrites	VM 057-2	mg N/l	<0.1
Ammonium ion	SRPS H.Z1.184:1974	mg N/l	0.28
Total inorganic nitrogen	calculated	mg N/l	1.26
Oils and fats	EPA M 1664 A:1999	mg/l	<1.4
Phenols	SRPS ISO 6439 B:1997	mg/l	<0.002
Mineral oils C10-C40	VM 056-2	mg/l	<0.05
Detergents	SRPS EN 903:2009	mg/l	<0.1
Iron	VM 090	mg/l	<0.01
Chrome	VM 090	mg/l	<0.007
Zinc	VM 090	mg/l	<0.006
Copper	VM 090	mg/l	<0.006
Nickel	VM 090	mg/l	<0.008
Lead	VM 090	mg/l	<0.005
Cadmium	VM 090	mg/l	<0.003
Total phosphorus	SRPS EN ISO 6878:2008	mg/l	0.017
TOC	VM 093	mg/l	1.51
Sulphides	EPA M 376.2	mg/l	<0.1
Cyanides	SRPS H.Z1.139	mg/l	<0.01
Mercury	EPA M 245.1	mg/l	<0.0007
Arsenic	VM 090	mg/l	0.008

Since ammonium ion occurs in the presence of organic matter, one of the assumptions for increased ammonium ion concentration may be the appearance of residual parts of the wooden pit support and bitumen. For increased pH, a more detailed analysis would have to be done to explain why such water is alkaline to this extent. Such information would assist in the treatment of wastewater.

CONCLUSION

In order to improve the technical and technological procedure for the separation of pine ore, the procedure for trench ore washing is imposed as a first step. As a product of the washing of pine ore, a certain amount of waste water is generated which has to be tested and determined whether it can freely enter the watercourses. This experiment was performed to serve as an initial assumption of water quality for further exploration of the possibility of treating such wastewater. The test results show that the found pH values and the found values of ammonium ion concentration increased in relation to the limit values prescribed by the Decree on limit values of pollutants in surface and groundwater and sediment and deadlines for their attainment (Official Gazette RS No. 50/2012), indicating that such filtered water does not qualify for discharge as such into watercourses. It is necessary to create a plant for the preparation of mineral raw materials where the water would be brought to a condition that would meet the legal requirements during the technological purification process, so that it could flow into the watercourses. This should be a mandatory part of all future projects that would address any type of separation in raising the quality of boron concentrate.

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REMOVAL OF PHOSPHORUS AND NITROGEN IN MODIFIED FLOATING TREATMENT WETLAND

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Abstract

There is a recognised need for the protection of water integrity by using environmentally friendly, efficient and cost-effective solutions. Floating treatment wetlands (FTW) have emerged as a powerful and innovative technology for the removal of a vast spectrum of pollutants from contaminated water. This research set out to determine the efficiency of P and N removal in modified FTW constructed on the bank of the polluted urban river. The results showed that after the whole treatment P concentrations in polished water were reduced by 87%. This green technology was also very efficient in removing NH_4*-N,* NO_2*-N,* NO_3*-N and total N by decreasing its concentrations 96%, 97%, more than 94% and more than 86%, respectively. Further studies should focus on the research on the required number and arrangement of cells with aerobic and anaerobic conditions in FTW.*

Keywords: floating treatment wetlands, water pollution, phytoremediation, nutrient removal

INTRODUCTION

Finding an efficient, environmentally friendly and economically justified solution for the treatment of degraded urban rivers and lakes has received increased attention across many disciplines in recent years. Floating treatment wetlands (FTW) are one of the innovative phytoremediation techniques [1] that are often described as more cost-effective and efficient compared to widely used constructed wetlands [2,3]. Floating treatment wetlands consist of a series of cells with floating islands. The platform, which carries the substrate for the growth of terrestrial and aquatic plants forms the floating island. To start the revitalization of the polluted urban river, pilot-scale FTW was constructed on its bank. Because of numerous sources of anthropogenic pollution this river is mainly classified as a river with bad ecological status (class V) based on its chemical, physiochemical and microbiological water parameters [4]. Phosphorus (P) and nitrogen (N) are one of the most important elements in ecosystems. However, the problem arises when the excess amounts of these macronutrients occur in water. This will lead to a deplete of dissolved oxygen in the water and the appearance of eutrophication [5]. This paper evaluates the efficiency of modified FTW in the removal of P and N.

MATERIALS AND METHODS

The FTW consisted of a pump for drawing water from the river, a closed collection tank, four open rectangular cells with floating islands, and one open rectangular cell with algae [4]

(Figure 1). In each of 4 cells, there were 3 floating islands with seedlings planted in the substrate (stone wool). The coverage of the cells with plants was 100%.

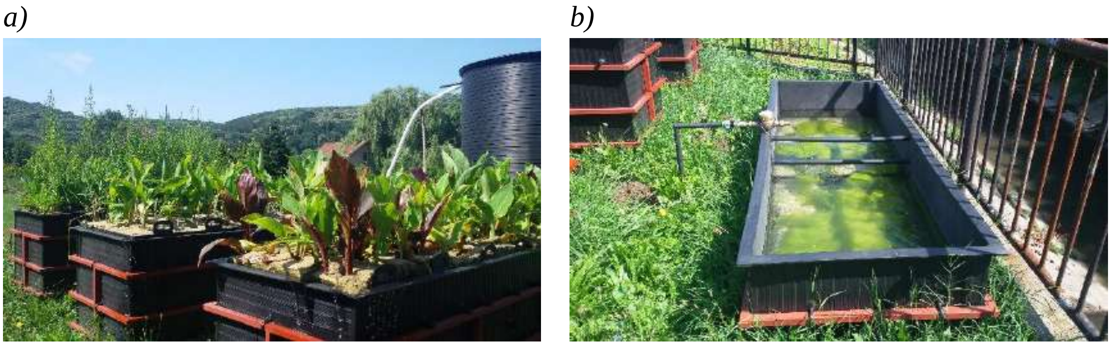

Figure 1 *The cells with plants a month after the planting (a) and the cell with algae (b)*

The floating islands of the Cell 1 were planted with 25 seedlings of *Phragmites australis* (Cav.) Trin. ex Steud each. The Cell 2 was planted with 25 seedlings of *Canna indica* L. per floating island. The Cell 3 contained a mix of those 2 species, with 25 seedlings on each island. Each floating island of the Cell 4 was planted with 30 seedlings of mix decorative macrophytes: *Iris pseudacorus* L., *Iris sibirica* 'Perry's Blue', *Alisma plantago - aquatica* L., *Lythrum salicaria* L. and *Menyanthes trifoliata* L. The algae (*Cladophora* sp.) were introduced to the Cell 5 directly from the river.

A 12-day treatment was conducted to assess efficiency of modified FTW for removal of P and N from water. The treatment cycle began with the pumping of polluted water from the river to the collection tank. Water was then simultaneously transported by gravitation to 4 open cells with floating islands. Polluted water stayed in Cells 1 - 4 for 6 days and then it was moved to the Cell 5 for the same period. At the end of this phase, the treatment cycle was completed. Samples of polluted water were collected at the beginning of the treatment cycle at the outlet of the pump. Treated water was sampled in cells with plants after 6 days. Polished water in the cell with algae was sampled at the end of the cycle (after 12 days). The composite sample represented 1L of water collected from 5 spots within each cell.

Temperature, pH and dissolved oxygen (DO) in water samples were measured with HACH HQ 40d Digital Multi 2-channel Meter with automatic temperature calibration (HACH, USA) according to US EPA 170.1:74, SRPS EN ISO 10523:2016 and HACH 10360 LDO methods, respectively. Total P was determined by SRPS ENISO 6878:2008 method. Concentration of ammonia nitrogen (NH_4-N), nitrites (NO_2-N), nitrates (NO_3-N), and total N were determined according to SRPS EN ISO 14911:2009, SRPS EN 26777:2009, APHA 4500-$NO3^-$ B and SRPS EN 12260:2008 methods, respectively.

RESULTS AND DISCUSSION

The polluted water had the characteristics of a slightly alkaline medium (Table 1). There was a decrease in pH in each cell with plants after the first six days of treatment. However, the pH value increased again at the end of treatment (after 12 days). Extremely low DO values were detected in Cells 1 - 4 due to 100% cell coverage with floating islands (Table 1). After water polishing in Cell 5, the amount of DO increased and had higher values than DO concentrations in the polluted water.

Table 1 *Temperature, pH and dissolved oxygen in polluted and treated water*

Parameter	Tank	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5
t (^{o}C)	14.50	12.80	12.10	12.40	12.10	14.00
pH	7.66	7.33	7.29	7.37	7.33	8.15
DO (mg/L)	6.98	0.40	0.63	1.33	1.43	18.77

Low concentrations of phosphorus (0.31 mg/L) were detected at the inlet of FTW. Content of P increased within the cells with floating islands after 6 days of treatment. However, by the end of treatment, the removal efficiency of total P in Cell 5 was 87% (Table 2).

Settling is the main physical process for the removal of P from polluted water [1,6]. During this process, P binds to solid particles in water and sinks to the bottom of the FTW. The removal of P is much more efficient in the FTW compared to other constructed aquatic ecosystems [7]. The large free root surface of floating islands allows rapid filtration of solid particles from the water which are then precipitated with P. White and Cousins [8] have shown that the removal efficiency of P in the FTW can reach 81%. The results of this research are in accordance with these claims if the efficiency of the entire FTW is considered. However, the results also showed that there was no reduction of P concentrations in the Cells 1 - 4 and that there was higher content of P in the outlet of these cells than in the collection tank. It was presumed that the anaerobic conditions in the cells with floating islands have led to the release of sequestered and precipitated P back into the water body. It was also assumed that at extremely low DO content in the water, sulfate was reduced, sulfides were created, and thus prevent the binding of P to Fe and Al oxides [9]. Also, the cause of the additional P resuspension in the FTW could be the turbulence caused by the introduction of new quantities of water into the cells or the occurrence of gases (oxygen, methane and carbon dioxide) from the bottom of the cells [5]. Algae have a high affinity for P removal from polluted water, and the removal process is rapid [10]. The results have shown that algae accumulate large amounts of P during the experimental period [4]. Since there was no removal of P in the Cells 1 - 4, it can be concluded that algae were responsible for the biological removal of P in the modified FTW. Together with the settling and sorption processes in the aerobic environment, algae were able to remove this element with high efficiency.

Confirmation of the high efficiency of the modified FTW in the removal of P can also be supported by the following data. Based on the concentration of P as a parameter for the assessment of the ecological status of waters [11] water at the inlet of the modified FTW was classified as water with moderate ecological status (class III). After 12-day treatment, water at the outlet of the modified FTW had characteristics of water with excellent ecological status (class I).

Table 2 *Efficiency of the removal of total phosphates, ammonia nitrogen, nitrite, nitrate and total nitrogen (%)*

Parameter	Cell 1	Cell 2	Cell 3	Cell 4	FTW outlet
P	-55	-294	-71	-58	87
NH_4 - N	83	45	81	78	96
NO_2 - N	15	-137	-26	-100	97
NO_3 - N	79	56	63	67	>94
N	77	22	64	67	>86

The initial concentration of ammonia (NH_4-N) in polluted water was 3.12 mg/L. After the treatment cycle the concentration was reduced to 0.14 mg/L and thus a removal efficiency of 96% was achieved (Table 2). Reduction of NH_4-N concentration was significant even after six days of treatment in the cells with plants. The highest NH_4-N removal efficiency in the Cells 1 - 4 was achieved in the Cell 1 where *P. australis* was planted (Table 2). The removal efficiency of nitrite (NO_2-N) and nitrate (NO_3-N) was also high, considering the entire treatment cycle, with NO_2-N removed up to 97% and NO_3-N by more than 94% (Table 2). After six days of treatment, NO_2-N concentrations decreased in the Cell 1 (15%) compared to the inlet value (0.27 mg/L), while in other cells with plants concentration increased (Table 2). The reduction of NO_3-N content was significant in the cells with floating islands and ranged from 56% to 79% (Table 2). The maximum removal efficiency was achieved in the Cell 1 with *P. australis* compared to other cells with plants. The concentration of total nitrogen (N) in the inflow was 7.00 mg/L. As with nitrates, removal of N was significant after six days of experiment in the Cells 1 - 4 (Table 2). The highest removal efficiency was achieved in the Cell 1 with *P. australis*, and the lowest in the Cell 2 with *C. indica*. At the end of the treatment and polishing of the water with algae, the removal efficiency of N was more than 86% (Table 2).

The removal of organic N in the modified FTW was accomplished primarily due to the metabolism of nitrifying and denitrifying microorganisms [12]. The decomposition of these pollutants in water begins with the process of ammonification. This process takes place in both aerobic and anaerobic environments [1]. The rhizosphere of plants in the modified FTW is a convenient place within which the organic N compounds can be decomposed to NH_4-N and CO_2. An aerobic environment in which nitrification takes place is required for the further decomposition process. Based on the obtained results about the efficiency of NH_4-N removal in the Cells 1 - 4 and the fact that cells had anaerobic conditions, it can be concluded that the amount of oxygen present in the rhizosphere of the plants was sufficient for the unobstructed execution of this process. Also, the decrease in the pH of the water in the Cells 1 - 4 can serve as an indication that nitrification in the cells with plants took place despite the low DO in the water surrounding the rhizosphere. However, when analysing the results obtained for the efficiency of NO_2-N removal, it can be noticed that the nitrification process was still not complete thus that all available NH_4-N was not utterly converted to NO_3-N. Bernet *et al.* [13] state that low DO concentrations in water can lead to the formation of toxic NO_2-N, as an intermediate phase for the conversion of NH_4-N to NO_3-N. The reduction of NO_2-N concentration occurred only in the Cell 1 with *P. australis*, with removal efficiency being relatively low compared to removal of other forms of N from polluted water. Anaerobic water conditions in the cells with plants enabled high NO_3-N removal through denitrification. Through their metabolism, denitrifying microorganisms have decomposed NO_3-N to harmless gaseous N and CO_2. Despite the relatively low and seasonally dependent efficiency of plants in N removal [14], it cannot be said that they had no significance in the removal of this element from the polluted waters. The primary role of plants in FTW was water aeration. However, plants also adopted inorganic N as a macronutrient thus removing it from water. For its growth, *C. glomerata* can use N in both NH_4-N and NO_3-N form [15]. Although the removal of various forms of N was mainly due to microorganisms, the efficiency of the Cell 5 with algae was very high for NH_4-N, NO_3-N and total N. Due to the aerobic conditions in the Cell 5, NO_2-N was reduced with an efficiency of 97% (Table 2).

Dodkins and Mendzil [1] state that the removal efficiency of total N and NH_4-N in the FTW is about 40% and 50%, respectively. By comparing the efficiency of the modified FTW in this research with the results obtained by other authors [2,3,8,16] for a similar type of FTW it can be concluded that the modified FTW was far more efficient in removing the various forms of N, both in the cells with plants and algae, especially in the case of NH_4-N.

The high efficiency of the modified FTW in the removal of various forms of N can also be indicated by comparing the contents of NH_4-N, NO_2-N, NO_3-N and total N, as a parameter for the assessment of the ecological status of water [11], in inlet and outlet of modified FTW. Based on the content of NH_4-N, the polluted water had characteristics of waters with bad ecological status (class V). According to the concentration of NO_2-N polluted water had poor ecological status (class IV). Based on the total N and NO_3-N concentrations polluted water was characterised as water with moderate ecological status (class III). After treatment in modified FTW water had high ecological status (class I) for parameters NO_2-N, NO_3-N and total N, and good ecological status (class II) based on NH_4-N concentration.

CONCLUSION

The present study was designed to determine the removal efficiency of P and N in the modified FTW. Taken together, presented results suggest that proposed green technology can provide efficient removal of P and N from polluted water if appropriate conditions are created for the unobstructed execution of the main physical and biological processes for the removal of these pollutants. These findings have significant implications for the understanding of how alternating changes in aerobic and anaerobic conditions can lead to successful treatment of polluted water. The most important limitation for high P removal in this research lies in the fact that the cell coverage with the floating island was 100%. There is, therefore, a definite need for the reduction of the vegetation coverage in order to leave enough free space for the contact between water and air, which will allow the necessary oxygen input into the water. Since P is removed mainly through the processes of filtration and settling, to avoid its resuspension to water it is important to organize periodical removal of the accumulated sediments from the bottom of the cells. Another important practical implication of this study is that for an efficient N reduction in the FTW it is necessary to provide both aerobic and anaerobic conditions. This means that, as in the case of P, the percentage of the cell coverage should be reassessed. Based on the presented results it is also recommended to provide a series of cells with algae at the end of the FTW for additional water polishing. Further studies should focus on the research on the required number and arrangement of cells with aerobic and anaerobic conditions in FTW, bearing in mind that such biological systems should be also able to remove a vast range of pollutants, other than P and N.

ACKNOWLEDGEMENT

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NUMERICAL ANALYSIS OF THE INDUSTRIAL POLLUTANTS DISPERSION IN URBAN AREA

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Abstract

The concentration of pollutants in the atmosphere is constantly increasing every day which affects human population, as well as complete ecosystem. Present work utilizes Computational Fluid Dynamics based on the control volume to analyse influence of meteorological conditions on the dispersion of pollutants from stationary industrial sources in populated areas. Measured emission values from the Thermal Power Plant Sisak and INA Sisak Refinery were used as input data together with the boundary wind conditions taken from the meteorological model. The computational domain covers the area of the City of Sisak and the time horizon encompass period of 24 hours, i.e. one characteristic day. Simulation results demonstrate spatial evolution of pollutant dispersion for the SO_2 *emissions along the domain height. It was concluded that the legally prescribed emission limit value for* SO_2 *in the populated part of the city is not exceeded during the simulation period, making the air quality satisfactory.*

Keywords: numerical simulation, SO_2 emission, pollutant dispersion

INTRODUCTION

The increase in world population together with strong economic development has led to the increase in environmental burden, especially pollutant emissions which have adverse impact on human health. Most of the energy today is obtained through the combustion of fossil fuels, which lead to an increase in the concentration of greenhouse gases, as well as other harmful products such as CO, NOx and SOx. The negative impact of these substances on the environment is reflected through the formation of photochemical smog, ozone depletion, global warming, the occurrence of acid rain etc. [1]. Anthropogenic sources of pollutants include traffic, industry, households, agriculture, energy sector etc., while forest fires, volcano activity, dust dispersion caused by the action of wind, could be classified into natural sources. During its development, humanity has recognized the negative impacts and has begun to take action to control and reduce it. Today, environmental protection is receiving greater attention and cases of such disasters are very rare [2].

The aim of the present work is to study the dispersion of pollutants from stationary industrial sources by the control volume method. The emission data for simulation were taken from the Sisak Thermal Power Plant and the INA Sisak Refinery, whereas for wind data the meteorological model was employed. Those stationary industrial sources have a significant influence on the pollution of the city of Sisak and the simulation of the movement of pollutants under different wind speeds and directions was being studied. The rest of the work is organized in a few steps. First, the research method is presented by giving the most important conservation laws in differential form which lead to general transport equation as the basis for numerical method. Afterwards, most important numerical settings are given together with boundary conditions for emissions. Finally, most important results are presented as spatial distributions and average values of SO_2 and most important findings are summarized in conclusion section.

RESEARCH METHOD

In this section, the most important equations behind the method are given together with numerical simulation settings and boundary conditions.

Mathematical model

Mass conservation law for differential element of fluid in Cartesian coordinate system can be expressed by the following equation:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j}\left(\rho u_j\right) = 0 \tag{1}$$

where ρ is fluid density, t represents time, x_j Cartesian coordinates and u_j velocity vector components. For incompressible fluid, equation (1) states that the divergence of velocity is equal to zero. Momentum conservation law for differential, incompressible element of Newtonian fluid can be written in the following form:

$$\frac{\partial}{\partial t}\left(\rho u_i\right) + \frac{\partial}{\partial x_j}\left(\rho u_i u_j\right) = -\frac{\partial p}{\partial x_i} + \mu \frac{\partial^2 u_i}{\partial x_j x_j} + \rho f_i \tag{2}$$

Equations (1) and (2) are also known as Navier-Stokes equations. Energy conservation law is written as:

$$\frac{\partial}{\partial t}\left(\rho i\right) + \frac{\partial}{\partial x_j}\left(\rho i u_j\right) = -p \frac{\partial u_j}{\partial x_j} + \frac{\partial}{\partial x_j}\left(\lambda \frac{\partial T}{\partial x_j}\right) + \rho f_i v_i + \frac{\partial\left(\tau_{ji} v_i\right)}{\partial x_j} \tag{3}$$

where i is specific internal energy of fluid.

The observed commonalities between presented governing equations enable introduction of a general scalar variable φ, with whom general conservative form of all fluid flow equations can be stated:

$$\frac{\partial}{\partial t}\left(\rho \varphi\right) + \frac{\partial}{\partial x_j}\left(\rho \varphi u_j\right) = \frac{\partial}{\partial x_j}\left(\Gamma_\varphi \frac{\partial \varphi}{\partial x_j}\right) + S_\varphi \tag{4}$$

In the above equation four characteristic members can be distinguished each with distinct physical meaning: first term on the left hand side represents time rate of change of scalar variable φ, second term on the left hand side is convective transport of the same variable, first term on the right hand side describes diffusional transport of φ, whilst the last term of the equation is source/sink of the variable φ due to various other mechanisms. General transport equation (4) represents foundation for the numerical theory of CFD. In this work conservation equations of mass, momentum and energy based on Reynolds averaging were solved.

Simulation settings

Computational domain was made which encompasses boundaries of the city of Sisak (Figure 1). The domain is 2000 m high, 8230 m wide and 5530 m long. The boundary conditions for wind in the form of velocity components and turbulent kinetic energy were taken from the Weather Research and Forecasting (WRF) model for locations of 4 boundary points depicted in Figure 1 in red colour. Data were given for the entire height of the domain, more precisely from the ground up to two kilometres in height. The boundary conditions between those points were obtained by linear interpolation.

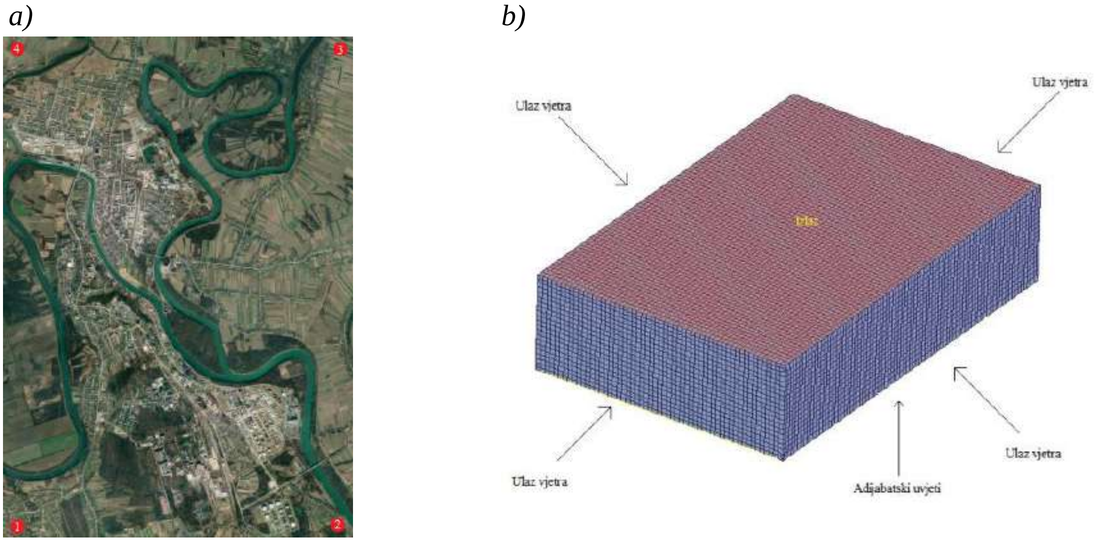

Figure 1 *City of Sisak   a) satellite image; b) computational mesh* [3]

Initial concentrations of chemical species were set within the domain, amounting to 79% for nitrogen and 21% for oxygen. Emission sources in simulation domain come from 5 chimneys (Table 1), of which 2 chimneys belong to the thermal power plant (TE blok A and TE blok B) and 3 belong to the refinery (FCC, WB3 and main chimney).

Table 1 *Data for industrial chimneys used in the simulation as emission sources*

CHIMNEY	**Temperature**	**Mass flow**	**Mass fraction SO_2**
	K	**kg/h**	**ppm**
FCC	620	67980	695
WB3	484	47652	443
main chimney	423	361902	552
TE block A	433	202767	2142
TE blok B	433	271391	2046

At the top of the domain constant pressure of 0.8 bar was imposed which linearly increases towards the bottom of the domain where adiabatic and no-slip boundary conditions were set. Well established *k-ε* model was used for the description of turbulence which is numerically robust and gives reasonable compromise between results accuracy and computational demands. Solution is considered converged when residuals of conservation equations fall below four orders of magnitude compared to initial guessed solution. SIMPLE algorithm was used for pressure velocity coupling. Euler first order implicit scheme was utilized for the time discretization. Central differencing scheme was used for continuity equation, whereas combined scheme of central and upwind schemes with blending factor of 0.5 was used for momentum equation. Energy and scalar equation employed upwind differencing scheme.

RESULTS AND DISCUSSION

Following section presents spatial distribution of SO_2 concentration at different hours of simulated characteristic day and emission profiles at different domain heights.

Spatial distribution of SO_2

The green area in the following Figures represents densely populated Sisak area. The concentrations in the scales are set according to the limit values for SO_2 emissions following national legislation. The limit value for the concentration of SO_2 in the air should be below 350 µg/m^3 during the one-hour averaging period, and this value was converted to mass fraction.

Figure 2 presents spatial distribution of SO_2 concentration at 10th hour of characteristic day. Smoke plums are quite narrow, which in combination with fairly uniform wind direction, results in longer retention of pollutants in the air and low concentrations near the ground surface emission concentration. The area around the chimneys is most affected at a height of 2 m, and considering the terrain, the area around the chimney is mostly affected. At 400 m, a smoke plume is only visible from the thermal power plants chimneys.

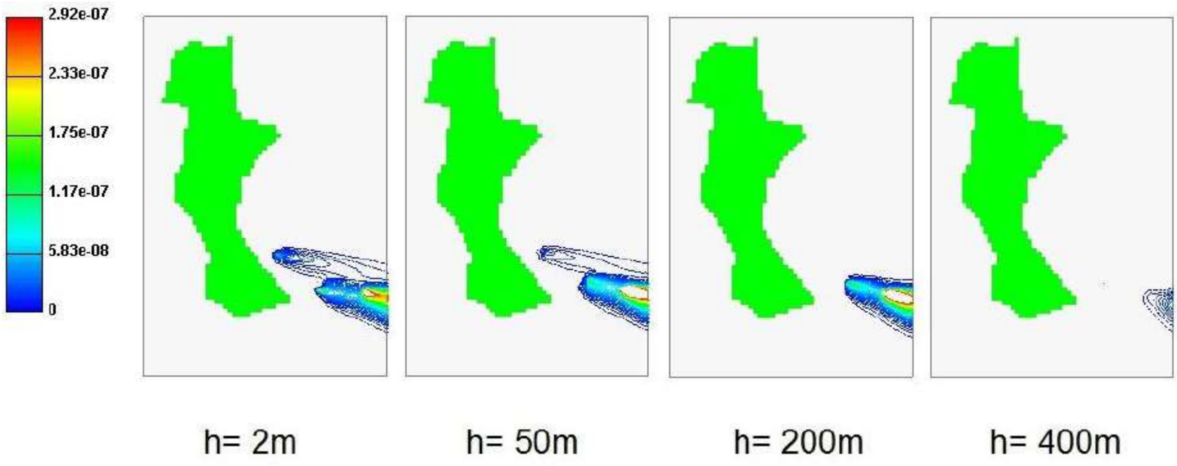

***Figure 2** Spatial distribution of SO_2 mass concentration at various heights for 10th hour*

Figure 3 presents results for 15th hour of the characteristic day and is selected because the emissions cover a wider area, including the densely populated area of the city.

Also, it can be seen that fairly similar concentration pattern is conserved regardless of height. The reasons for this can be reflected in the state of the atmosphere, the time of day, meteorological conditions and other influences. Stationary industrial sources of the city of

Sisak present a potential risk of contamination even for areas located at larger distances from the industrial zone. SO_2 concentrations are increased compared to the 10^{th} hour.

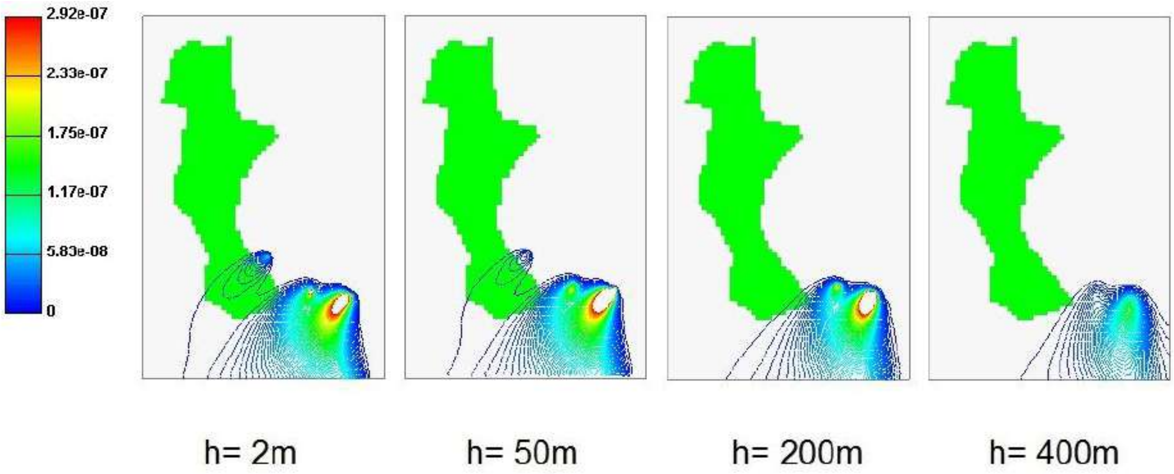

Figure 3 *Spatial distribution of SO_2 mass concentration at various heights for 15^{th} hour*

Emission profiles at different domain heights

Emission profiles along the line that goes across the green zone of the densely populated part of the city (Figure 4a) is considered representative to check whether the SO_2 concentration limits defined by law were surpassed.

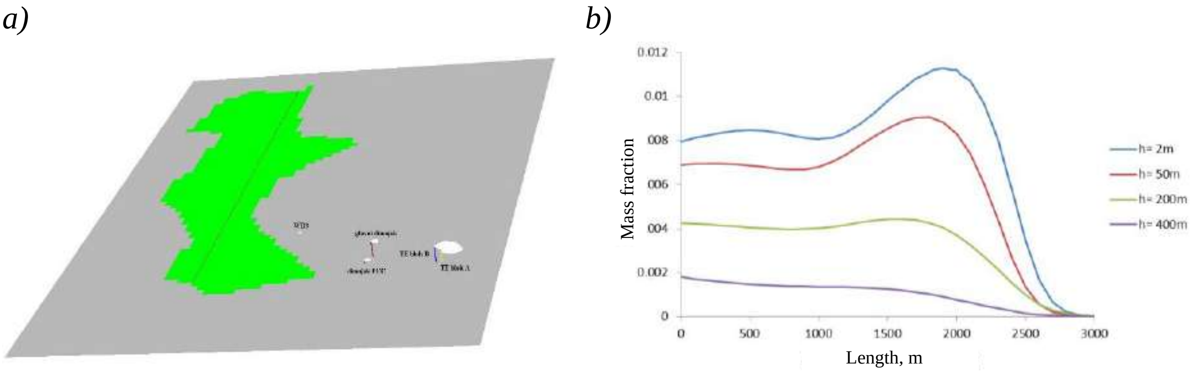

Figure 4 *Concentration profiles a) line position within the city; b) SO_2 profiles at various heights*

It can be seen that the conenctration is highest near the ground and becomes more uniform and lower with increased height. Emission limit is not reached at any simulated hour in the green zone, bringing the conclusion that air quality is satisfactory with respect to SO_2 concentrations during the the cahracteristic day. It was also shown that numerical simulations are valid tool for study of urban pollution which can be used for environmental studies and urban planning.

CONCLUSION

The simulation performed within this work shows the results of the dispersion of pollutants with the associated concentration values at specific parts of the domain and at certain altitudes. The highest concentrations were noticed at the ground level at a height of 2 meters. It should be pointed out, as an important conclusion, that the limit value for SO_2 emissions in the populated part of the city was not exceeded during any hour of simulated time period. The recommendation for further work is to validate the presented method and to analyse the dispersion of suspended particles that have a negative effect on human health. It was also shown that numerical simulations are valid tool for study of urban pollution which can be used for environmental studies and urban planning.

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WALNUT SHELL AS A BIOSORBENT FOR REMOVAL OF HEAVY METAL IONS FROM DIFFERENT SAMPLE SOLUTIONS

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Abstract

The purpose of this study was to investigate possibility of walnut shell for heavy metals ions removal from rivers into which wastewater is discharged from Mining and Smelting Complex Bor, ZiJin Bor Copper. Concentration of metal ions (Cu (II), Cr (II), Ni (II), Cd (II)), in treated sample solutions, were determined using inductively coupled plasma optical emission spectrometer. Maximum biosorption efficiencies for Cd (II), Cr (II), Cu (II) and Ni (II) of walnut shell was determined to be 96%, 91.6%, 97.6% and 91.5%. According to the results walnut shell can be used as an efficient biosorbent for removal of metal ions from wastewater solutions.

Keywords: walnut shell, biosorption efficiency, biosorbent

INTRODUCTION

Industrial activities influenced the flow of materials in nature, so that in aquatic environments, besides naturally occurring, appeared and some other substances, such as textile dyes, phenols, pesticides, detergents, heavy metals, etc. Many industries, such as mining, metallurgy, pesticide and fertilizer production, create wastewater with a relatively high content of heavy metals whose impact on the ecosystem is of great economic and health importance [1]. Today, wastewater treatment can remove 30-90% of harmful elements. Such purified waters are further discharged into surface water, which is practically harmless if wastewater treatment is applied, which is not yet the case in Serbia [2].

One of the most commonly used methods is adsorption with activated carbon, but its application is limited due to the high cost of production and regeneration of activated carbon. The last ten years have been invested in finding new, cheaper and more efficient materials for wastewater treatment [3]. Most attention is paid to natural materials, most often to agro-industrial waste that is readily available in large quantities. The biosorption as a method for removal of heavy metals from water has been studied for more than twenty years [4]. The advantages of this method relative to traditional methods are the low cost, high efficiency, minimization of chemical or biological sludge, the ability to regenerate biosorbent and the ability to extract metals. Jalayeri and Pepe, 2019 [5] showed that pistachio green hull is sutible sorbent for Cu (II) removal from aqueous solutions. Corn silk can be used as efficiant sorbent for effective removal of Cu (II) and Zn (II) and grape pomace waste is sutible for cadmium ions removal from solutions [6,7].

Walnut shell is rich in lignin and cellulose that contains many functional groups which have a strong affinity for heavy metal ions. So, it is widely used in the removal of heavy metal in a solution. Some authors showed that the walnut shell have an adsorption effect on heavy metals ions in aqueous solutions [8,9].

The purpose of this study was to investigate possibility of walnut shell for heavy metals ions removal from seven sample solutions. Sampling was carried out from rivers into which wastewater is discharged from Mining and Smelting Complex Bor, ZiJin Bor Copper. In this study, by interpreting the results of biosorption experiments, the answers about the efficiency of this biosorbent were obtained.

MATERIALS AND METHODS

Seven different water samples were collected from rivers at locations Krivelj (K), spring of Bor River (I), Timok (T), Slatina (S), Robule (P), Bor River (B) and Jaruga (J). The samples were collected according to The Official Gazette of Republic of Serbia, no. 33/2016. Walnut shell as biosorbent was collected from rural households. Biosorbents were previously air-dried to constant mass, and then grounded in a vibrating mill with Mesh-Tyler rings. Subsequently, the walnut shell samples were dried in a laboratory oven at 105° C for almost 1 hour. All the formed walnut shell samples were passed through a 200 mm sieve. A mass of 20 g/L of walnut shell was added in each water sample and stirred with magnetic stirrer (600 rpm) during 60, 120 and 240 min at the room temperature. After filtration, metal ions concentration (Cu (II), Cr (II), Ni (II), Cd (II)), in treated sample solutions, were determined using inductively coupled plasma optical emission spectrometer (ICP-OES Optima 8300; Perkin Elmer, USA).

The biosorption efficiency, R (%) of heavy metal ions from wastewater was determined according to equation (1):

$$R\,(\%) = \frac{C_0 - C_f}{C_0} \qquad (1)$$

where C_o and C_f are the initial and final heavy metal ion concentrations (mg/L) in aqueous solution, respectively.

RESULTS AND DISCUSSION

Heavy metal ion removal by the biosorbent was investigated at various initial concentrations and the results obtained are presented in Table 1. The concentrations of metal ions before treatment decreased with time. For example, the initial concentration of Cu (II) ions, 76.7 mg/L in sample S is reduced to a value of 5.1 mg/L. While in the same sample a reduction of Cd ions from 0.97 mg/L to 0.18 mg/L and Ni ions from 0.89 mg/L to 0.24 mg/L was observed. The Cr concentration in initial sample B of 0.39 mg/L is reduced to 0.05 mg/L.

Table 1 *Concentrations of metal ions in sample solutions before and after biosorption*

Sample solutions	Cd(II)	Cr(II)	Cu(II)	Ni(II)
	Concentrations (mg/L)			
J_o	*0.0863*	*0.0752*	*0.8933*	*0.3069*
J$_1$	0.0168	0.0447	0.5546	0.2547
J$_2$	0.0078	0.0092	0.2004	0.1347
J$_4$	0.0034	0.0063	0.1856	0.0262
K_o	*0.0105*	*0.0086*	*0.7951*	*0.0125*
K$_1$	0.0078	0.0015	0.5006	0.0097
K$_2$	0.0046	0.0010	0.2469	0.0076
K$_4$	0.0027	0.0009	0.1865	0.0053
I_0	*0.0146*	*0.0066*	*0.6883*	*0.0894*
I$_1$	0.0090	0.0025	0.5843	0.0686
I$_2$	0.0077	0.0016	0.2826	0.0526
I$_4$	0.0070	0.0009	0.2549	0.0234
T_o	*0.0105*	*0.0199*	*0.8861*	*0.5627*
T$_1$	0.0085	0.0191	0.7121	0.2886
T$_2$	0.0073	0.0191	0.3364	0.1807
T$_4$	0.0028	0.0157	0.2610	0.0418
S_o	*0.9691*	*0.3733*	*76.676*	*0.8861*
S$_1$	0.6862	0.0907	7.5221	0.6186
S$_2$	0.2271	0.0665	5.3418	0.3008
S$_4$	0.1883	0.0709	5.0956	0.2379
P_o	*0.0040*	*0.0451*	*7.3515*	*0.1253*
P$_1$	0.0033	0.0408	1.3574	0.0951
P$_2$	0.0022	0.0263	0.6666	0.0870
P$_4$	0.0018	0.0206	0.1779	0.0229
B_o	*0.0778*	*0.3954*	*40.076*	*0.5685*
B$_1$	0.0223	0.1238	3.3453	0.4884
B$_2$	0.0205	0.1114	3.1804	0.3719
B$_4$	0.0178	0.0532	2.7812	0.2824

Walnut shell showed high affinity for heavy metal ions in all samples (Figure 1). The highest biosorption efficiency of the walnut shell for metal ions was determined after 4 h in all water samples. Those results point out to best contact time between investigated biosorbent and treated water. Maximum biosorption efficiencies for Cd (II) were detected in samples J (96%), S (80.6%) and B (77%), respectively. In samples J, K, I, B and S, high efficiency of Cr biosorption after 4h was determined: 91.6%, 89.9%, 86.9%, 86.5% and 80.9%, respectively. Also, copper ions were effectively removed from the studied samples P (97.6%), B (93.1%) and S (93%). Biosorption efficiency of Ni after 240 min was most effective in samples J (91.5%), T (86.2%) and P (81.7%).

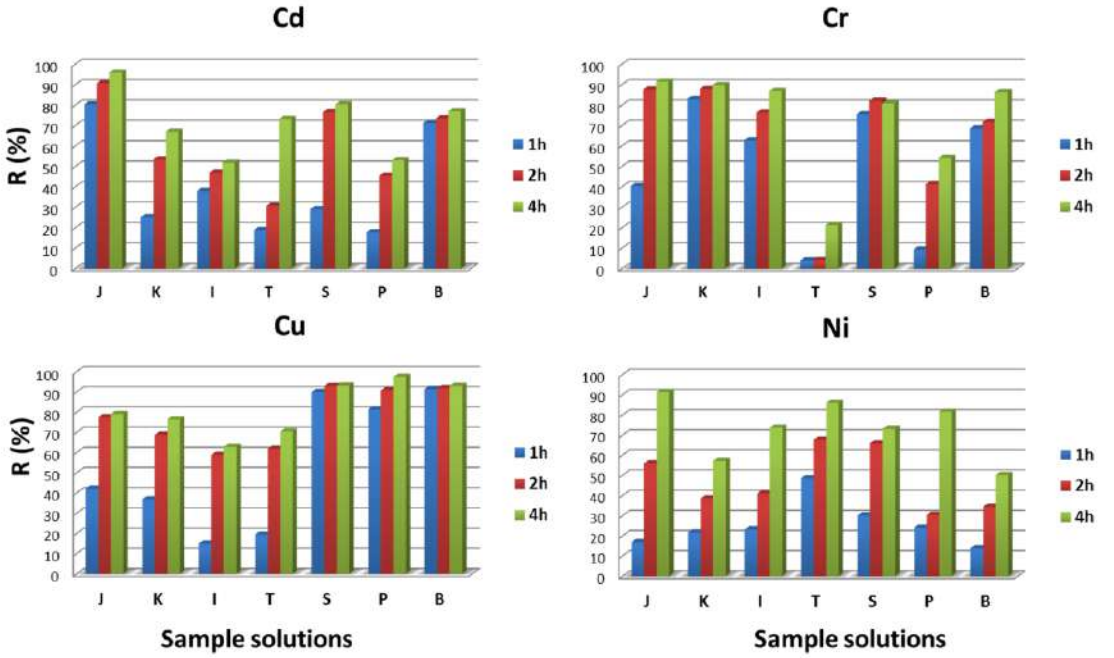

Figure 1 *Efficiency of heavy metals ions removal from different sample solutions by walnut shell*

CONCLUSION

Walnut shell has been found to have a high sorption capacity for Cd (II), Cr (II), Cu (II) and Ni (II). The highest efficiency removal of Cu (II) with the walnut shell occurred in the samples that contained the highest initial copper ions. According to the results, a high biosorption efficiency for Cd (II), Cr (II), Cu (II) and Ni (II) removal from different sample solutions revealed that the walnut shell can be used as an eco-friendly and low-cost adsorbent, in particular in those areas where this material is abundant.

ACKNOWLEDGEMENTS

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DETECTION OF PAHs AS MICRO-POLLUTANTS IN ENVIRONMENTAL SOIL AND PLANT SAMPLES

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Abstract

The examples of the exploitation of various methods for isolation and detection of polycyclic aromatic hydrocarbons (PAHs), as typical micro-pollutants present in environmental soil and plant samples are numerous, and over the years, their combinations became more and more original. It can be said that during the latest decades of 20th century, the development of different procedures practically exploded, especially in terms of screening of PAH presence in the environment, as well as for different risk assessments. However, gas chromatographic-mass spectrometric (GC/MS) method, in combination with various extraction/purification procedures, showed as one of the most appropriate because it provides a fast, safe, and accurate analysis. In this work, a brief overview of some of the most interesting and important examples of GC/MS application in PAH determination is represented, including the descriptions of methods for PAH extraction from the investigated soil and plant samples (together with the subsequent clean-up steps).

Keywords: PAHs, environmental samples, GC/MS

INTRODUCTION

Polycyclic aromatic hydrocarbons, PAHs, are hazardous substances belonging to a group of the so called persistent organic pollutants, POPs. The number of individual PAH compounds that can be found in the environment is pretty high (over 100) but 16 of them are recognized as extremely dangerous and they are included in the list of priority pollutants; they are: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), phenanthrene (Phe), fluoranthene (Flt), fluorene (Flr), anthracene (Ant), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (CHR), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), dibenz[a,h]anthracene (DhA), benzo[g,h,i]perylene (BgP), and indeno[1,2,3-cd]pyrene (IcP); several compounds such as BaP, BkF, BbF, BaA, DhA, CHR, and IcP are anticipated as possible carcinogenic and mutagenic [1].

Although present in micro-quantities in the environment, it was shown that PAHs may pose serious risk for all living organisms. Their main natural sink is surface soil, where some significant quantities may be accumulated over the years. Edible plants growing in PAH-contaminated soil may also accumulate many PAH compounds representing in that way a potential danger for human health [2]. In terms of protecting human health and the complete environment, a constant monitoring of 16 priority PAHs is recommended by many relevant world organizations, together with the related methods for their precise and accurate detection. In most cases, gas chromatographic-mass spectrometric (GC/MS) method was a method of choice and it was applied to different environmental matrices with great success [3]. In this paper, a brief overview of some of the most interesting and important examples of

GC/MS application in PAH determination is represented, including the descriptions of methods for PAH-extraction from the investigated soil and plant samples, as well as of the subsequent clean-up steps.

VARIOUS COMBINATIONS OF ISOLATION AND DETECTION METHODS FOR PAHs IN THE SOIL AND PLANT SAMPLES

The development of different procedures practically exploded during the latest decades of 20th century, especially in terms of screening of PAH presence in the environment, as well as for different risk assessments.

For example, at the end of 20th century, in far 1999, Kipopoulou *et al.* [4], applied the method of high performance liquid chromatography, HPLC (with fluorescence detector) in PAH detection in edible parts of several vegetables such as: carrot (*Daucus carota*), cabbage (*Brassica oleracea capitala*), lettuce (*Lactuca sativa*), endive (*Chichorium endivia*), and leek (*Allium porrum*), growing in an industrial area of Thessaloniki (Greece). PAHs were extracted from the dried plant samples but also from the corresponding soils, in a Soxshlet-apparatus, using solvents such as dichloromethane (for plants) and cyclohexsane (for soil). For each sample clean-up, i.e. for the separation of PAHs from the polar compounds (chlorophyll, etc.), solid-phase extraction, SPE, was applied, using Florisil cartridge (Florisil fibers are typical silica micro-columns properly conditioned by n-hexsane, containing also anhydrous Na_2SO_4).

Only few years later, in 2004, Tao *et al.* [5] were investigating the content of 16 priority PAHs in agricultural soil and plants in the area of Chinese town Tianjin, using the method of GC/MS. The selected plants were celery (*Apium graveolens*), Chinese cabbage (*Brassica rapa, Pekinensis group*), sweet violet (*Coriandrum sativum*), spinach (*Spinacia oleracea*), turnip (*Brassica rapa*), cauliflower (*Brassica oleracea*), carrot (*Daucus carota*), and Chinese mustard (*Brassica juncea*). Soil PAHs were extracted using accelerated solvent extraction, ASE, with 1:1 mixture of dichloromethane and acetone. Clean-up was performed on silica gel column (with anhydrous Na_2SO_4 and dichloromethane). The solvents used in different procedural phases were as follows: cyclohexsane, n-hexsane, and pentane/dichloromethane. Similar extraction and clean-up methods were also used for plant samples, with the notification that the step of sulfonation was included during the clean-up (in terms of removing the lipids and other co-extracted substances that could jeopardize PAH analysis).

Two years later, Tao *et al.* [6] were also investigating the content of 16 priority PAHs in the samples of soil and different organs of rice (*Oryza sativa*) collected at the same territory (Tianjin, China), and using the same GC/MS method together with the same extraction and clean-up techniques. The applied procedure provided a safe evolving of important conclusions related to the level of PAH bioaccumulation in the investigated rice organs, as the main food in the region of interest.

In the same year, 2006, Meudec *et al.* [7] were using GC/MS method for the identification and quantification of PAHs in marine plants, especially in halophytic *Salicornia fragilis*. For elimination of pigments and other compounds that may endanger the analysis of PAHs, they used the saponification method with KOH and SPE (with Florisil fibers). The solvents used in different procedure steps were – ethanol, hexane, and dichloromethane.

During 2006, Ratola *et al.* [8], collected and used *Pinus pinea* needles (from Barcelona, Spain) for the analysis of 16 priority PAHs by GC/MS method. They also used this opportunity for the development and comparison of the three different extraction methods: Soxhlet, ultrasonic and pressurized liquid extraction, using always the same mixture of solvents such as hexane/dichloromethane (1:1, v/v). Several clean-up procedures were also tested, namely: Florisil, silica and alumina in cartridges or glass column format using the same solvent mixture. Among several investigated extraction and clean-up methods tested, ultrasonic extraction followed by alumina cartridge clean-up was the method that provided the best recoveries of PAHs and limits of detection.

Already in 2010, Liao *et al.* [9] used an advanced GC/MS apparatus equipped with triple-quadrupole in terms of the detection of PAHs in surface soils. Microwave-assisted extraction, MAE, and SPE were used for PAH extraction and clean-up. Used solvents were dichloromethane/hexane and acetone. The applied procedure provided average recoveries in the range of 66.59–122.07% with relative standard deviations generally less than 20%.

In terms of investigating plant phytoremediation potentials, in 2011, Smith *et al.* [10] used the method of HPLC with an UV diode array detector in the analysis of PAHs in 5 different plant species: *Festuca rubra* (red fescue), *Festuca arundinacea* (tall fescue), *Trifolium pratense* (red clover), *Lolium perenne* (perennial ryegrass), and *Trifolium repens* (white clover). Extraction was accomplished by Soxhlet-method using dichloromethane/acetone (1:1, v/v).

In 2012, Wang *et al.* [11] applied the method of GC/EI-MS (GC/electron-ionization MS) in the investigation of PAH content in the samples of native plants, vegetables and rice (but also in their corresponding soils) growing near the electronic (e-) waste situated at the territory of Guangdong province in south China. PAH extraction from the soil samples was accomplished by Soxhlet-method with dichloromethane as an extraction solvent, while plant samples were extracted using mixture dichloromethane/acetone (3:1, v/v). After the concentration, both kinds of extracts were dissolved in hexane. Their purification was performed in a multi-layer silica gel - alumina column (with anhydrous Na_2SO_4) using eluent hexane/dichloromethane (1:1, v/v). In terms of elimination of lipids, the extracts obtained from the plant samples were additionally purified on a gel-permeation chromatography column.

Three years later, Banach-Szott *et al.* [12] determined the content of the selected PAHs (fluorene, anthracene, pirene, and chrizene) in the samples of agricultural soils from the regions of Kujawy i Pomorze (Poland) using HPLC (with fluorescence detector). pAHs were extracted in a standard way using Soxhlet-apparatus and cyclohexane as an extraction solvent. Extracts were evaporated, whereas the residue was dissolved in acetonitrile.

In terms of investigating of the influence of PAH speciation in industrial soil on their latter assimilation by plants (practicallt, Chinese cabbage, *B. chinensis*), in 2016, Zhang and Fan [13] used the method of GC/MS and the accelerated solvent extractor with dichloromethane as a solvent; it was later replaced with the series of different combination of solvents with the aim of determination of PAH speciation in the samples of soil and plant). The extracts were purified on an alumina and silica gel chromatography column and the extractable PAHs were obtained through elution with 30 mL dichloromethane/n-hexane (2:1, v/v); the extractable aliphatic hydrocarbons were obtained through elution with n-hexane.

In 2017, Shi *et al.* [14] monitored the content of 6 PAHs (phenanthrene, anthracene, pyrene, benz[a]anthracene, benzo[a]pyrene, and benzo[g,h,i]perylene) in the samples of leaves of 6 varieties of winter wheat (*Triticum aestivum* L.). Analyses were done on HPLC-FLD aparatus with ultraviolet detector and a fluorescence detector. For the extraction, Soxhlet-apparatus and mixture of solvents acetone/dichloromethane (1:3, v/v) were used. The extracts were purified on Florisil column using mixture hexane/dichloromethane (1:1, v/v).

During 2013 and 2014, Sadowska-Rociek *et al.* [15,16] introduced a significant novelty in PAH extraction from plant samples but also from the samples of different types of tea; namely, they applied and optimized the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) methodology, a method combining the extraction: liquid–liquid with the later purification on dispersive SPE. The method was originally developed for pesticide residues analysis operating normally with the pollutant micro-quantities. Sadowska-Rociek *et al.* [15, 16] examined several types of solvents (acetonitrile, ethyl acetate), sorbents (PCA, GCB, SAX, NH_2), and preparation methods (solvent evaporation to dryness and dissolving of residues in hexane and liquid–liquid extraction, LLE, with the solvent exchange). The results showed that, for different types of teas, acetonitrile extraction, clean up with SAX and final LLE represented the best approach providing the most purified extracts and the best compound recoveries. The final extracts were analyzed by GC/MS.

A couple of years later, Cvetkovic *et al.* [17] adopted the QuEChERS methodology for PAH analysis in real soil samples (collected in urban-industrial locations in Niš, Serbia), applying again, different combinations of the extraction solvents (acetonitrile/water and hexane/water) and purification sorbents (PSA, florisil, C18, diatomaceous earth and clinoptilolite). Detection was done on GC/QqQ/MS system in the selected ion monitoring (SIM) mode. The results showed that the most effective combination was: extraction by acetonitrile/water as the extraction solvent and diatomaceous earth as the dispersive SPE sorbent.

Following previous examinations, in 2016 and 2017, Alagić *et al.* [2,18] used the QuEChERS method for PAH analysis in the samples of roots of wild blackberry from the region of Bor (Serbia), as well as in the corresponding soil samples with the aim of estimating the usability of this plant species in biomonitoring and phytoremediation. Practically, extraction was performed using mixture acetonitrile/water (1:1, v/v), the clean-up was done on a PSA-sorbent, while the detection of PAHs was done on the same GC/QqQ/MS system. The results confirmed the proficient biomonitoring and phytostabilization potentials of the investigated plant species.

CONCLUSION

Today, the researchers have mighty analytical instruments, which provide very precise detection of organic pollutants such as PAHs, even in the case of their micro-quantities (typically found in the environmental samples). However, GC/MS method is one of the most appropriate because it provides a fast, safe, and accurate analysis; the detection of PAHs by this method is of great importance for environmental preservation and protection. It should be mentioned here that the preparation of samples also represent an important step in the complete analysis, including the suitable methods for PAH extraction and later purification where PAHs should be properly separated from other substances that may jeopardize the correct final results. In recent time, the QuEChERS method appears as one of the best solutions for micro-pollutants such as PAHs.

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SOURCES AND AVAILABILITY OF INORGANIC PHOSPHOROUS IN THE SOIL

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Abstract

Increasing needs for agricultural products require significant use of phosphorus fertilizers, that has seriously disrupt natural cycle of this element in the soil. Phosphorus fertilizers are primarily used to increase concetration and availability of phosphorus, as an essential element for plant development and growth. However, more than 80% of phosphorus originating from fertilizers, soon after application turn into the form that cannot be absorbed by the plants, due to very slow diffusion process and high fixation degree. There are numerous factors influencing phosphorus availabilty in soil solution, such as easily accessible Pi adsorption and desorption processes, soil texture, type and pH value as well as method of soil treatment. It is necessary to understand dynamics and nature of the process of phosphorus absorption and factor influencing phosphorus availiability in soil solution in order to reduce production of phosphorus fertilizers and improve efficiency of its consumption. This paper describes factors affect phoshorus availiability and concentration in soil solution and methods for increasing phosphorus availability in soil solution.

Keywords: soil, inorganic P, phosphorus fertilizers, P availability, phosphorus activators

INTRODUCTION

In addition to nitrogen and potassium, phosphorus (P) is one of seventeen essential elements required for normal plant growth and development [1,2]. Phosphorus stimulates seed germination, root and stem development, flower and seed formation, crop yield and quality. Also, it has significant role in numerous cell processes including maintenance of membrance structures, synthesis of biomolecules and high energy molecules. Phosphorus deficiency reflects in the disruption of many physiological, biochemical and metabolic processes, so the plants growing under such conditions are underdeveloped with smaller, curled dark–green leaves. Younger plants have greater need for phosphorus in relation to the plants that finished their growth and development process, and that is the reason why the symptoms of its deficicency are more visible at young plants [3].

As Balemi and Negisho [1], at more than 40% of the worldwide soil, P content available for plants, is not sufficient to satisfy the needs of the plants [1]. During last decades, much greater quantities of phosphorus fertilizer have been used, to satisfy needs for agricultural products in the world. Shen *et al.* [4] indicated that consumption of phosphorus fertilizers in China has been drastically increased from 1.18 Mt P in 1985 to 4.80 Mt P in 2005 [4]. Excessive application of phosphorus fertilizers can lead to an increase in the amount of phosphorus that accumulates in the soil and/or leads to leakage from the soil into aquatic systems, which can further lead to artificial eutropia and red tide [5,6]. In South China, about

68 kg P/h accumulates in agricultural land annually [5]. The results of study conducted by Heckrath [7] indicate that if the amount of accumulated Olsen P is greater than 60 mg/kg, there will be a loss of phosphorus from agricultural land to aquatic ecosystems [7]. The disruption of natural phosphorus cycles imposes the risk to complete environment.

This paper present factors affecting phosphorus availability and concentration in soil as well as methods for reducing phoshorus fertilizers and maximum recovery of the phosphorus present in the soil.

PHOSPHORUS IN THE SOIL

Phosphorus in soil exists both in organic (Po) and inorganic (Pi) form. Literature data of organic and inorganic phosphorus content is presented in Table 1. P concentration in the surface layer of soil (0–15 cm) is from 50 to 3000 mg P/kg soil, whereas P concentration in soil solution is from 0.05 to 0.30 µg/ml. Although most soil contains significant amounts of phosphorus, only small part (<1%) of total P has been dissolved in soil solution [8]. Such low phosphorus concentration and poor availability in soil solution has conditioned application of phosphorus fertilizers [9]. Phosphorus fertilizers are primary used for increasing concentration and availability of phosphate ion in soil solution. The most commonly used phosphorus fertilizers are: shredded phosphate rock, super phosphate, triple super phosphate, NPK and ammonium phosphate fertilizers [10]. P_2O_5 content in different types of phosphorus fertilizers is given in Table 2.

Table 1 *Content of organic and inorganic phosphorus in soil*

	Content of P (%)	Sapling location	Ref.
Po	20–80	Newark (USA)	[9]
Po	30–60	Beijing (China)	[4]
Pi	35–70		
Po	30–50	Beijing (China)	[8]
Pi	60–80		
Po	15–80	Novi Sad (Serbia)	[11]

Table 2 *P_2O_5 content in different types of phosphorus fertilizers [2]*

Types of phosphorus fertilizers	Content (%)
Single superphosphate	17–20
Triple superphosphate	44–48
Phosphate rock	26–37
Dicalcium phosphate	35–52

FACTORS INFLUENCING Pi CONCENTRATION AND AVAILABILITY IN SOIL SOLUTION

The great number of reactions taking place in soil (Figure 1) affect P concentration and availability in soil solution. Soon after application, more of 80% of P originating from fertilizers, turns into form that cannot be absorbed by the plants, because of the sorption process, precipitation or microbial immobilization [8].

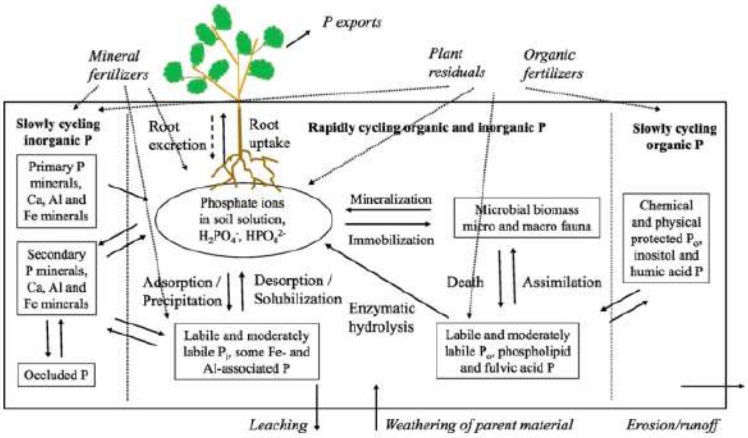

Figure 1 *Phosphorus cycles in soil [8]*

P concentration in soil solution is primarily controlled by balance between adsorption and desorption process of labile Pi [8]. In acidic soil, P can be adsorbed at Al and Fe oxides/hydroxides and clay mineral, whereas in neutral and carbonate soil, on the surface of Ca carbonate and clay minerals [4]. Taking into consideration that clay minerals are characterized by large surface for P adsorption, clay–rich soil is characterized by small amount of P that can be extracted [12].

Phosphorus adsorbed at aluminium or iron oxide, as well as calcium phosphate minerals are sensitive to changes of pH. Increasing of soil pH leads to increasing of Fe and Al phosphate solubility (Figure 2), whereas the solubility of the Ca phosphate decreases until pH=8. Increasing of soil pH (pH>8) leads to increasing of Ca phosphate solubility.

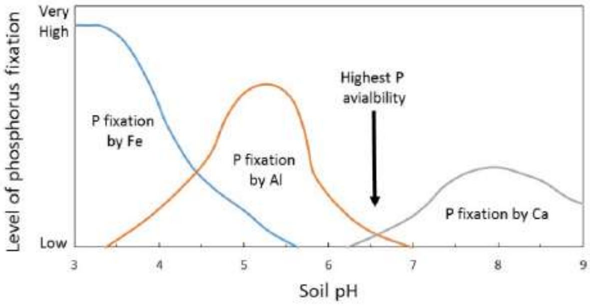

Figure 2 *Influence of soil pH value to P availability [13]*

Different forms of Ca, Al and Fe phosphates can influence P concentration in soil solution. Dissolution of minerals in acidic, neutral and alkaline soil is presented in the following reactions (1–9) [8]:

$$FePO_4 \cdot 2H_2O_{(s)} \leftrightarrow Fe^{3+} + PO_4^{3-} + 2H_2O \quad (1)$$

$$Fe_3(PO_4)_2 \cdot 8H_2O_{(s)} \leftrightarrow 3Fe^{2+} + 2PO_4^{3-} + 8H_2O \quad (2)$$

$$AlPO_4 \cdot 2H_2O_{(s)} \leftrightarrow Al^{3+} + PO_4^{3-} + 2H_2O \quad (3)$$

$$Ca_3(PO_4)_{2(s)} \leftrightarrow 3Ca^{2+} + 2PO_4^{3-} \quad (4)$$

$$CaHPO_{4(s)} \leftrightarrow Ca^{2+} + PO_4^{3-} + H^+ \quad (5)$$

$$CaHPO_4 \cdot 2H_2O_{(s)} \leftrightarrow Ca^{2+} + PO_4^{3-} + H^+ + 2H_2O \quad (6)$$

$$Ca_5(PO_4)_3F_{(s)} \leftrightarrow 5Ca^{2+} + 3PO_4^{3-} + F^- \quad (7)$$

$$Ca_5(PO_4)_3OH_{(s)} \leftrightarrow 5Ca^{+} + 3PO_4^{3-} + OH^- \quad (8)$$

$$Ca_8H_2(PO_4)_6 \cdot 5H_2O \leftrightarrow 8Ca^{2+} + 6PO_4^{3-} + 6H_2O \quad (9)$$

Some metal cations present in soil solution can form metal–phosphate complexes with $H_2PO_4^-$ and HPO_4^{2-} ions. Complexed P can present significant part of total P present in the soil [14]. Low molecular weight organic acids can form organo–metal complexes with Fe, Mn, Zn, Cu or Ca, whereby P releases from metal–phosphate complexes. Plants that grow on soil rich in $CaCO_3$ contribute to increase of organic acid content in the soil and thus affect the concentration of P that plants can absorb [15].

METHODS FOR INCREASING Pi AVAILABILITY IN SOIL

Phosphorus activators transform insoluble P into forms that can be absorbed, leading to a reduction in the amount of phosphorus that accumulates in the soil and/or flows into aquatic ecosystems. They can be divided into three groups: (1) bio–inoculants and bio–fertilizers; (2) organic substances and (3) zeolites and other substances [8]. The effect of applying different bio-fertilizers is shown in Table 3.

***Table 3** Effect of bio-fertilizers application*

Microorganisms in bio-fertilizers	Soil type	Results of applied bio-fertilizers	Ref.
Aspergillus versicolor	Silt clay soil (India)	The applied bio–fertilizer improved the uptake of P in maize and rice by 25.95–50.56% and 18.58–44.09%, respectively	[16]
Bacillus licheniformis			
Bacillus subtilis			
Streptomyces cellulosae			
Pseudomonas synxantha	Loamy soil (India)	Improved phosphorus uptake by 103%	[17]
Serratia marcescens	Loamy soil (India)	Improved phosphorus uptake by 121%	
Aspergillus niger	Sandy soil (Egypt)	Application with superphosphate improved P uptake by 29 mg/pot and 30 mg/pot for wheat and faba bean, respectively	[18]
Aspergillus fumigatus	Sandy soil (Egypt)	Application with superphosphate improved P uptake by 129 mg /pot and 39 mg /pot for wheat and faba bean, respectively	
Penicillium pinophilum	Sandy soil (Egypt)	Application with superphosphate improved P uptake by 125 mg/pot and 112 mg/pot for wheat and faba bean, respectively	

The effects of applied organic acid on P transformation are shown in Table 4.

The use of humic acid, biochemical humic acid and lignosulfonate sodium as activators reduced the amount of phosphorus that flows into aquatic ecosystems by 34.6%, 35.6% and 42.3%, respectively [5]. The impact of the application of phosphorus activators on the amount of P that flows into aquatic ecosystems is shown in Figure 3 [5].

Table 4 *Effects of applied organic acid on P transformation*

Organic compound	Concentration	Soil type	Results	Ref.
Humic acid	0.1 mg/kg soil	Calcareous soil (Pakistan)	Prevents the fixation of P in the soil and increases its availability to plants.	[19]
Maleic acid	10 mM/kg soil	Natural forests or plantation from subtropical and tropical areas (Australia)	Effective in mobilizing P from soil	[20]
Citric acid				
Oxalic acid				

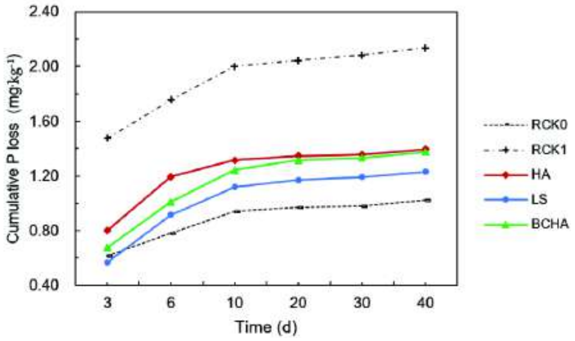

Figure 3 *Cumulative phosphate loss via P leaching from the paddy soil [5]*
(RCK0–without the addition of agents; RCK–superphosphate; HA–humic acid; LS– lignosulfonate sodium; BCHA– biochemical humic acid)

In addition to activators, availability of phosphorus in soil solution can be affected by changes in physical and chemical soil properties as well as crops planting approach. Results of the study conducted by Shen *et al.* [4] indicated that if the corn and broad beans are grown on the same agricultural land, the amount of absorbed P can be increased. Broad beans secrete organic acids that leads to decreasing of rhizosphere pH value and contributes to increasing of P concentration that can be absorbed by the plants [4]. Considering that P diffusion in the soil is a very slow process, applying phosphorus fertilizers near the crop seeds can increase its availability for the plants. By applying phosphorus fertilizer out of root area, the efficiency of the applied fertilizer is reduced.

CONCLUSION

Due to the very low concentrations and poor availability of phosphorus in soil solution and high demand for agricultural products, phosphorus fertilizers have been used in increasing quantities in recent decades. In order to reduce quantity of phosphorus fertilizers in the world, it is necessary to understand factors affecting P availability in soil, dynamics and nature of P absorption from the soil. A number of factors influence phosphorus availability, such as: soil pH value, method of soil treatment, content of Fe, Al, Ca, clay mineral and organic substances. The activators, which facilitate phosphorus accumulated in the soil to be transformed in the form easily absorbed by the plants, can be used in order to reduce the quantity of phosphorus fertilizers application worldwide. Also, the use of activators can reduce the amount of P that flows into aquatic ecosystems, thus preventing environmental pollution.

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CONTRIBUTION TO THE KNOWLEDGE OF THE DISTRIBUTION OF *Gyas titanus* Simon, 1879 (OPILIONES, PHALANGIIDAE) IN THE TERRITORY OF BOSNIA AND HERZEGOVINA

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Abstract

According to the literature so far, a total of Gyas titanus is present in nine localities in Bosnia and Herzegovina. Our surveys from 2001 to 2018 recorded it in 21 localities. All our findings of Gyas titanus do not deviate from other habitats of other authors where it is found, which is a forest on the bank of a stream-river or terrain overgrown with shrubs and mostly beneath a rock or rotten tree. As we can see, it mainly inhabits the forests of the most old age with a strong set, whose canopy cover is not less than 70% and slightly smaller canyons and gorges with high almost vertical cliffs overgrown with dense vegetation. During our study, the elevation zonation of this species ranged from about 600 above the sea level in Kozara to almost 1700 above the sea level in Mount Cincar. If we look at the sites cited by Novak et al. [4] we notice that some localities are repeated, i.e. our research has confirmed their presence in the wider area, which indicates our continuity of presence in the area. If we compare the literature data with ours, we can see that for most of our localities these are new findings in Bosnia and Herzegovina. It is reasonable to assume that the species and inhabits areas that have not been extensively explored before, as these new localities in Bosnia and Herzegovina show. Considering the findings from the literature as well as these new locations in Bosnia and Herzegovina, we can conclude that G. titanus is more or less constantly present in the western and central Balkans. In addition to some isolated mountains in the Pannonian Plain, the species population has a continuous Alpine-Balkan-Carpathian distribution.

Keywords: *Gyas titanus*, Bosnia and Herzegovina, new location

INTRODUCTION

European phalangidae of the genus *Gyas*, are represented by two species *Gyas titanus* Simon, 1879 and *Gyas annulatus* (Olivier, 1791) and both represent Mountainean species. In the subalpine and hilly regions, *G. titanus* occurs in forests on the banks of streams and there have been rare sporadic findings in caves. *G. titanus* species has been recorded in Croatia, Bosnia and Herzegovina (B&H), Montenegro and Serbia.

In the description of the area we will stick to the Mountainean pre-alpine and hilly region, which is cultivated and inhabited. The territory of B&H has an area of 51129 km^2 and is an integral part of the geomorphostructure of the Dinarides. The Dinaric Mountain Morphosystem is a sub-continent of the western part of the Alpine-Himalayan belt. It originated in the geotectonically moving, Mediterranean subduction zone (Mediterranean geosynclinal area), during the Cenozoic phase of the Alpine cycle of orogenic closure by the Neothetical Ocean. The formation of the Dinaric Orogen was influenced by complex tectonic processes [1]. The relief structure of Bosnia and Herzegovina is expressed by: mountain massifs and hills with foothill stairs, surfaces, mountain elevations and hills, karst fields, valleys, bays and valleys. The high mountain dinaric zone morphologically expresses the mountainous areas of northern Herzegovina, central, southeast and southwestern Bosnia. Therefore, it is an extremely mountainous area with the highest altitudes (the peak of Maglic 2386 above the sea level) and the highest values of vertical distribution in B&H [2]. The northeastern part of the high mountain Dinaric zone, in the area of the Central Dinarides, is represented by mountain ranges and ridges of Vlasic (1943 above the sea level), Jahorina (1913 above the sea level), Bjelašnica (2067 above the sea level), Zelengore (2015 above the sea level), Maglića (2386 above the sea level). The southwestern highland frame is represented by the boring-folding and scaly mountain morphostructures of the High Karst zone in the Outer Dinarides. Orographically, the linear elevations of the mountain ridges predominate. These are: Pljecevica 1645 above the sea level, Klekovača 1961 above the sea level, Staretina 1607 above the sea level, Dinara 1912 above the sea level, Vitorog 1907 above the sea level, etc. The mountain massifs in the high Dinaric Orographics reflect orographically: Tent 1873 above the sea level, Grmeč 1604 above the sea level, Prenj 2123 above the sea level, etc. The mentioned mountains are morphotectonically separated by relief depressions of karst fields and larger bays. Morenan deposits are a reliable indicator of the glacial process found in the high bays and low foothills of Pranja, Velez, Dinara, Tent, etc., while higher parts of the mentioned mountains are marked by forms of Pleistocene glacial relief. The high mountain belt of the Dinarides of B&H is bordered from the northeast and southwest, by slightly lower mid-mountain morphostructures of average altitudes of 1000-1600 above the sea level. The southwestern highlands, extending to eastern and western Herzegovina, represented by the backs and massifs of Radovan 1133 above the sea level, Vranić 1117 above the sea level, Bjelašnica 1395 above the sea level, Viduše 1328 above the sea level, etc., while the northeastern mountain range in central and eastern [1].

This paper aims to complete the picture on the distribution of *Gyas titanus* in B&H.

MATERIALS AND METHODS

The material is ordered by rolling stones, rotting trees and stumps mainly in the bed of a stream or mountain river in the forest. Specimens in most localities were not collected, only photographed. It covers the period from 2001 to 2018 when field surveys were conducted in the territory of Bosnia and Herzegovina. Determination was done according to Luhan [3].

RESULTS AND DISCUSSION

According to the authors Novak *et al.* [4] *Gyas titanus* is present in Bosnia and Herzegovina in eight localities:

Kupreška vrata, **XJ87**, Bugojno, 1200 m, 10.09.1983, Coll. BIOS 2606, SIVEC leg.: 1 m (TN 406/1985; PMSL); **Kozarac**, **XK48**, Prijedor, 06.05.1987, SIVEC, HORVAT leg.: 2 subad. (TN 1096/1998; PMSL); **Ravan**, **YJ38**, Busovača, Zenica, 13.05.1986, SIVEC, HORVAT leg.: 1 subad., 1 iuv. (TN 1234/1998; PMSL); **Konjuh Mountain**, **CQ00**, 890 m, 16 km north of Kladanj, 14.10.1990, SIVEC, HORVAT leg.: 2 iuv. (TN 1256/1998; PMSL);

Vranica Mountain., **YJ27**, 1400 m, 5 km southwest of Fojnice, 17.10.1990, SIVEC, HORVAT leg.: 2 iuv. (TN 1264/1998; PMSL); **Ponor** cave **Bijambare**, Čevljanovići, **BP37**, 28.07.1968, PRETNER leg.: 1 iuv. (TN 233/1985; JH); **Radačići**, **CP09**, Kladanj, 680 m, 15.10.1990, SIVEC, HORVAT leg.: 1 iuv. (TN 1271/1998; PMSL); **Maglić Mt**., **CN19**, 25 km south of Foča, AUSOBSKY leg. (MARTENS, 1978).

The data of Jakšić [5], PhD for Prokoško Lake on Vranica Mountain, where the description of biodiversity indicates the presence of this species. Thus, in total, *Gyas titanus* is present in nine localities in Bosnia and Herzegovina. In the period 2001-2018 *Gyas titanus* was recorded in 21 localities (Figure 1), which are listed as:

Zelengora Mountain: Canyon of Hršćanka River, 20. 08.2008, river bank below stone, 1 individual; Donje Bare Lake, 22.08.2008, lake shore, below stone, 2 individuals; rainforest Perucica, 19.08.2009, forest, under rotting tree, 3 individuals; 23.05.2001, forest under stone along Perucac creek, 5 individuals;

Maglić Mountain: Trnovac Lake, 19.08.2009, forest around the lake, under a rotting tree, 1 individual; Suha River Canyon, 19.08.2009, forest under a rotting tree, 2 individual;

Sutjeske canyon: 21.08.2009, coast, forest under stone, 1 individual;

Cincar Mountain: Dragnjic place, 17.08.2010, under the stone, 1 individual;

Šator Mountain: place Rare, under the stone, 18.08.2010, 1 individual; place Štekerovci, 19.08.2010, under the stone, 1 individual;

Lisine Mountain: Podrašnica, Zelenkovac, 24.08.2010, under a tree in the forest, 2 individuals; 25.08.2010, and 21.08.2011, along Zelenkovački creek below the stone, 1 individual each;

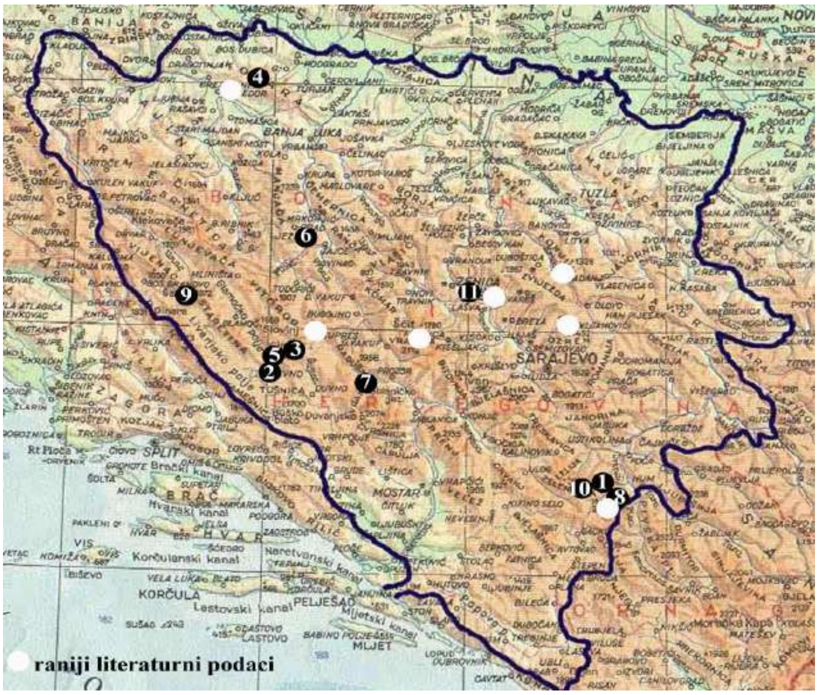
Krug Mountain: place Zagoričani, 25.08.2010, under the stone, 2 individuals;

Ljubuša Mountain: place of Mokronoge, 29.08.2010, under the stone, 2 individuals; the surroundings of Rama Lake, 29.08.2010, below the stone 1 individual;

Livno: Jaruga River, 25.08. 2011, river bank below the rock, 2 individuals;

Zenica: Kraljeva Sutjeska, 20.04.2012, beneath the extinct tree in the forest, (one dry specimen);

Kozara Mountain: Crna River, 17.08.2012, 20.08.2014. and 22.08.2013, under the deciduous tree in the forest, 2 + 5 + 3 individuals; Pasini konaci, 21.08.2013. below the extruded tree in a wet meadow (swamp) 2 individuals, Gumlin cave, 28.08.2015, in the furnace walker in complete darkness, 3 individuals, Gumlin creek 28.08.2015, in the gorge of the stream below the stone at coast, 3 individuals., Starenica river, 30.08.2018., below the stone on the coast, 1 individual. Figure 2 shows *Gyas titanus* in Kozara NP in the Gumlin creek gorge below a rock on the shore.



● New data from 2001-2018

Figure 1 *21 localities in Bosnia and Herzegovina where Gyas titanus was recorded*

Localities surveyed: 1. Sutjeske Canyon (1); 2. Livno: Jaruga River (2); 3. Cincar Mountain: Dragnjic Town (3); 4. Kozara Mountain: Black River (4), Pasha Strands (5), Gumlin Cave (6), Gumlinski brook (7), Starenica River (8); 5. Krug Mountain: Zagoricani Town (9); 6. Lisina Mountain: Podrasnica, Zelenkovac (10) and Zelenkovack creek (11); 7. Ljubuša Mountain: the place of Mokronog (12) and the vicinity of Rama Lake (13); 8. Maglić Mountain: Trnovac Lake (14) and Suha Reka Canyon (15); 9. Šator Mountain: Rare (16) and Štekerovci (17); 10. Zelengora Mountain Canyon of the Christian (Hršćanke) River (18); Donje Bare Lake (19); rainforest Perucica (20); 11. Zenica: Kraljeva Sutjeska (21)

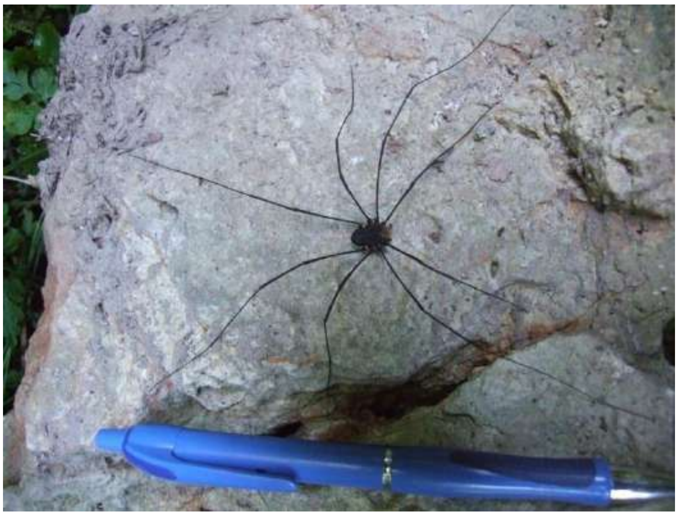


Figure 2 *Gyas titanus in Kozara NP in the Gumlin creek gorge below a rock on the shore (Photo by M. Stanković)*

All our findings of *Gyas titanus* do not deviate from other habitats where it is found, which is a forest on the bank of a stream or terrain overgrown with shrubs and mostly under rock or decayed wood. As we can see, it mostly inhabits the forests of the most old age with a strong set, whose canopy cover is not less than 70% and slightly smaller canyons and gorges with high almost vertical cliffs overgrown with dense vegetation. In terrains that have a predominantly open merocarst type where sparse shrubby or only grassy vegetation is present, specimens are found under the rock, usually in slightly higher grass or denser shrub assemblages.

The finding of the species in the Gumlin creek gorge and in the Gumlin Cave shows its trogloxene character. That is, the species uses the interior of the cave temporarily during the summer dry season. Visiting the cave itself, specimens were found in the cave corridor over 100 m from the entrance in complete darkness due to optimal humidity during the summer when the temperature reached 40ºC and the water level in the stream was very low. This is not the first case that opilions are found both around and inside the cave.

During fieldwork, it was observed that in vegetation terms *Gyas titanus* inhabits from hardwood to mixed to purely coniferous communities as well as to communities in pastures above the forest border, or from canyon communities with Salix, through mesophilic oak communities, as well as from hilly and mountain beech communities to subalpine conifer or mixed communities (*Abieto-Fagetum, Abieto-Fageto-Picetum, Picetum submontanum*, etc.) The presence of this species was recorded in four localities belonging to the protected areas, namely the Sutjeska and Kozara National Parks, while the Lisine Mountains are under previous protection.

If we look at the sites cited by Novak *et al.* [4] we notice that some localities repeat like Maglic (finding in 1978) where we also found it, which only confirms its continuity. At two localities Kozarac near Prijedor (finding in 1987) and Ravan near Zenica (finding in 1986), our research confirmed their presence in the wider area. In the work of Novak *et al.* [6] we find data on the zoogeographical distribution of *Gyas titanus* where the authors state that it belongs to the Alpine, Iberian, Central European, Dinaric and Carpathian elements.

During our study, the elevation zonation of this species ranged from about 600 above the sea level in Kozara to almost 1700 above the sea level in Mount Cincar.

If we compare the literature data with ours, we can see that for most of our localities these are new findings in B&H. It is reasonable to assume that the species and inhabits areas that have not been extensively explored before, as these new localities in B&H show.

CONCLUSION

According to the literature so far, a total of *Gyas titanus* is present in nine localities in Bosnia and Herzegovina. Our research in the period 2001-2018 recorded it in 21 localities.

All our findings of *Gyas titanus* do not deviate from other habitats of other authors where it is found, which is a forest on the bank of a stream-river or terrain overgrown with shrubs and mostly beneath a rock or rotten tree. As we can see, it mainly inhabits the forests of the most old age with a strong set, whose canopy cover is not less than 70% and slightly smaller canyons and gorges with high almost vertical cliffs overgrown with dense vegetation. During our study, the elevation zonation of this species ranged from about 600 above the sea level in Kozara to almost 1700 above the sea level in Mount Cincar.

If we look at the sites cited by Novak *et al.* [4] we notice that some localities are repeated, i.e. that our research has confirmed their presence in the wider area, which indicates to us its continuity in the area.

If we compare the literature data with ours, we can see that for most of our localities these are new findings in B&H. It is reasonable to assume that the species and inhabits areas that have not been extensively explored before, as these new localities in B&H show.

Considering the findings from the literature as well as these new locations in B&H, we can conclude that *G. titanus* is more or less constantly present in the western and central Balkans. In addition to some isolated mountains in the Pannonian Plain, the species population has a continuous Alpine-Balkan-Carpathian distribution.

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23 YEARS OF THE NATURAL COLLECTION OF ZASAVICA RESERVES

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Abstract

The Zasavica Nature Reserve study collection includes the Paleontological-Geological Section and the Biological Section. About 50 specimens of minerals, rocks and fossils have been deposited in the paleontological-petrological collection from the area of the reservoir and the surrounding area.The paleontological part of the collection consists of a collection of quaternary vertebrates with parts of the mammalian quaternary fauna skeletons, and here we have the mammoth atlas (Mammuthus sp.) found in Crna bara (Jovaca); then a collection of invertebrate macrofauna with the remains of Bivalvia, Gastropoda and other freshwater or marine invertebrates in limestone and other sediments (silt, clay, etc.) and a paleobotanical collection consisting of parts of the tree found in silt and peat and peat samples. The petrological part of the collection contains minerals and rocks found in alluvial deposits or averaged fractions of deposits from sources on the Zasavica coast. The biological part of the collection includes: Mycological collection of 111 liquid mushroom preparations; Botanical collection with 2500-3000 specimens herbaceous material and 82 bottles and vials with liquid preparations of plants and algae and Zoological collection in which we have a total of 113 samples of 64 species + 1 subspecies and include: Ichthyology collection with 34 samples in ethanol and one dry preparation; Batrachological collection of ethanol from 28 samples in ethanol (9 from Caudata and 19 from Anura); Herpetological collection with 23 samples in ethanol and dry preparations (armor and hairpieces); Ornithological collection of 8 prepared birds of 7 species; Mammological collection of 20 exhibits (whole specimens and horned heads prepared), followed by skulls of small mammals, rodents' nests and liquid preparations; Entomological collection and collection of other invertebrates with 10 entomological boxes and about 300 vials and vials with liquid sample preparations in ethanol and dry preparations. The collection so far contains the only specimens found so far in the reserve in the past 23 years, namely those of fish: Neogobius fluviatilis, Gobio albipinnatum and Barbus peloponesus; from amphibians Rana temporaria and from reptiles black (melano) specimen of the species Vipera berus bosniensis.

Keywords: Natural History Collection, Zasavica Reserve

INTRODUCTION

The purpose of forming a natural collection is to serve the present and future interest of research, protection and presentation to a wider range of stakeholders. Collecting material for collections can be done by various ways. One way is to donate an item or an entire assembly. The exhibits can be purchased through purchase, exchange or field research. Any material to be included in the collection must be recorded in the inventory book with all necessary basic and additional information. The material thus processed is stored either in a depot usually inaccessible to visitors and used for scientific research or placed in collections for display in an exhibition space [1].

An important segment in the scientific work of each protected area is to study natural history collections, which represent significant scientific, historical and archival material of the area. It preserves significant and valuable scientific material that proves the presence of certain species and populations in the area, and from a historical point of view it is significant because it also preserves species that have disappeared in the meantime or are rarely encountered in the field. It is a significant material for various comparative analyzes, evolutionary, morpho-anatomical and genetic studies on species and populations. In addition to the scientific value of the collection, they also have an educational role for both visitors and young professionals and scholars. All preparations in any collection in order to be scientifically valid must have the following information: name (Latin) species, date of collection, locality, habitat, legator and who has determined and prepared the specimen, and of the additional data such as the method of preparation, the dimensions of the preparation, ect. [2].

There are two methods of preparation in natural collections: dry and liquid preparations. By dry preparation we mean all specimens that are dehydrated, pressed, stuffed specimens (animals), osteological material (skeletal and skull parts), dermo preparations, etc. Liquid preparations are specimens immersed in a certain substance (ethanol, formalin, glycerin, etc.) to be preserved and thus stored in adequate containers [2].

The Zasavica Nature Reserve Study Collection Fund covers the period from 1996 to 2019 and has the following parts: Paleontological-geological part and biological part, which includes: Mycological, Botanical and Zoological Collection, which include: Ichthyological, Batrachological, Herpetological, Ornithological, Mammological, Entomological and other invertebrate collections. The reserve collection includes dry and liquid preparations.

This paper deals with vertebrate artifacts in more detail in the study's natural collection of reserves by groups, as this is the most central part of the collection so far.

MATERIALS AND METHODS

The methodology consists in listing the exhibits and their basic data, which are later sorted by systematic affiliation. For herbarium, algological and paleontological material and collections related to the invertebrate fauna, only the total number of specimens has been given, because a large part of the material has not yet been determined. Part of the material stored in the collection is dry preparations specimens (herbarium, dermo and osteological material, prepared (stuffed) animals (birds, mammals), entomological material, fruits, galls, shells, nests of birds or insects, etc.), while a considerable proportion are liquid preparations most often in ethanol (specimens of fish, amphibians, reptiles, smaller mammals (rodents, cockroaches, bats) and most of the invertebrate fauna samples). Preparation of all but stuffed animals is done by our expert associate, while the preparation of birds and mammals is done by our professional preparer at the Provincial Institute for Nature Conservation in Novi Sad.

RESULTS AND DISCUSSION

For the past 23 years, the following material has been deposited in the reserve's natural history collection:

Paleontological-petrological collection: includes found paleontological and geological material (minerals and rocks) in the area of the reservoir and in the immediate vicinity. A total of about 50 specimens have been deposited in this collection. The paleontological part of the collection can be divided into three parts: the collection of quaternary vertebrates, the collection of invertebrate macrofauna and the paleobotanical collection. The collection of quaternary vertebrates consists of parts of the mammalian quaternary fauna skeletons, and this part of the collection has one exhibit, which is the mammoth atlas (Mammuthus sp.) found during the gravel excavation at the Black Bar near Jovaca. By looking at certain parameters and comparing the measured values of the length and width of the atlas, the obtained value is 1.7 to 1.8, which is between the species Mammuthus primigenius (Blumenbach) and Mammuthus trogontherii Pohlig. with Mammuthus sp. The collection of invertebrate macrofauna consists of the remains of shellfish (Bivalvia), snails (Gastropoda) and other freshwater or marine invertebrates in limestone and other sediments (silt, clay, etc.), and in this collection there are about a dozen pieces of limestone and other material with remains of marina or freshwater fauna. The paleobotanical collection consists of parts of a tree found in silt and peat and peat samples. The petrological part of the collection contains found pieces of minerals and rocks (sedimentary, metamorphic and magmatic) in the alluvial deposition of the Sava or Drina during field work (digging) or as a result of hydroerosion. This collection also contains one box with averaged fractions of alluvial deposit from a single source on the Zasavica coast.

Mycological collection - a total of 111 specimens of liquid mushroom preparations in ethanol have been deposited.

Botanical Collection - consists of collected herbarium material of pressed plants, fruits, twigs with buds, algae and lichen samples, etc. The collection contains between 2500-3000 excipients of herbarium material and 82 bottles and vials with liquid preparations of samples of plants and algae in ethanol.

Zoological Collection - Includes collected complete material related to the reserve fauna. The zoological collection can be divided into two major sections: the invertebrate collection, which includes the Entomological Collection and the collection of other invertebrates, and the vertebrate collection.

A total of 300 vials and vials containing liquid sample preparations in ethanol have been deposited in the invertebrate collection and one smaller part is the dry preparation, i.e. samples in boxes (cocoons, plant damage, gals, litters, etc.). Also, 10 entomological boxes containes the collected entomological material (insect fauna) from the reserve area.

The vertebrate collection includes: Ichthyological, Batrachological, Herpetological, Ornithological and Mammological collections.

A total of 106 specimens of liquid and dry preparations have been deposited in the vertebrate collection.

Review of the spine collection (vertebrate)

Below will be analyzed and commented on the collection of vertebrates, which is the best processed and arranged, in the brackets [] the number of specimens in the collection is given.

Ichthyological collection

The collection has a total of 34 samples in ethanol and one dry head preparation. The collection includes exhibits of 19 species of fish.

Review of ichthyological collection: **1)** *Umbra krameri*: Banovo Polje, Trebljevine, 26.07.1997 and 26.07.1998, Leg./Det. Stanković. M., [by 1]; **2)** *Scardinius erithrophthalmus*: Zasavica II, Valjevac, 13.05.2004 and 11.07.2000, Leg/Det.: Stanković. M., [by 1]; **3)** *Cobitis elongatea* [checkup. *Cobitis taenia*]: Banovo Polje, well, 26.07.2007, Leg: Stanković. M., Det: Sekulić. N., [by 1]; **4)** *Cobitis taenia*: Salaš Noćajski, Sadžak, 13.07.2011, Leg. Stanković. M., Det. Simić.V., [by 1]; **5)** *Abramis sapa*: Zasavica II, Valjevac, 20.07.2007, Leg. Stanković. M., Det. Sekulić. N., [1]; **6)** *Misgurnus fossilis*: Radenković, Batar, 20.06.2005, Leg./Det. Stanković. M., [1]; **7)** *Carassius carassius*: Ravnje, Prekopac, 22.06.2004, Leg. Stanković. M., Det. Simić. V., [1]; **8)** *Barbus peloponesus*: Radenković, Batar, 03.05.2004, Leg. Stanković. M., Det. Simić. V., [1]; **9)** *Ictalurus nebulosus*: Zasavica II, Valjevac, 07.07.2007, Leg./Det. Stanković. M., [1]; Zasavica I, Šumareva ćup., 2010, Leg./Det. Stanković. M., [10 juv.]; **10)** *Lepomis gibosus*: Zasavica II, Valjevac, 20.07.2007, Leg./Det. Stanković. M., [1]; **11)** *Silurus vulgaris*: Zasavica I, Šumareva ćup., 14.06.2007, Leg./Det. Stanković. M., [1]; **12)** *Rutilus rutilus*: Zasavica II, Valjevac, 20.07.2007, Leg. Stanković. M., Det. Simić. V., [1]; Zasavica I, Šumareva ćup., 03.05.2003, Leg. Stanković. M., Det. Simić. V., [1]; Radenković, Vrbovac, 20.07.2007, Leg. Stanković. M., Det. Simić.V., [1]; **13)** *Pseudorasbora parva*: Zasavica II, Valjevac, 27.09.2007, 21.07.2007, 20.07. 2007, Leg. Stanković. M., Det. Simić. V., [by 1]; **14)** *Abramis brama*: Noćaj, Preseka, 04.05.2006, Zasavica II, Valjevac, 20.07.2008, Zasavica II,Valjevac, 13.05.2007, Leg. Stanković. M., Det. Simić. V., [by 1]; **15)** *Gobio albipinnatus*: Radenković, Batar, 20.09.2002, Leg. Stanković. M., Det. Simić. V., [1]; **16)** *Esox lucius*: Zasavica I, Šumareva ćup., 18.05.2005, Zasavica II, Valjevac, 30.05.2006, Leg./Det. Stanković. M., [1]; **17)** *Carassius auratus*: Noćaj, Preseka, 05.05.2005, [3]; Zasavica II, Valjevac, 20.07.2002, Leg. Stanković. M., Det. Simić. V., [1]; **18)** *Perca fluviatilis*: Noćaj, Preseka, 19.03.2006, Zasavica I, Šumareva ćup., 08.04.2005, Zasavica II, Valjevac, 21.07.2007, [by 1]; Banovo Polje, izvori, 26.07.2007, [1 juv.]; **19)** *Neogobius fluviatilis*: Zasavica II, Valjevac, 05.07.2008., Leg. Stanković. M., Det. Simić.V., [1].

It is important to mention that for the three species of fish in the collection the only data for the reserve in the past 23 years are: *Neogobius fluviatilis*, found in 2008 in a watercourse on Valjevo; *Gobio albipinnatum*, found in 2002 in Batar and *Barbus peloponesus*, found in 2004 in Batar.

Batrachological collection

The collection has a total of 28 samples in ethanol, of which 9 are from Caudata and 19 from Anura. In 9 samples of Caudat there are three species, two from the genus Triturus and one species from the genus Salamandra, while in 19 samples from the Anura there are 10 species. All specimens are stored as a liquid preparation in ethanol.

Review of the Batrachological Collection: Caudata: **1)** *Salamandra salamandra*: Ravnje, Prekopac, 11.08.1997, Leg./Det. Stanković. M., [1]; Crna bara, Jovača, 27.04.1996, Leg./Det. Stanković. M., [1 juv]; **2)** *Triturus vulgaris*: Radenković, Vrbovac., 18.06.1998, Zasavica I, Valjevac, 21.07.1997, Ravnje, Široka bara, 06.08.2006, Leg./Det. Stanković. M., [by 1 larva]; Radenković, Batar, 31.03.2000, Radenković, Pačija bara, 22.12.1997, Leg./Det. Stanković. M., [by 1 juv.]; Ravnje, Prekopac, 07.05.1997, Leg./Det. Stanković. M., [1]; **3)***Triturus dobrogicus*: Ravnje, Prekopac, 10.09.1997, Leg./Det. Stanković. M., [1]; Anura: **1)** *Rana ridibunda*: Salaš Noćajski, Sadžak, 22.08.1997, Mačv. Mitrovica, Modran, 20.07.1996, Leg./Det. Stanković. M, [by 1]; **2)** *Rana temporaria*: Radenko vić, Batar, 17.09.2005, Leg./Det. Stanković. M., [1]; **3)** *Bufo viridis*: Noćaj, Preseka, 25.05.1998, Salaš Noćajski, canal, 14.04.1998, Leg./Det. Stanković. M., [by 1]; **4)** *Bufo bufo*: Banovo Polje, Panjevine, 25.08.1998, [1 ad.]; Radenković, Batar, 04.11.2005, [1 ad.], **5)** *Pelobates fuscus*: Radenković, Vrbovac, 25.06.2000, Radenković, Gajića ćup., 30.03.2005, Banovo Polje, Batar, 23.04.2003, [by 1]; Ravnje, Široka bara 16.07.2010, larvae (tadpoles); Zasavica I, run over, 01.08.2010, [1 juv]; **6)** *Rana dalmatina*: Crna bara, Jovača, 13.05.1997, Leg./Det. Stanković. M., [1]; **7)** *Bombina bombina*: Salaš Noćajski, Ostrovac, 07.02. 2008.; Crna bara, Jovača, 03.08.2006, Leg./Det. Stanković. M., [by 1]; **8)** *Rana esc.complex*: Zasavica II, Valjevac, 20.07.1996, Leg./ Det. Stanković. M., [1]; **9)** *Rana lessona*: Salaš Noćajski, Sadžak, 03.08.1996, Leg./Det. Stanković.M., [1]; **10)** *Hyla arborea*: Radenković, Batar, 29.07.1998, Leg./Det. Stanković. M., [1 juv]; Ravnje, 13.07.1998, Leg./Det. Stanković. M., [1].

One specimen of the species *Rana temporaria* found in Batar (Radenković) in 2005 is also kept in the Batrachological collection, and it is the only specimen found so far in the reserve. From the Caudat, the collection contains only two specimens of the Salamandra salamandra species found in the reserve found in the forests around Jovaca near Crne Bara.

Herpetological collection

The collection has a total of 23 samples in ethanol and dry preparations (armor), of a total of 10 reptile species. Ordo Testudines: Out of 23 samples in a collection of 8 samples, it belongs to the Testudines ordo within three types. The collection contains found armor, parts of armor or whole turtle specimens as dry preparations and their eggs in ethanol. The collection contains pieces of armor of the allochthonous species *Pseudemys scripta elegans* for the time being the only finding in the reserve.

Review of the testudines collection: **1)** *Emys orbicularis*: Noćaj, Preseka, 07.08.2000, Leg./Det. Stanković. M., [1 oocit]; Zasavica I, Valjevac, 14.05.2008, Leg./Det. Stanković. M., [1 juv]; Noćaj, Preseka, 07.08.2009, Leg./Det. Stanković. M., [2 armors]; Mačvan. Mitrovica, Modran, 23.05.2000, Leg./Det. Stanković. M., [1. ad]; Noćaj, Preseka, 27.07.2008, Leg./Det. Stanković. M., [1 turtle armor]; **2)** *Testudo hermanni*: Banovo Polje, Kupalište, 28.07.1999, Leg./Det. Stanković. M., [1 juv]; Ravnje, Staniševac, 08.08.2008, Leg./Det. Stanković. M., [1 turtle armor]; **3)** *Pseudemys scripta elegans*: Zasavica II,Valjevac, 31.07.2008, Leg. Grujić, D., Det. Stanković, M., [parts of the armor].

Ordo Sauridae: out of a total of 23 specimens in a collection of 6 specimens belong to the Sauridae order within three species. In addition to whole ethanol-stored specimens, the collection also stores dried scum found in the field.

Review of the Sauridae collection: **1)** *Podarcis muralis*: Zasavica II, Turske livade, 10.12.2006, Leg./Det. Stanković. M., [1. ad]; Zasavica II, Turske livade, 18.04.2004, Leg./Det. Stanković. M., [1. ad]; **2)** *Lacerta viridis*: Salaš Noćajski, Sadžak, 20.07.1996, [1 juv]; *Lacerta sp*.: Ravnje, Široka bara, 06.08.2006, Leg./Det. Stanković. M., [1 juv]; **3)** *Lacerta agilis*: Crna bara, Jovača, 09.06.1996, Leg./Det. Stanković. M., [1 svlak]; Salaš Noćajski, Sadžak, 20.07.1996, Leg./Det. Stanković. M., [2. ad].

Ordo Serpentes: of the total of 23 specimens in the collection of 9 specimens belong to the Serpentes order within three species and one intraspecific form. All specimens are stored as a liquid preparation in ethanol. Special segments of this collection are snake hairs that are stored in clear thin PVC boxes.

Review of the Serpentes collection: **1)** *Natrix natrix persa*: Banovo Polje, Ribnjača bara, 13.02.1997, Leg./Det. Stanković. M., [1. ad]; Banovo Polje, Trebljevine, 28.08.2008, Leg./Det. Stanković. M., [1. juv]; **2)** *Natrix natrix*: Radenković, Batar, 29.09.2000, Leg./Det. Stanković. M., [1]; Zasavica I, Valjevac, 20.07.1996, Leg./Det. Stanković. M., [1]; Salaš Noćajski, Sadžak, 06.07.1996, Leg./Det. Stanković. M., [1. ad]; **3)** *Vipera berus bosniensis melano*: Radenković, Batar, 26.08.2005, Leg./Det. Stanković. M., [1. ad]; **4)** *Elaphe longissimus*: Mač. Mitrovica, Modran (Bogaz), 25.01.1998, Leg./Det. Stanković. M., [1. ad]; Zasavica II, Turske livade, 12.06.2011, Leg./Det. Stanković. M., [oocit]; Banovo Polje, Trebljevine, 07.07.2004, Leg./Det. Stanković. M., [snake old skin].

The herpetological collection also preserves one black (melano) specimen of the species *Vipera berus bosniensis* found in Batar (Radenković) in 2005, and it is the only specimen found so far in the reserve.

Ornithological collection

The collection has a total of 8 specimens of prepared birds within 7 species. Please note that all specimens of birds in the collection were found dead in the wild except in one instance when the specimen was seized by hunter-gatherer hunters for illegal hunting of predators and donated to us for collection as it comes from the reserve area. There are also several specimens of bird nests in the collection.

Review of ornithological collections: **1)** *Phalacrocorax pygmeus*: Salaš Noćajski, 05.01.2002, Leg. Nedić. Z., Det. Stanković. M., [1. ad]; Zasavica I, 16.09.2006, Leg. Simić. S., Det. Stanković. M., [1. ad]; **2)** *Anas plathyrrhinchos*: Zasavica II, Valjevac, 2002, Leg. Papić. S., Det. Stanković. M., [1.♂ad]; **3)** *Gavia arctica*: Zasavica II, 05.02.2007, Leg. Simić. S., Det. Stanković. M., [1.♂ad]; **4)** *Recurvirostra avosetta*: Zasavica II, Valjevac, 2008, Leg./Det. Stanković. M. [1. ad]; **5)** *Accipiter nisus*: Salaš Noćajski, Sadžak., 19.12.1998, Leg. Papić. S., Det. Stanković. M., [1. ad]; **6)** *Phaesanus colchicus*: Salaš Noćajski, Sadžak-Ostrovac, 13.12.1998, Leg. Papić. S., Det. Stanković. M., [1. ad]; **7)** *Strix aluco*: Salaš Noćajski, Sadžak, 2000, Leg. Papić. S., Det. Stanković. M., [1. ad].

Mammological collection

It possesses a total of 20 specimens of prepared mammals within 16 species. In addition to the prepared whole specimens, the collection includes the preparation of horned heads, rodents' nests and skulls of small mammals and several specimens in ethanol as liquid preparations (*Erinaceus europaeus*, *Apodemus agrarius*, *Sorex araneus*, *Microtus arvalis*, *Talpa europaea* and *Nyctalus noctua*). Material that is only a year old has been received as a gift and entered the year the copy was presented to us. All specimens that we have collected and after preparation are in the collection were found dead in the wild or killed on the road (e.g. *Castor fiber*).

Review mammological collections: **1)** *Castor fiber*: Zasavica, 22.03.2008, Leg. Papić. S., Det. Stanković. M., [1. ad]; **2)** Rattus norvegicus: Mačv. Mitrovica, Modran, 2002, Leg./Det. Stanković. M., [1. ad-present]; **3)** *Ondatra zibethica*: Zasavica I, Šumareva ćup, 15.04.2002, Leg. Simić. S., Det. Stanković. M., [1. ad]; **4)** *Erinaceus europaeus*: Zasavica II, Turske livade, 12.08.2000, Leg./Det. Stanković. M., [1. ad]; Ravnje, Staniševac, 27.07.2004, Leg. Stanković. M., Det. Paunović, M., [skull]; **5)** *Micromys minutus*: Ravnje, Bostanište, 24.07.2007, Leg./Det. Stanković. M.; Radenković, Poljansko, 24.07.2007, Leg./Det. Stanković. M., [∑=2 nests]; **6)** *Martes martes*: Mačvan. Mitrovica, 15.12.1998, Leg./Det. Stanković. M., [1. ad]; Noćaj, 07.01.2004, Leg. Stanković. M., Det. Paunović, M., [♀skull]; **7)** *Sciurus vulgaris*: Noćaj, Preseka, 2002, Leg./Det. Stanković. M., [1. ad-present]; **8)** *Felis silvestris*: Ravnje, 2005, Leg./Det. Stanković. M., [1. ad] (seized from hunters); **9)** *Capreolus capreolus*: Noćaj, 1997, Leg. Papić. S., Det. Stanković. M., [1 head, present]; **10)** *Apodemus agrarius*: Banovo Polje, Panjevine, 11.04.2005, Leg. Stanković. M., Det. Paunović, M., [1. ad]; **11)** *Lutra lutra:* Ravnje, 25.10.2005, Leg./Det. Stanković. M., [1. ad]; Zasavica I, 2006, Leg./Det. Stanković. M., [1. ad-present]; **12)** *Meles meles*: Salaš Noćajski 03.01.2002, Leg./Det. Stanković. M., [1. ad]; **13)** *Sorex araneus*: Radenković, Batar, 29.08.2000, Leg./Det. Stanković. M., [1. ad]; **14)** *Microtus arvalis*: Zasavica II, Turske livade, 04.08.2004, Leg. Stanković. M., Det. Paunović, M., [1. ad]; **15)** *Talpa europaea*: Ravnje, Bostanište, 23.07.1998, Leg./Det. Stanković. M., [1. ad]; **16)** *Nyctalus noctua*: Radenković, Vrbovac, 08.07.1998, Leg. Stanković. M., Det. Paunović. M., [1. ad].

By analyzing the natural collection of the vertebrates of the Zasavica Reserve, we see that all classes of vertebrates are represented.

CONCLUSION

The Zasavica Nature Reserve Study Collection includes the Paleontological-Geological Section and the Biological Section. For the past 23 years, the following material has been deposited in the reserve's natural history collection. A total of 50 specimens of minerals, rocks and fossils have been deposited in the paleontological-petrological collection from the area of the reservoir and the immediate environment. The paleontological part of the collection includes a collection of quaternary vertebrates composed of parts of the skeletons of mammals of the quaternary fauna, and here we have one exhibit, namely the mammoth atlas (*Mammuthus* sp.) Found in Black Bar near Jovaca, then a collection of invertebrate macrofauna consisting of the remains of shellfish shells (Bivalvia), snails (Gastropoda) and other freshwater or marine invertebrates in limestone and other sediments (silt, clay, etc.) and a paleobotanical collection consisting of parts of trees found in silt and peat and peat samples. While the petrological part of the collection contains pieces of minerals and rocks found in the alluvial deposit of the Sava or Drina or the average fraction of deposits from sources on the Zasavica coast. The biological part of the collection includes: Mycological collection with a total of 111 specimens of liquid preparations of fungi; Botanical collection with about 2500-3000 exotic herbaceous material and 82 bottles and vials with liquid preparations of plants and algae and the Zoological collection. In the zoological collection, we have a total of 113 samples with 64 species + 1 subspecies and include: ichthyological collection with a total of 34 samples in ethanol and one dry head preparation. For the three fish species in the collection, these are the only data for the reserve in the past 23 years (*Neogobius fluviatilis*, *Gobio albipinnatum* and *Barbus peloponesus*). A collection of ethanol from a total of 28 specimens of ethanol (9 are from the Caudata order and 19 from the Anura order) where the only specimen found so far is found in the *Rana temporaria* species in the reserve. Herpetological collection with a total of 23 samples in ethanol and dry preparations (armor), and the only black (melano) specimen of the species *Vipera berus bosniensis* found so far is kept in the collection. The ornithological collection consists of a total of 8 specimens of prepared birds within 7 species, and the mammological collection has a total of 20 exhibits (whole specimens prepared and head with horns), followed by small mammal skulls, rodent nests and liquid preparations. The entomological collection has 10 entomological boxes containing the collected entomological material, as well as a collection of other invertebrates where about 300 vials and vials with liquid sample preparations in ethanol have been deposited and one smaller part are dry preparations i.e. samples in boxes.

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SUITABILITY OF PROCEDURAL CALIBRATION STANDARDS AFTER LONG-TERM STORAGE FOR PESTICIDE ANALYSIS IN APPLE PEEL

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Abstract

An ever-present problem in the pesticide residue analysis - the matrix effect, can lead to the misleading results. Procedure-matched standards which compensate both for the matrix effect and the recovery are one of the best options for the matrix effect overcoming. Since procedural standard preparation is often time consuming, its storage for a prolonged usage can be valuable. For how long procedural standards can be stored was evaluated by monitoring the main parameters of the apple peel-matched calibration graphs for 5 pesticides over 57 days. The preparation procedure itself consisted of a liquid-liquid and solid-phase extraction, common steps in sample preparation procedures. Limited storage stability of pyrimethanil determined the storage period of less than 9 days.

Keywords: apple peel, procedural standards, GC-MS, storage

INTRODUCTION

When analyzing complex matrices such are fruits or vegetables, the matrix effect appears as a certain problem in the domain of quantitative analysis. Abundant matrix compounds can affect analyte response in two ways. The response enhancement effect, characteristic for gas-chromatographic analysis, was originally described by Erney *et al.* [1]. Matrix compounds from sample extracts block the active sites, primarily in the GC injector, thus leading to the lesser analyte adsorption and consequently to the signal enhancement and vice-versa, the growth of the new active sites number by gradual accumulation of non-volatile matrix compounds in the GC inlet and front part of the chromatographic column could decrease the analyte response as matrix – induced diminishment effect [2]. Therefore, the matrix effect can lead to the misleading results in pesticide residue analysis, both in quantitation or validation procedures and must be in some way overcome. Several approaches are nowadays frequently applied, such as the use of analyte protectants [3], matrix matched [4] or standard addition calibration method [5] or even the combination of matrix matching and multiple isotopically labeled internal standards [6].

Since the matrix effect is matrix-type dependent, the reliable approach of analyte quantitation should be the matrix-matching. Between the procedure-matched (pre-extraction fortified standards) and matrix-matched standards (post-extraction fortified standards), the usage of procedure-matched standards is more useful since it represents the straightest method of quantitation, simultaneously compensating for the recovery and for the matrix effect. Although this is the straightest method it is not the quickest one. Along with the positive features, the time-consuming preparation stands as the major negative feature. Thus, an adequate storage of the standards for the prolonged usage may be an alternative. The aim of this study was to evaluate the long-term conservation degree of procedural standards of several pesticides in apple peel as an example of complex matrix.

MATERIALS AND METHODS

Chemicals

High purity pesticide standards of trifloxystrobin, bifenthrin and boscalid were obtained from Sigma-Aldrich® (Germany). High purity pesticide standards of pyrimethanil and cyprodinil were obtained from AccuStandard® (USA). High purity dibutyl adipate (DBA), used as internal standard (IS), was purchased from Sigma-Aldrich Chemie® (Germany). HPLC grade ethanol, HPLC grade hexane and HPLC grade methanol were purchased from Fisher Scientific (USA). SELECTRA® (octadecyl, bulk form) was purchased from UCT (USA). Florisil® (60-100 mesh) was purchased from LGC Promochem (Germany).

Stock solutions preparation

Primary pesticides stock solutions of 1,000.00 µg mL^{-1} were made of high purity pesticide standards in ethanol. Secondary stock solutions of various pesticide concentration (single-pesticide solutions) were prepared in ethanol by diluting the primary stock solutions. Secondary stock solutions of various pesticide concentration (multi-pesticide solutions) were prepared in ethanol by mixing and diluting the primary stock solutions. Primary DBA stock solution of 1,000.00 µg mL^{-1} was prepared in ethanol; solutions of lower concentration were prepared in hexane, by diluting the primary stock solution. All solutions were stored in freezer at –15 °C.

Procedural standards preparation

[1] Fortification procedure: Apples of the *Granny Smith* variety were randomly chosen at the open-air market (JP "Tržnica", city of Niš, Serbia). One-kilogram sample was peeled. Peel was homogenized by blending after which six 10 g-portions were weighted. Each portion was mixed with 20 mL of water and additionally blended. The resulting mixture was transferred to a glass container and fortified with 5-pesticide mixture solution (multi-pesticide solution). The resulting concentration levels were: 0.000 mg kg^{-1} – blank procedural standard, 0.100, 0.200, 0.300, 0.400 and 0.500 mg kg^{-1}.

[2] Extraction procedure: After homogenization by shaking, mixtures were left to equilibrate for an hour and then subjected to a liquid-liquid extraction with two 10 mL-portions of hexane.

[3] Clean-up procedure: Ten milliliters of the obtained hexane extract were subjected to the SC, SE/LTP procedure, as detailed in Anđelković *et al.* [7] in order to remove waxes. Afterwards, partially cleaned-up extract was subjected to a SPE procedure in order to remove pigments. The SPE cartridge was filled with 500 mg of C18, then with 500 mg of Florisil® and at last with another 500 mg of C18, thus creating a three-layered form. Prior to sample

extract loading, the column was conditioned with 3 mL of methanol. Then, 1 mL of previously obtained methanol extract was loaded. The elution of analytes was performed with 2 mL of methanol, while the pigmentation was retained on the C18 part of the column. The obtained eluate was evaporated to dryness, re-dissolved in 0,5 mL of DBA hexane solution (1 μgmL^{-1}) and subjected to GC-MS analysis. Between each data acquisition standards were kept in refrigerator at 4 °C in closed 2-mL GC glass vials.

Instruments

In sample preparation procedure, following appliances were used: balance KERN KB 2000-2N, Germany (acc. ± 0.01 g); food processor TEFAL 0.9L BL142A, centrifuge Thermo Scientific Jouan C4i and TurboVap® LV evaporator, Zymark USA, Manifold SPE system Waters®, USA.

GC-MS analysis

The gas chromatographic analysis was performed on Agilent 6890 gas chromatograph equipped with 5973 Mass Selective Detector (MSD) and 7683 autosampler and SGE 25QC2/BPX5 0.25 capillary column (25 m×0.22 mm×0.25 μm, non-polar). The mass spectra were recorded under an electron ionization (EI) voltage of 70 eV. The gas chromatograph was operated in the splitless injection mode (purge time 1 min). The oven temperature was programmed from 90 °C (hold time 0 min) to 280 °C (4 min) at 20°C min^{-1} rate; post run: 300°C (2 min). Helium was the carrier gas with constant flow rate of 1.0 mLmin^{-1}. The target compounds were identified and confirmed at scan mode (*m*/*z* 50–400) and analysed at selected ion monitoring (SIM) mode with confirmation ions as given in Table 1. Both data acquisition and processing were accomplished by Agilent MSD ChemStation® D.02.00.275 software.

Table 1 *Properties and qualification parameters of tested pesticides (quantifier ion is given in bold)*

Pesticide	Class	Structure	MRL[a], mg kg^{-1}	Molecular mass	Log Kow	Retention time, min	Characteristic ions, m/z
Pyrimethanil	Fungicide	Anilinopyrimidine	15.00	199.25	2.84	6.79	**198**[b]
Cyprodinil	Fungicide	Anilinopyrimidine	2.00	225.28	3.59	7.95	**224**[b]
Trifloxystrobin	Fungicide	Strobilurin	0.70	408.37	4.50	9.06	**116**, 131, 145
Bifenthrin	Insecticide	Pyrethroid ester	0.01	422.86	6.00	9.61	**181**, 166, 165
Boscalid	Fungicide	Pyridine-carboxamide	2.00	343.20	2.96	12.08	**140**, 342, 112

[a] Maximum residual level (the highest level of a pesticide residue that is legally tolerated in or on food or feed when pesticides are applied correctly (Good Agricultural Practice)); [b] Besides ions specified in the table, EI ionization of pesticide molecules do not give other specific fragments.

RESULTS AND DISCUSSION

Internal standard overview

Internal standard was added to each calibration standard in the last part of the standard preparation procedure, and not prior to each data acquisition. This implies that possible variation in IS signal might be both the outcome of the instrument drift and/or the storage. IS signal variation as a function of storage time and instrument sequence is given in Figure 1.

Within-sequence variation in IS signal during the first data acquisition was about 2%. This variation is also low after 9 days of storage (about 5%), after which it increases (24-32%), mainly due to the different IS signal in blank sample (Figure 1, label 0). The percentage of within-standard IS variation ranged between 8.87% for 0.400 mg kg^{-1} procedural standard (label 0.4) to 24.60% for blank procedural standard (label 0). Based on the overall IS variation, its stability can be considered as good.

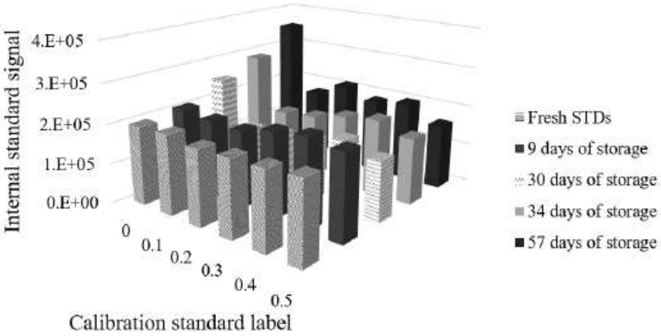

Figure 1 *Variation in internal standard signal within each sequence and within each standard*

Calibration graphs

Evaluation of pyrimethanil calibration plots (Figure 2) and residual plots (not presented in the paper) suggests that between the signals and the concentration of freshly prepared standards and standards after 9 day of storage exists good linearity. Calibration plot parameters assessed from standards after longer period of storage are quite altered. Both lower slope and intercept values were observed, with no signal-to-concentration correlation (Figure 2). Lower signal was measured for the same standard over period, suggesting the decomposition of the pesticide original form. Comparison of 1st day and 9th day acquisition plots indicate that although the signal-to-concentration correlation is still good after 9 days of storage, the graphs would not give comparable quantitation result, owing to the clearly distinct both the slope and the intercept. Thus, for the quantitation purposes of pyrimethanil in apple peel, freshly prepared procedural standards should be used, or the longevity of pyrimethanil standards should be additionally investigated and confirmed for periods <9 days.

The similar conclusion can be made either for cyprodinil plots (Figure 2), with the note that calibration based on the same standards is also appropriate after 9 days of storage, since the parameters are not altered (Table 2) and linearity is preserved. After that period significantly lower signals were measured over the full concentration range, indicating certain changes in the pesticide original form. Trifloxystrobin procedural standards, on the contrary, preserved good signal-to-concentration correlation over the whole concentration range and period of storage (Figure 2). The correlation coefficients were always higher than 0.95. Similar was observed for boscalid calibration plots, where correlation coefficients ranged from 0.9666 to 0.9899 indicating well-preserved correlation after storage (Table 2).

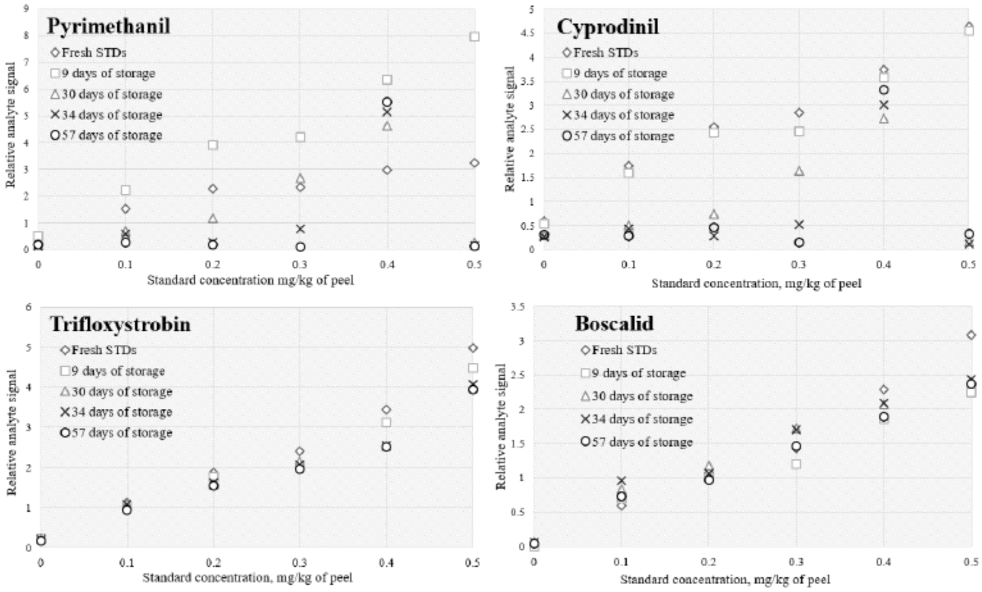

Figure 2 *Procedure-matched calibration plots for pyrimethanil, cyprodinil, trifloxystrobin and boscalid; relative analyte signal was calculated as absolute signal / IS signal*

Table 2 *Parameters of the procedure-matched calibration graphs for five pesticides in the 0.00 – 0.50 mg kg^{-1} concentration range*

Analyte	Time range	Slope	Intercept	Correlation coefficient
Pyrimethanil	1st day acquisition – fresh standards	5.26	0.81	0.9273
	Acquisition after 9 days	14.23	0.63	0.9788
	Acquisition after 30 days	3.92	0.63	0.1785
	Acquisition after 34 days	4.07	0.15	0.1516
	Acquisition after 57 days	4.39	-0.03	0.1420
Cyprodinil	1st day acquisition – fresh standards	7.57	0.79	0.9807
	Acquisition after 9 days	7.44	0.66	0.9650
	Acquisition after 30 days	1.97	0.52	0.1393
	Acquisition after 34 days	2.06	0.26	0.1221
	Acquisition after 57 days	2.55	0.17	0.1491
Trifloxystrobin	1st day acquisition – fresh standards	8.95	0.10	0.9731
	Acquisition after 9 days	7.96	0.12	0.9643
	Acquisition after 30 days	6.82	0.23	0.9554
	Acquisition after 34 days	6.91	0.21	0.9508
	Acquisition after 57 days	6.86	0.13	0.9596
Bifenthrin	1st day acquisition – fresh standards	4.70	0.05	0.9117
	Acquisition after 9 days	4.14	0.09	0.9014
	Acquisition after 30 days	3.49	0.31	0.9048
	Acquisition after 34 days	3.54	0.30	0.8559
	Acquisition after 57 days	3.75	0.27	0.8485

***Table 2** continued*

Boscalid	1st day acquisition – fresh standards	5.90	-0.06	0.9791
	Acquisition after 9 days	4.25	0.11	0.9762
	Acquisition after 30 days	4.54	0.25	0.9784
	Acquisition after 34 days	4.53	0.25	0.9666
	Acquisition after 57 days	4.44	0.14	0.9899

When compared to other plots, bifenthrin calibration plots (Figure 3) showed somewhat weaker signal-to-concentration correlation from the beginning of storage, but the initial correlation was linear. Stronger correlation and similar slope and intercept values were maintained until the 9th day of storage, after which alteration was observed (Table 2). The correlation coefficient ranged from 0.9117 at the beginning to 0.8485 after 57 days of storage.

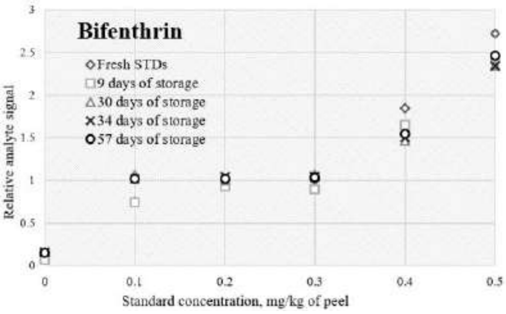

***Figure 3** Procedure-matched calibration plots for bifenthrin*

CONCLUSION

Freshly prepared 5-pesticide mixture procedural standards showed good linear signal-to-concentration correlation, ranging from 0.9117 for bifenthrin to 0.9807 for cyprodinil. Similar calibration plot parameters *i.e.* slope and intercept, as well excellent correlation coefficient, were preserved even after almost two months of trifloxystrobin and boscalid procedural standards storage. Bifenthrin procedural standards showed slightly weaker linear correlation than other 4 pesticides and slow decrease in slope until 30th day of storage with preserved correlation. Pyrimethanil and cyprodinil procedural standards are suitable freshly prepared and until 9 days of storage, respectively.

Regarding the feasibility of simultaneous analysis as a desirable feature, the overall conclusion is that mixed procedural standards are suitable for quantitation only up to 9 days of storage or even less, due to the limited storage stability of pyrimethanil.

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LABORATORY SCALED EVALUATION OF SORPTION BEHAVIOR FOR FIVE PESTICIDES IN APPLE PEEL: EFFECT OF CONTACT TIME

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Abstract

Apple fruit is frequently exposed to pesticide treatment, especially in the latest stages of apples production. When a pesticide gets the fruit, its interaction with the cuticle and the cuticular waxes starts via absorption mechanisms. Sorption behavior, that ultimately depends on the pesticide and the peel waxes characteristics, tends to affect the fate of the pesticide as well as its persistence in the fruit. This laboratory scaled study was designed to determine the residue levels of four fungicides and one insecticide in apple peel after immersion in solution of commercial pesticides for different periods of time. The study revealed that the amount of the fungicides and the insecticide in peel increases linearly and exponentially, respectively.

Keywords: fruit, sorption, fungicides, insecticides

INTRODUCTION

Apple fruit is frequently exposed to pesticide treatment, especially in the latest stages of the apples production. The first point of contact of pesticide molecule and fruit is the peel, the fruits natural barrier. Peel is considered to have an ability to accumulate most of the applied pesticides. The principal reason for this consideration is the cuticle and its structure and composition.

Cuticle represents an extracellular coating comprising a polymeric matrix of cutin and soluble cuticular waxes. The waxy part is mainly consisted of C16–C18 chain compounds i.e. saturated and unsaturated dihydroxy hexadecenoic, trihydroxy and epoxy hydroxy octadecanoic acids and a triterpenoid-rich cuticular wax mixture [1].

When a pesticide gets the fruit, its interaction with the cuticle and the cuticular waxes starts, via absorption mechanisms. A study dealing with the effectiveness of washing agents in the removal of surface and internalized pesticide residues from apples revealed pesticides sorption phases [2]. Namely, after applying a pesticide solution to the apple surface, pesticide was firstly absorbed onto the surface of epicuticular wax and then diffused into the wax and cuticle. Equilibrium of the pesticide on the epicuticular wax and the pesticide in the wax and cuticle is established when the amounts of pesticides in wax and cuticle no longer increase and upon reaching the equilibrium, pesticides begin to penetrate the living cells below, making this fraction of the pesticide permanently retained.

Although there is a range of factors such as the pesticide formulation applied, the applying conditions etc., absorption processes and their magnitude ultimately depend on the pesticide and the peel waxes characteristics. This includes the polarity characteristics of pesticides and its mode of action (penetrating, non-penetrating), the maturity stage of apple fruit, the growth season and even the apple variety. For sure, sorption behavior tends to affect the fate of the pesticide as well as its persistence in the fruit.

This study was designed to determine the residue levels of four fungicides and one insecticide in apple peel after immersion in commercial pesticides solution for different periods of time and thus to assess if the pesticides sorption process is time dependent.

MATERIALS AND METHODS

Chemicals

High purity pesticide standards of trifloxystrobin, bifenthrin and boscalid were obtained from Sigma-Aldrich® (Germany). High purity pesticide standards of pyrimethanil and cyprodinil were obtained from AccuStandard® (USA). High purity dibutyl adipate (DBA), used as internal standard (IS), was purchased from Sigma-Aldrich Chemie® (Germany). HPLC grade ethanol, HPLC grade hexane and HPLC grade methanol were purchased from Fisher Scientific (USA). SELECTRA® (octadecyl, bulk form) was purchased from UCT (USA). Florisil® (60-100 mesh) was purchased from LGC Promochem (Germany).

The following commercial formulations of pesticides were used: *Botrystock®* - pyrimethanil (Stockton Crop Protection AG, Swizerland), *Cormax®* – cyprodinil (Shanghai Mio, China), *Bosco®* – boscalid (Ningbo Synagrochem, China), *Zato 50 WG®* – trifloxystrobin (Bayer AG, Germany) and *Talstar 10 EC®* – bifenthrin (FMC Corporation, USA).

Stock solutions preparation

Primary pesticides stock solutions of 1,000.00 µg mL^{-1} were made of high purity pesticide standards in ethanol. Secondary stock solutions of various pesticide concentration (single-pesticide solutions) were prepared in ethanol by diluting the primary stock solutions. Primary DBA stock solution of 1,000.00 µg mL^{-1} was prepared in ethanol; solutions of lower concentration were prepared in hexane, by diluting primary stock solution. All solutions were stored in freezer at –15°C. The stock solution of commercial pesticide formulations, containing 100.00 µg mL^{-1} of each of five pesticides was prepared prior to experiment set-up by dissolving commercial formulations in distilled water.

Experiment set-up

Apples of the *Granny Smith* variety, similar in shape, mass and maturity stage, were chosen at the open-air market (JP “Tržnica”, city of Niš, Serbia). The average mass of 15 apple units used in this study was 153.64±8.89 g. Apples were cleaned from any visible dirtiness by wiping. Pesticides sorption was studied by soaking each apple unit in 300 mL of aqueous solution fortified with five pesticides with final concentration of 1.00 mg L^{-1}, in a 500 mL glass beaker. The submersion period was 0.50, 1.50, 4.00, 5.50 and 7.50 minutes. Each submersion was performed in triplicates. Immediately after submersion has finished, the excess of immersion solution was removed from apple surface by 2-3 times short immersion in tap water and wiping, after which apples were peeled.

Analysis: The complete peel mass obtained from apple unit was homogenized by blending after which a 10 g-sub portion was weighted for analysis. Each portion was mixed with 20 mL of water and additionally blended. The resulting mixture was transferred to a glass container and subjected to liquid-liquid extraction with two 10 mL-portions of hexane.

Clean-up procedure: Ten millilitres of the obtained hexane extract were subjected to the SC, SE/LTP procedure, as detailed in Anđelković *et al*. [3] in order to remove waxes. Afterwards, partially cleaned-up extract was subjected to a SPE procedure in order to remove pigments. The SPE cartridge was filled with 500 mg of C18, then with 500 mg of Florisil® and at last with another 500 mg of C18, thus creating a three-layered form. Prior to sample extract loading, the column was conditioned with 3 mL of methanol. Then, 1 mL of previously obtained methanol extract was loaded. The elution of analytes was performed with 2 mL of methanol, while the pigmentation was retained on the C18 part of the column. The obtained eluate was evaporated to dryness, re-dissolved in 0.50 mL of DBA hexane solution (1 µg mL^{-1}) and subjected to GC-MS analysis.

Note: In order to check for the possible migration of pesticides during the immersion period, beside peel, the first layer of flesh (approx. 1 mm) was peeled and analysed. Although there are no waxes in flesh, flesh samples were prepared according to the same procedure due to the comparability of the results.

Quantitation: For the quantitation purposes procedure-matched standards representing the mixture of five pesticides were prepared in the following analytical range: 0.000 – 0.050 – 0.100 – 0.200 – 0.300 – 0.350 – 0.400 – 0.500 – 0.600 – 0.700 mg per kg of apple peel and 0.000 – 0.010 – 0.030 – 0.050 – 0.075 – 0.100 – 0.200 mg per kg of apple flesh. Calibration plots for peel (linear calibration range) at the end included following levels: pyrimethanil and cyprodinil (0.00, 0.10, 0.30, 0.35, 0.40, 0.50 and 0.70 $mgkg^{-1}$), trifloxystrobin (analytical range), bifenthrin (0.000, 0.050, 0.100, 0.350, 0.400, 0.500, 0.600 and 0.700 mg kg^{-1}) and boscalid (0.000, 0.050, 0.100, 0.200, 0.350, 0.400, 0.500 and 0.700 mg kg^{-1}).

Instruments

In sample preparation procedure, following appliances were used: balance KERN KB 2000-2N, Germany (acc. ± 0.01 g); food processor TEFAL 0.9L BL142A; Manifold SPE system Waters®, USA; centrifuge Thermo Scientific Jouan C4i and TurboVap® LV evaporator, Zymark USA.

GC-MS analysis

The gas chromatographic analysis was performed on Agilent 6890 gas chromatograph equipped with 5973 Mass Selective Detector (MSD) and 7683 autosampler and SGE 25QC2/BPX5 0.25 capillary column (25 m×0.22 mm×0.25 µm, non-polar). The mass spectra were recorded under an electron ionization (EI) voltage of 70 eV. The gas chromatograph was operated in the splitless injection mode (purge time 1 min). The oven temperature was programmed from 90°C (hold time 0 min) to 280°C (4 min) at 20°C min^{-1} rate; post run: 300°C (2 min). Helium was the carrier gas with constant flow rate of 1.0 mL min^{-1}. The target compounds were identified and confirmed at scan mode (m/z 50–400) and analyzed at selected ion monitoring (SIM) mode with confirmation ions as given in Table 1. Both data acquisition and processing were accomplished by Agilent MSD ChemStation® D.02.00.275 software.

Table 1 *Properties and qualification parameters of tested pesticides (quantifier ion is given in bold)*

Pesticide	Class	Structure	MRL[a], mg kg^{-1}	Molecular mass	Log Kow	Retention time, min	Characteristic ions, m/z
Pyrimethanil	Fungicide	Anilinopyrimidine	15.00	199.25	2.84	6.79	**198**[b]
Cyprodinil	Fungicide	Anilinopyrimidine	2.00	225.28	3.59	7.95	**224**[b]
Trifloxystrobin	Fungicide	Strobilurin	0.70	408.37	4.50	9.06	**116**, 131, 145
Bifenthrin	Insecticide	Pyrethroid ester	0.01	422.86	6.00	9.61	**181**, 166, 165
Boscalid	Fungicide	Pyridine-carboxamide	2.00	343.20	2.96	12.08	**140**, 342, 112

[a] Maximum residual level (the highest level of a pesticide residue that is legally tolerated in or on food or feed when pesticides are applied correctly (Good Agricultural Practice)); [b] Besides ions specified in the table, EI ionization of pesticide molecules does not give other specific fragments.

RESULTS AND DISCUSSION

Amount of tested pesticides in the first layer of flesh was for all intervals of immersion below the limit of quantitation of the method. The amount of pyrimethanil and cyprodinil in apple peel ranges from 0.087 and 0.045 after immersion for 0.50 min, to 0.393 and 0.378 mg kg^{-1} after immersion for 7.50 min, respectively (Table 2). The highest tendency for sorption to apple peel was observed for bifenthrin (3.686 mg kg^{-1} after 7.50 min of immersion), while boscalid showed the lowest tendency, not being detected in peel after 0.50 min and reached only 0.094 mg kg^{-1} after 7.50 min of immersion. Linear *in-peel amount vs. immersion time* correlation can be observed for all pesticides, with exception of bifenthrin for which it is exponential (Figure 1).

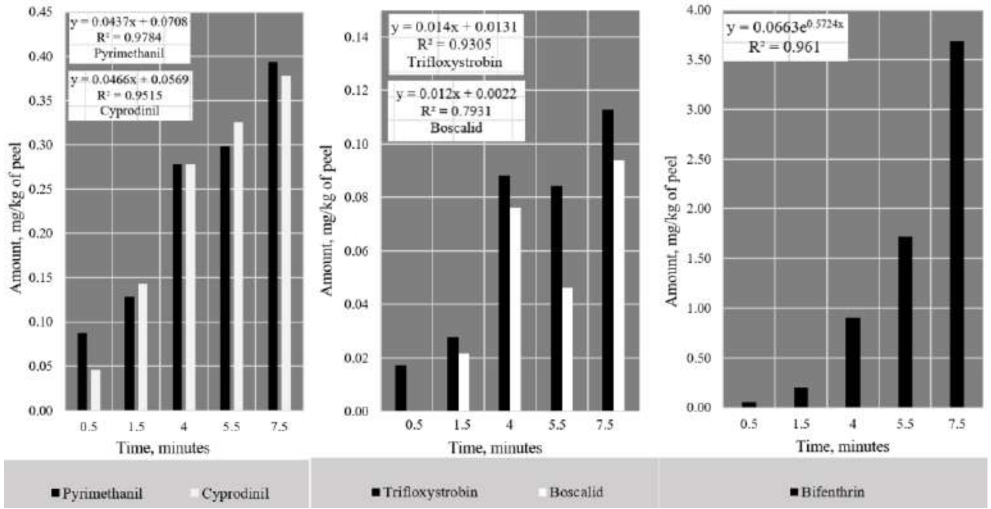

Figure 1 *Relationship between pesticide solution-apple contact time and detected amount of pesticide*

Considering the average peel mass of the three immersion period replicates and the pesticide concentration in 300 mL immersion solution (1 mg L^{-1} each), the pesticide concentration in peel (mg kg^{-1}) in case of a 100% sorption was calculated; theoretical maximum of each pesticide concentration in peel would be: 19.75 mg kg^{-1}, 21.30 mg kg^{-1}, 21.79 mg kg^{-1}, 18.83 mg kg^{-1} and 19.00 mg kg^{-1} in apple units submerged for 0.50, 1.50, 4.00, 5.50 and 7.50 min, respectively. Thus, the sorption percentage for each pesticide over the period of 7.50 minutes can be calculated (Table 2). The correlation between the immersion period and the percentage of sorption was evidenced. For pyrimethanil, cyprodinil, trifloxystrobin and boscalid linear correlation was observed with the correlation coefficient of 0.9974, 0.9762, 0.9755 and 0.8628, respectively. For bifenthrin exponential correlation was evidenced (R^2=0.9709).

***Table 2** Pesticides residues and sorption percentage in apple peel (n=3) after being in contact with 1 mg L^{-1} pesticides solution during different time intervals*

Time, min	Pesticide:	Pyrimethanil	Cyprodinil	Trifloxystrobin	Bifenthrin	Boscalid
0.50	mg kg^{-1} (*RSD, %*)	0.087 (*32.35*)	0.045 (*24.80*)	0.017 (*27.16*)	0.058 (*15.75*)	n.d.
	% of sorption	0.44	0.23	0.09	0.29	n.a.
1.50	mg kg^{-1} (*RSD, %*)	0.128 (*31.09*)	0.143 (*18.76*)	0.028 (*7.01*)	0.204 (*15.25*)	0.022 (*32.18*)
	% of sorption	0.60	0.67	0.13	0.96	0.10
4.00	mg kg^{-1} (*RSD, %*)	0.278 (*35.68*)	0.278 (*18.83*)	0.088 (*29.64*)	0.903 (*26.67*)	0.076 (*17.49*)
	% of sorption	1.28	1.28	0.41	4.15	0.35
5.50	mg kg^{-1} (*RSD, %*)	0.297 (*32.08*)	0.325 (*26.69*)	0.084 (*44.25*)	1.720 (*23.72*)	0.046 (*25.85*)
	% of sorption	1.58	1.73	0.45	9.13	0.25
7.50	mg kg^{-1} (*RSD, %*)	0.393 (*21.54*)	0.378 (*13.13*)	0.113 (*23.64*)	3.686 (*8.69*)	0.094 (*1.23*)
	% of sorption	2.07	1.99	0.59	19.39	0.49

CONCLUSION

Apple peel sorption experiments for four fungicides and one insecticide show that sorption process leads to a linear increase of the fungicides amount in peel, with decreasing sorption rate in following order: pyrimethanil, cyprodinil > trifloxystrobin > boscalid. Sorption process for the insecticide bifenthrin leads to an exponential increase of the amount of this pesticide in apple peel. The sorption percentage confirms the decreasing sorption tendency in following order: bifenthrin > pyrimethanil, cyprodinil > trifloxystrobin > boscalid. Pesticides amount in flesh, as determined by the first layer analysis, was below the method limit of quantitation.

ACKNOWLEDGEMENT

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THE MIGRATION OF DEHP FROM PLASTIC PACKAGING INTO DAIRY PRODUCTS WITH DIFFERENT FAT CONTENT

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Abstract

Objective of this study was to determine the effect of fat content of dairy products on the migration of di-(2-ethylhexyl) phthalate (DEHP) from plastic packaging into different dairy products. Migration of DEHP from plastic packaging into three dairy recipients with different fat content was observed: infant formula, whey powder and water under the influence of increased temperature. Amount of leached DEHP from plastic packaging into different recipients was determined by liquid-liquid extraction followed by gas chromatography-mass spectrometry (GC/MS).The ion of base peak m/z 149 for DEHP was selected for the screening studies. The acquisition was performed at the selected ion monitoring mode (SIM). The mass-selective detector (MSD) response for GC/MS DEHP calibration standards was linear between 0.25 and 2.50 µg mL^{-1}*. The study demonstrated an increase of the amount of migrated DEHP from packaging material into dairy product with higher percentage of fat. The mass of migrated DEHP was the highest in the sample of infant formula, followed by whey powder and water. Also, the results show that longer exposure to high temperature results in reaching the plateau on the graph Mass of migrated DEHP vs time, which means that further exposure to high temperature does not result in increase of DEHP leaching.*

Keywords: DEHP migration, dairy products, fat content, plastic packaging, GC/MS

INTRODUCTION

Phthalates, known as dialkyl or alkyl aryl esters of 1,2-benzenedicarboxylic acid, are a type of chemical compounds used to soften plastics, making plastics more suitable for a wider range of uses. Plastics treated with such plasticizers are softer and more flexible, with a suitable odour and colour. As such, plastics are used to manufacture medical equipment, children's toys, food packaging and other different plastic packaging. However, the phthalates are not chemically bonded to the polymer but are only impregnated in the polymer, making phthalates more accessible to the environment (phthalates can easily migrate to their environment - food, drink, air, soil, *etc.*).In this way, human health can be affected by phthalates, so the European Food Safety Authority (EFSA) had set the tolerable daily intake (TDI) for the most commonly used phthalate - DEHP and amounts 0.05 mg kg^{-1} body weight of adult human day^{-1} [1]. Various studies have shown that DEHP exposure may induce reproductive toxicity, liver damage, and carcinogenesis in humans [2]. Given that DEHP affects human health, and that DEHP is easily leached into food from plastic packaging materials, it is of great importance to determine the concentration of DEHP in the investigated matrices as well as to test the impact of fat content to a DEHP migration.

Determination of DEHP can be performed using different techniques, depending on the investigated matrix. Gas chromatography coupled with mass spectrometry (GC/MS) is the most used technique for DEHP determination [3].

In this experiment, the migration of DEHP from plastic packaging materials of known percentages of DEHP was done under the influence of increased temperature, while dairy products with different fat content were used as the receiving matrix for the leached DEHP. The quantification of leached DEHP from plastic packaging into different dairy products was performed by GC/MS. In this way, the impact of fat content of dairy products on migration of DEHP from plastic packaging was determined.

MATERIALS AND METHODS

Reagents and materials

HPLC grade *n*-hexane was purchased from Sigma–Aldrich (St. Louis, MO, USA). Di(2-ethylhexyl) phthalate (DEHP) was purchased, in the highest available purity, from Sigma–Aldrich (St. Louis, MO, USA). Dibutyladipate (DBA) was purchased from Fluka (Buchs, Switzerland) and used as an internal standard. Water from a Milli-Q system (Millipore, Bedford, MA, USA) was used. Dialysis bag (Baxter, USA) was used. Whey powder and infant formula were purchased from commercial manufacturers offered at the Serbian market.

All stock, intermediate and working solutions were prepared in *n*-hexane. The stock solutions of DEHP and DBA were prepared at a concentration of 1.0 mg mL^{-1}. The stock standard was diluted stepwise with *n*-hexane to prepare working solutions of DEHP. The calibration standard series was obtained with DEHP in the concentration range of 0.25, 0.50, 1.00, 1.50 and 2.50 µg mL^{-1} with DBA as the internal standard, at a concentration of 1 µg mL^{-1}. The calibration curve was linear in the range from 0.25 to 2.5 µg mL^{-1} with a correlation coefficient higher than 0.99. The linear dynamic range was broader and covered the range from 2.50 to 50 µg mL^{-1}.

GC-MS technique

Gas chromatographic analysis was performed by gas chromatograph 6890 (Hewlett-Packard, USA) equipped with a mass selective detector (MSD) 5973 (Hewlett-Packard, USA) and Autosampler 7683 (Agilent, USA) and a DB-5 MS capillary column (30 m × 250 mm × 0.25 mm) (Agilent, USA). The gas chromatograph was operated in the split less injection mode. The oven temperature was programmed from initial temperature 60 °C (hold time 1 min) to 220 °C (hold time 1 min) at a rate of 20 °C min^{-1}and then to 280 °C (hold time 4 min) at a rate of 5 °C min^{-1}. Helium was the carrier gas (flow rate of 1.0 mL min^{-1}) and the inlet temperature was 250 °C. The operating temperature of the MSD was 280 °C with the electron impact ionization (EI) voltage of 70 eV. The dwell time was 100 ms. The MSD was used in the single ion-monitoring mode (SIM), the quantification ion was*m/z* 149 for DEHP and ion *m/z* 185 was chosen as representative ion of DBA. Analyte response was normalized to DBA as internal standard. The identification and quantification of target compound was based on the relative retention time, the presence of target ion and its relative abundance. Both data acquisition and processing were accomplished by Agilent MSD ChemStation® D.02.00.275 software.

Sample preparation

In the migration experiment, recipients for migrated DEHP from plastic packaging materials under the influence of temperature were infant formula, whey powder and water. Dairy products (infant formula and whey powder) were non-polar and had different fat content, unlike water which was polar and without fat, and it was taken for comparison. Fat content for infant formula and whey powder were 22.8 and 2 %, respectively.

Whey powder (65 g) and infant formula (45 g) were dissolved in 1 L of water from a Milli-Q system, respectively, according to the producer instruction. Fresh samples were always prepared immediately before analysis.

The dialysis bag was used as a plastic packaging material with high phthalate content. This reliable source of DEHP which contains about 35.8 % of DEHP compared to the total weight was used to examine DEHP migration [4]. The measured pieces of 1 cm^2 of dialysis bag were covered with 35 mL of dairy samples (infant formula and whey powder) and water.

Migration experiment and extraction procedure

The conditions of a migration experiment were set up to determine the effects of exposure time and temperature to DEHP migration into dairy products: dairy products with plastic packaging materials were heated up to 60 °C for up to 60 min, with repetition of cooling and heating processes with the total heating time up to 60 hours.

Dairy samples with 1 cm^2 of dialysis bag were vigorously stirred and heated to a temperature up to 60 °C, for 60 min. After cooling the samples at room temperature and filtering, 20 mL of *n*-hexane, as effective extraction agent[5], was added to the samples. Extracts were manually shake for 15 minutes followed by extraction inthe ultrasonic bath for 30 minutes. After clarification of blurred extracts, the *n*-hexane layers were separated and concentrated to the volume of 1 mL. DBA was added to concentrated *n*-hexane extracts such that its concentration in each sample was 1 $\mu g\ mL^{-1}$.

Pieces of dialysis bag, were subjected to repeated migration tests into dairy products, providing total heating time of 60 hours. The test was performed until the plateau was reached on the curve $m = f(t)$, where m is mass of the migrated DEHP and t time of exposure.

Blank samples (dairy products without plastic pieces from dialysis bag) were treated in the same way as the dairy samples with plastic pieces from dialysis bag. The laboratory contamination was thus monitored.

All experiments were performed in triplicate and quantification on GC/MS was repeated twice.

Glassware control

In order to minimize the contamination by phthalates from the laboratory, only glassware equipment was used. All glassware was washed with soap, tap water and ultrapure water, then washed with acetone and n-hexane and dried at 200 °C in the oven for 4 hours [6].

RESULTS AND DISCUSSION

The chromatogram of a standard solution of DEHP and DBA, given in Figure 1, shows good separation of DEHP and DBA occurred within a running time of 20 minand retention times for DBA and DEHP were 9.990 and 18.426 min, respectively. The calibration curve was linear in the range from 0.25 to 2.5 µg mL^{-1} with correlation coefficient of calibration curve higher than 0.990.

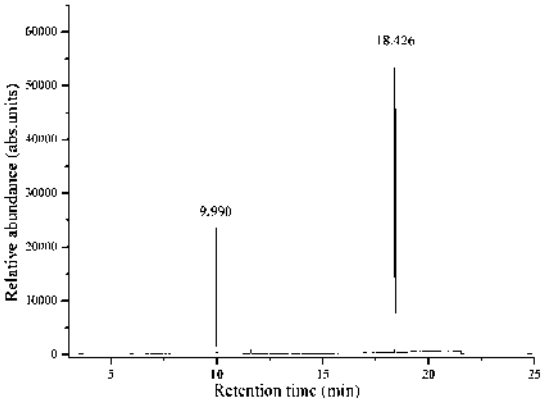
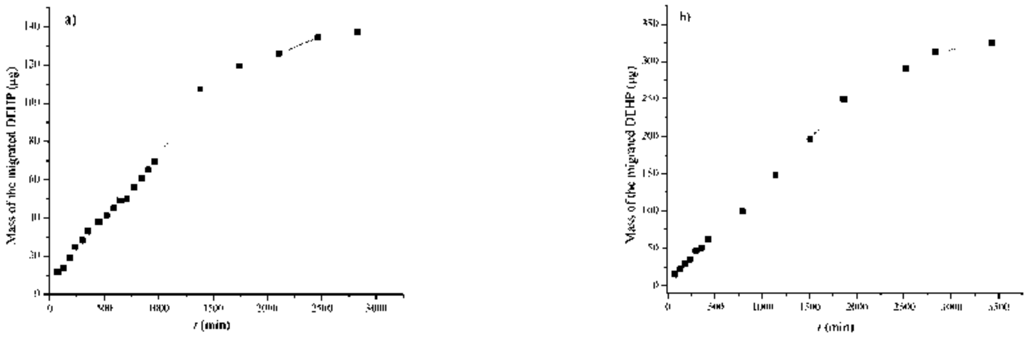


***Figure 1** GC/MS chromatogram of a standard solution of DEHP and DBA in a concentration of 2.5 µg mL^{-1} and 1.00 µg mL^{-1}, respectively*

Figure 2 shows the graphs of the mass of the migrated DEHP as the function of exposure time to increased temperature for three types of dairy products. The graphs show a linear increase of the mass of migrated DEHP over time under the influence of temperature, until the plateau is reached. Plateau indicates that after the maximum migration of DEHP has been reached DEHP no longer migrates into the food receiving matrices under the influence of increased temperature. Maximal amount of migrated DEHP, to water as recipient, is reached after 2500 min. The time required to achieve maximum DEHP migration into whey powder and infant formula were2950 and 3000 minutes, respectively.



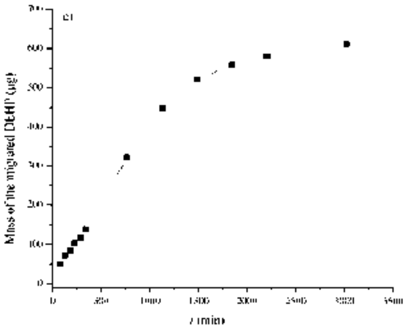


***Figure 2** The influence of temperature on the migration of DEHP in a) water, b) whey powder, c) infant formula*

The total migrated amount of DEHP follows the order: infant formula (601.29 µg), whey powder (311.83 µg) and water (135.67 µg), which is in correlation with the time of reaching plateau and with fat content of receiving matrix.

Figure 3 shows two regions in the mass vs. time graphs. Graph (a) shows the dependence of the mass of the migrated DEHP relative to the total exposure time of the samples to increased temperature and graph (b) shows the dependence of the mass of migrated DEHP in the first 450 min of exposure. The second graph shows higher slope of curve of migrated DEHP over time and curve is almost linear. During this period of 450 min about 30 % of total amount of migrated DEHP migrated into recipients. Unlike this rapid migration in the first 450 min, the migration in the remaining exposure time is slower, and slope of curve of migrated DEHP over time was smaller then of the above noted.

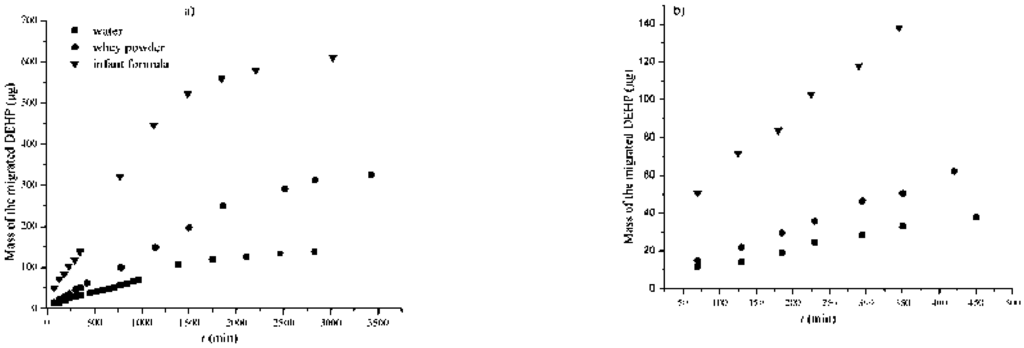


***Figure 3** Mass of the migrated DEHP under the influence of temperature a) in a time period of 3500 min and b) in a time period of 450 min*

The aim of this migration experiment was to determine the total mass of the migrated DEHP from plastic packaging materials into dairy products after repeated migration, related to temperature. The effects of temperature and fat content of dairy products on DEHP leaching are presented in Table 1.The results show that the highest mass of migrated DEHP was determined in the dairy product with the highest percentage of fat, which was expected, since DEHP is a non-polar molecule and is more soluble in non-polar media such as the infant formula with 22 % of fat. Water as a polar medium was not a suitable recipient for migrated

DEHP, while whey powder was second recipient for DEHP due to a fat content of 2 %.In all three cases, the percentage of DEHP leaching was low and ranged from to 0.02-0.12 % relative to the mass of DEHP in plastic materials.

Table 1 *Migration of DEHP influenced by temperature and fat content of food receiving matrix*

Food receiving matrix	Mass of dialysis bag (g)	Mass of DEHP in dialysis bag (g)[4]	Maximal amount of migrated DEHP (µg)	Percentage of migrated DEHP (%)
Water	1.7410	0.6233	135.67±1.23	0.02
Whey powder	1.6113	0.5768	311.83±1.40	0.05
Infant formula	1.4560	0.5212	601.29±2.73	0.12

CONCLUSION

Migration of DEHP from plastic packaging materials to dairy products depends on exposure temperature, exposure time and fat content of dairy product. Obtained data showed the following: amount of migrated DEHP decreases by following order infant formula > whey powder > water. In this order the fat content also decreases, which indicates that the highest migration is for dairy product with highest fat content. Results indicate that increasing temperature increases the migration of phthalates into diary matrices. Thus, during period of 450 min about 30 % of total amount of DEHP migrated into recipients, while the migration in the remaining exposure time is slower.

ACKNOWLEDGEMENT

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OPTIMIZATION AND APPLICATION OF LIGNOCELLULOSIC-Al_2O_3 BIOSORBENT FOR COPPER IONS REMOVAL FROM WATER

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Abstract

The chemically modified lignocellulosic biomass with an inorganic oxide (Al_2O_3) was tested as a new sorbent for the removal of copper (Cu (II)) ions from aqueous solution in batch conditions. As a lignocellulosic base material woodchips from an oak tree (Quercus rubra) were used. In order to define optimal conditions for sorption of Cu (II) ions from water by lignocellulosic-Al_2O_3 hybrid (LC-Al_2O_3), effects of initial pH, sorbent dosage and initial Cu(II) ions concentration, were studied. The increase in the solution pH from 1.0 to 6.0 led to an increase of removal efficiency of Cu (II) ions. The highest removal efficiency of Cu (II) ions was observed at pH 6 reached 99.08%. The increase of biosorbent dose from 0.5 to 8.0 g dm^{-3} led to an increase of removal efficiency of Cu (II) ions. Optimal sorbent dosage was 2.0 g dm^{-3}. With the increase of initial Cu (II) ions concentration, the removal efficiency decrease. In addition to the high removal efficiency, LC-Al_2O_3 biosorbent possesses other benefits, like mechanical stability, ease of synthesis, cost-effectiveness, biocompatibility and environmental-friendliness, which all makes it a promising material for the removal of heavy metal ions from water.

Keywords: optimization, biosorption, removal, copper, wastewater treatment

INTRODUCTION

Water bodies can be polluted by a wide variety of substances and the largest source of it are small and big industries. One of the most basic environmental pollutants discharged to water or wastewaters are heavy metals which may originate from wastewater of many industries, such as batteries, tanneries, electrical, electroplating, mining, refining ores, fertilizers, pesticides, etc. [1,2]. Heavy metals can pose a risk to the human and environmental health due to their hazardous effects, persistency and accumulation tendency causing damage to many parts of human bodies, even at very low concentrations [3,4]. Therefore, the removal of heavy metals from aqueous solutions is of extreme importance. Numerous processes and technologies have been used for heavy metal removal, such as: precipitation, ion exchange, membrane filtration, electroplating [1]. Among them, biosorption, using inactive and dead biomasses as sorbents, has emerged as a promising technique as compared to other methods of wastewater treatment in terms of cost, the simplicity of design and operation, availability, effectiveness, insensitivity to toxic substances and potential metal recovery [5].

In this paper, application of a chemically modified lignocellulosic biomass with a small amount of Al_2O_3 (LC-Al_2O_3) for removal of copper (Cu (II)) ions from water was studied. As a lignocellulosic base material woodchips from an oak tree (*Quercus robur*) were used. Woodchips were generated from wood industries, particularly from furniture manufacturing, so in that manner reusing this kind of material we can reduce waste and increase reuse/recycle options. In order to investigate principal operational process parameters effects of pH, temperature, sorbent dose and Cu (II) ions concentration on the sorption process were examined.

MATERIALS AND METHODS

The experiments have been performed using a woodchips residue generated from an oak tree (*Quercus robur*), which were fractionated by size and washed with deionized water. Ten grams of the biomass was acid treated (0.3 M HNO_3) to remove bio-accumulated metals, then alkali treated (1 M NaOH) in the period of 60 min. After that the material was mixed with solution of 1g of $Al(NO_3)_3 \times 9H_2O$ dissolved in 100 cm^3 of deionized water and the suspension was stirred for 0.5 h at 25.0 ± 0.5°C. After that the solution was evaporated. The obtained material was washed with deionized water, and treated by trimethylamine, then washed with deionized water until neutral pH and dried at 55 ± 1ºC for 5h. This material was abbreviated as LC-Al_2O_3.

Working model solutions of Cu (II) ions was prepared by the appropriate dilution of the stock solutions (1.0000 g dm^{-3}). The pH of the solutions was adjusted with 0.1/0.01 mol dm^{-3} NaOH/HNO_3 solutions pH-metrically (Orion Star A214, Thermo Fisher Scientific, USA). All experiments were performed at 25.0 ± 0.2°C. The aliquots of the solution were taken before the sorption started, and after particular periods of time. The concentrations of Cu (II) ions in the solution were determined by an atomic adsorption spectrometer Analyst AA 300 (Perkin Elmer, USA).

The removal efficiency (RE) of Cu (II) ions by biosorbent was calculated using the equation (1):

$$\text{RE}(\%) = \frac{c_0 - c_t}{c_0} \text{x}100 \qquad (1)$$

where c_0 and c_t are the initial and final Cu (II) ions concentrations in the solution (mg dm^{-3}).

All experiments were performed in triplicate. Average values ± SD (error bars) are presented in all graphs. All parameters were evaluated with the non-linear regression method by means of Origin Pro 2016 software (Origin Lab Corporation, USA).

RESULTS AND DISCUSSION

Effects of initial pH

The removal of Cu (II) ions by LC-Al_2O_3 biosorbent is highly affected by the pH value of the solution. The experiments were studied by varying initial pH value from 1.0 up to 6.0, while other parameters were kept constant (initial metal concentration 20.0 mg dm^{-3}, sorbent dose 2.0 g dm^{-3}, temperature 25.0 ± 0.2ºC). Results show that an increase in the solution pH from 2.0 to 6.0 led to an increase in the removal efficiency of Cu (II) ions from 35.05 to 99.08% (Figure 1).

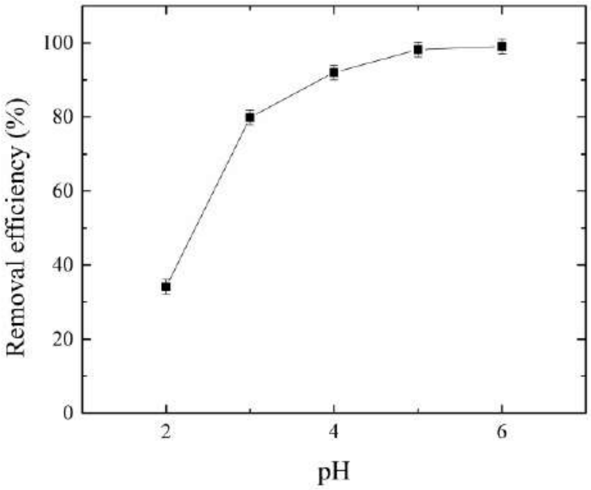

***Figure 1** Effect of pH on the Cu (II) ions removal with LC-Al_2O_3. Initial Cu (II) ions concentration 20.0 mg dm^{-3}, sorbent dose 2.0 g dm^{-3}, temperature 25.0 ± 0.2°C*

Therefore, when the pH decreased, concentrations of protons increased and competition in binding the active sites on the surface of biosorbent, between the H^+ and metal ions started. Protonated active sites were incapable of binding metal ions, leading to free ions remaining in the solution. With the increase in pH, the overall surface on LC-Al_2O_3 became negative and sorption was increased and the competing effect of hydronium ions decreased. Dominant species of copper in the pH range 3–5 are Cu^{2+} and $CuOH^+$, while the copper at above 6.3 occurs as insoluble $Cu(OH)_2$, so above pH 6.0, insoluble copper hydroxide starts precipitating from the solution and experiments could not be done [6,7]. From the obtained results, it can be concluded that the optimal pH value is 6.0 and this pH value was also used for all further experiments.

Effect of temperature

The temperature of the solution plays an important role in the sorption process. Increasing the temperature is known to cause an increase in the rate of diffusion of the sorbate molecules across the external boundary layer and in the internal pores of the sorbent, owing to the decrease in the viscosity of the solution. In that manner, changing the temperature will change the rate of the sorption [8]. The experiments were done at different temperatures: 10.0, 20.0, 35.0 and 50.0 °C, while the other parameters were kept constant (initial pH 6.0, initial pollutant concentration 20.0 mg dm^{-3} and sorbent dose 2.0 g dm^{-3}). Results show that an increase in the solution temperature from 10.0 to 50.0 °C led to an increase in the removal efficiency of Cu (II) ions from 84.12 to 99.9%, indicating the process to be endothermic in nature (Figure 2).

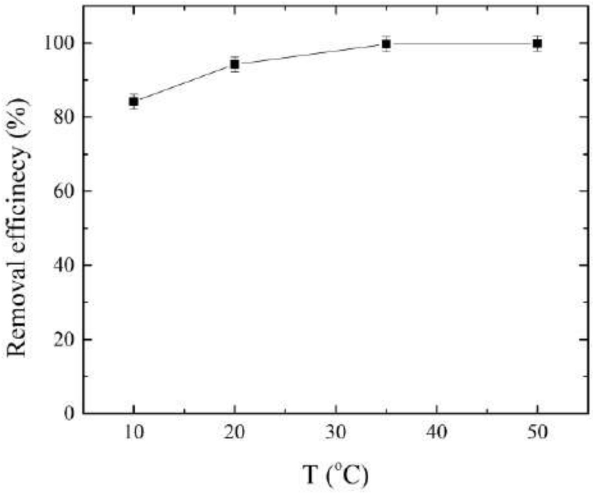

***Figure 2** Effect of temperature on the Cu (II) ions removal with LC-Al_2O_3. Initial pH 6.0, initial Cu (II) ions concentration 20.0 mg dm^{-3}, sorbent dose 2.0 g dm^{-3}*

Such influence of temperature may be a result of expected increase in the diffusion of Cu (II) ions in the water environment [8].

Effect of biosorbent dose

The removal efficiency of Cu (II) ions by LC-Al_2O_3 biosorbent significantly depends on amount of the biosorbent due to active surface area of the biosorbent and of available binding sites for Cu (II) ions. The effect of sorbent dose on the removal efficiency of pollutants by LC-Al_2O_3 was investigated in the range from 0.5 to 8.0 g dm^{-3}, while other parameters were kept constant (initial pH 6.0, initial pollutant concentration 20.0 mg dm^{-3} and temperature 25.0 ± 0.2 °C). Results show that an increase in the biosorbent dose from 0.5 to 8.0 g dm^{-3} led to an increase in the removal efficiency of Cu (II) ions from 34.05 to 99.8% (Figure 3).

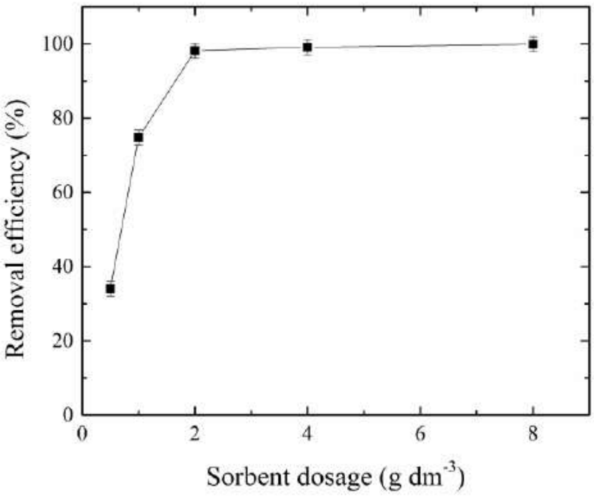

***Figure 3** Effect of biosorbent dose on the Cu (II) ions removal with LC-Al_2O_3. Initial pH 6.0, initial Cu (II) ions concentration 20.0 mg dm^{-3}, temperature 25.0 ± 0.2°C*

Removal efficiency of Cu (II) ions increased quickly from 34.05 to 98.21% with an increase in the sorbent dose from 0.5 to 2.0 g dm^{-3}, because of the increased active surface area of the biosorbent and the number of available binding sites for pollutants. Further increase in the sorbent dose to 4.0 g dm^{-3} slightly enhanced removal efficiency to 99.1%. The removal efficiency was without change at the sorbent doses of 6.0–8.0 g dm^{-3}. A negligible change in the removal efficiency at a biosorbent dosage higher than 2.0 g dm^{-3} may be attributed to the presence of the excess of active centres for pollutants binding on the biosorbent surface, with regard to the amount of Cu (II) ions initial concentration [9]. Therefore, a value of 2.0 g dm^{-3} was considered as the optimal biosorbent dose of LC-Al_2O_3 for removal of Cu (II) ions used in all other experiments.

Effect of initial Cu(II) ions concentration

Effects of initial Cu (II) ions concentration on the removal efficiency by LC-Al_2O_3 was investigated in the range from 5.0 to 100.0 mg dm^{-3}, while other parameters were kept constant (initial pH 6.0, sorbent dose 2.0 g dm^{-3} and temperature 25.0 ± 0.2 °C). Results show that an increase in initial Cu (II) ions concentration from 5.0 to 100.0 mg dm^{-3} led to an decreased in the removal efficiency of Cu (II) ions (Figure 4).

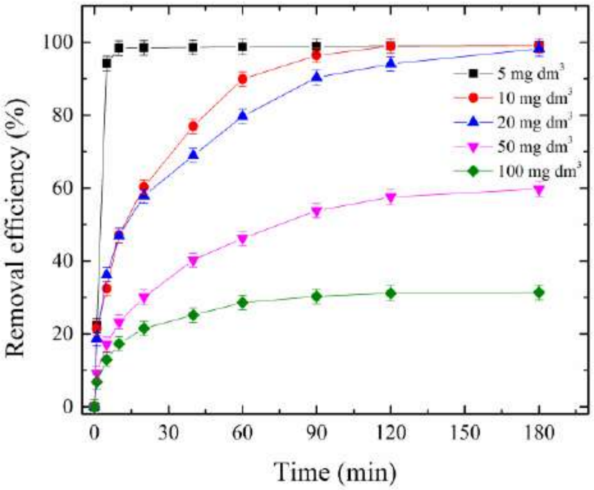

Figure 4 *Effect of initial Cu (II) ions concentration on the removal with LC-Al_2O_3. Initial pH 6.0, sorbent dose 2.0 g dm^{-3}, temperature 25.0 ± 0.2ºC*

With an increase in initial Cu (II) ions concentration, removal efficiency decreased. For initial concentrations of Cu (II) ions from 5.0 to 20.0 mg dm^{-3}, the removal efficiency was very high (99.11–98.21%). With further increase in concentrations to 50.0 mg dm^{-3}, the removal efficiency slowly decreased. With the increase in the initial Cu (II) ions concentration up to 100.0 mg dm^{-3}, removal efficiency decreased, reaching a value of 31.38%. In the case of a lower concentration range (5.0, 10.0 and 20.0 mg dm^{-3}), the ratio of initial number of sorbate molecules to the available sorption sites is low, and the biosorption becomes independent of initial concentration, which enabled the 99% ions uptake. At higher investigated concentrations (up to 100.0 mg dm^{-3}), a certain amount of molecules is left unsorbed in the solution due to a saturation of the limited available binding sites in the biomass [9,10].

CONCLUSION

A new material based on the chemical modification of lignocellulosic biomass with Al_2O_3 was synthesized in order to improve ability of starting biomass to remove heavy metal ions, such as Cu (II) ions. The initial pH strongly affects the sorption of Cu (II) ions onto LC-Al_2O_3. The optimal pH value for Cu (II) ions removal is 5 with very high removal efficiency (99.08%). It can be assumed that the main binding mechanism is ion exchange. The effect of temperature shows that the biosorption process for Cu (II) ions was endothermic in nature. The extent Cu (II) ions removal is directly related to the concentration of LC-Al_2O_3 in the suspension, with an optimal biosorbent dose of 2.0 g dm^{-3}. With the increase of initial metal ions concentration, the removal efficiency decrease. In addition to the high removal efficiency, LC-Al_2O_3 possesses other benefits, like mechanical stability, ease of synthesis, cost-effectiveness, biocompatibility and environmental-friendliness, which all makes it a promising material for the removal of heavy metal ions from water.

ACKNOWLEDGEMENT

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REACTIVE DYE CONTAMINATED WATER TREATED BY PHOTO DRIVEN ADVANCED OXIDATION PROCESSES

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Abstract

Reactive dyes are extensively used in the last years due to superior performance. This study examines, for the first time, heterogeneous advanced oxidation processes TiO_2/UV/$KBrO_3$, TiO_2/UV/$(NH_4)_2S_2O_8$ and TiO_2/UV/H_2O_2 for the purpose of decolorization of anthraquinone dye Reactive Blue 19 (RB 19). Decolorization is very fast for TiO_2/UV/H_2O_2 (87.79%), becomes even faster for TiO_2/UV/$KBrO_3$ (96.38%), after 10 min. On the other hand for TiO_2/UV/$(NH_4)_2S_2O_8$ process, complete dye decolorization was achieved in less than 10 min. In addition, experiments performed in three different matrixes were compared. In the surface water and dyebath effluent water, the removal efficiency of RB 19 was lower than that in the deionized water because of the interference of complex constituents in the surface water and effluent.

Keywords: AOPs, reactive blue 19, reactive dye, photocatalysis, electron acceptors

INTRODUCTION

Synthetic dyes are widely used in textile, cosmetics, printing, drug and food processing industries. Anthraquinone dyes represented the second most used class of commercial dyes after azo-compounds and are mainly used for dyeing wool, polyamide and leather. Dyes present in wastewater are of particular environmental concern since they not only give an undesirable color to the waters but also in some cases are themselves harmful compounds and can originate dangerous by-products through oxidation, hydrolysis, or other chemical reactions taking place in the waste phase [1]. A wide range of methods has been developed for the removal of synthetic dyes from natural and wastewaters to decrease their impact on the environment.

The main problem of heterogeneous photocatalysis is the undesired electron-hole pair recombination. This is the step in which the major energy-wasting occurs. This further leads to low quantum yield. These could be achieved by using electron acceptors or hole scavengers [2].

To the best of our knowledge, the study of photocatalytic decolorization of anthraquinone dye Reactive Blue 19 (RB 19) using heterogeneous advanced oxidation processes TiO_2/UV/$KBrO_3$, TiO_2/UV/H_2O_2 and TiO_2/UV/$(NH_4)_2S_2O_8$ has not been reported in the literature. The performance of these processes in terms of decolorization efficiency was compared. In addition, experiments performed in three different matrixes (lab deionized water, surface water collected from the Nišava River and dyebath effluent water from a local cotton dyeing) were compared.

MATERIALS AND METHODS

Reagents

The anthraquinone reactive dye C.I. Reactive Blue 19 (RB 19) (Mw = 626.55 g mol^{-1}) was obtained from Sigma-Aldrich (USA) and used without any purification. The hydrogen peroxide (H_2O_2) solution (30.0%), potassium bromate ($KBrO_3$) and ammonium persulfate ($(NH_4)_2S_2O_8$) were of analytical grade and purchased from Merck (Germany). TiO_2-P25 was received from Degussa (Frankfurt, Germany). TiO_2-P25 contains anatase 80.0 and rutile 20.0 with the mean particle size of 30.0 nm and BET surface area of 50.0 m^2 g^{-1}.

Photoreactor

Photochemical experiments were carried out in a batch photoreactor handmade in our laboratory. The UV lamps were turned on 10 min before performing each experiment. The intensity of UV radiation was measured by UV radiometer Solarmeter model 8.0 UVC (Solartech, USA). The total UV intensity was controlled by turning on different numbers of UV lamps and the maximum intensity was 1950 μW cm^{-2} (with all ten UV lamps on) at the distance of 220 mm, from working solution surface.

Procedures

A stock solution of RB 19 was made by dissolving 1.0 g dye in 1000.0 cm^3 of deionized water. Working solutions were prepared freshly, before irradiation, by diluting the stock to the desired concentration with deionized water. The pH of solutions was adjusted by addition of NaOH or HCl (0.1/0.01 mol dm^{-3}) with pH/ISE meter (Orion Star A214, Thermo scientific, USA). The suspensions of dye and TiO_2 were magnetically stirred in dark for 30 min to attain adsorption-desorption equilibrium between dye and TiO_2, and then the dye solutions are treated in the UV reactor.

During irradiation, the solution was magnetically stirred (Are, Velp Scientifica, Italy) in a constant rate and temperature was maintained at 25 ± 0.5ºC by thermostating. At required time intervals, 4.0 cm^3 of samples were withdrawn, centrifuged (3000 o min^{-1}, 15 min) and filtered through a 0.20 μm regenerated cellulose membrane filter (Agilent Technologies, Germany) to separate the catalyst. Absorbance at 592 nm was measured using a UV-vis spectrophotometer Shimadzu UV-1800 PC (Shimadzu, Japan) to determine the degree of decolorization of the solution. To ensure the accuracy, reliability, and reproducibility of the collected data, all experiments were carried out in triplicate, and mean values are recorded. OriginPro 2016 (OriginLab Corporation) software was used for statistical analysis and calculation of the data.

RESULTS AND DISCUSSION

The preliminary experiments were carried out in order to investigate the effect of UV radiation only, TiO_2 without UV radiation, electron acceptors ($KBrO_3$, H_2O_2 and $(NH_4)_2S_2O_8$) without UV radiation and UV irradiation in the presence of TiO_2 and electron acceptors. The solution of RB 19 dye (initial dye concentration was 50.0 mg dm^{-3}) was irradiated in the time period of 180 min to examine the effect of UV light radiation alone and there was no observable decrease of the residual dye concentration. It indicated that the direct photolysis of RB 19 dye by UV irradiation was slow. Experiments with only electron acceptors were done in the time period of 180 min in dark. The dye removal efficiency, in that case, was also negligible. No decolorization was observed for the dye solution with TiO_2 without UV radiation (Figure 1).

In order to optimize the process, a comparison was made between the three heterogeneous oxidation processes after 10 minutes of treatment under given conditions. The initial electron acceptors concentrations in these experiments were 30.0 mmol dm^{-3}, and the amount of TiO_2 was 1.0 g dm^{-3}. In the case of photocatalytic decolorization, $S_2O_8^{2-}$ is the most effective for the photodecolorization of RB 19 among the additives studied in this paper. The decolorization efficiency of RB 19 are in the following order $TiO_2/UV/(NH_4)_2S_2O_8$ (100%) > $TiO_2/UV/KBrO_3$ (96.38%) > $TiO_2/UV/H_2O_2$ (87.79%).

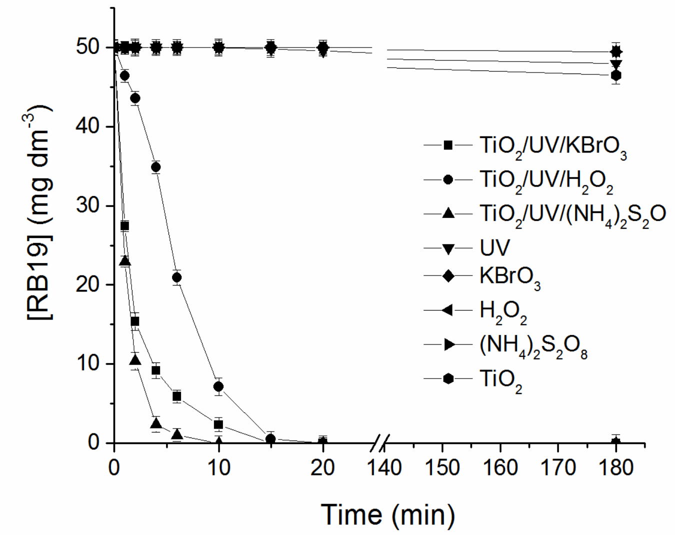

Figure 1 *Effect of UV light,* TiO_2*, electron acceptors,* $TiO_2/UV/KBrO_3$*,* $TiO_2/UV/H_2O_2$ *and* $TiO_2/UV/(NH_4)_2S_2O_8$ *processes on decolorization of RB 19.* $[RB19]_0 = 50.0$ *mg* dm^{-3}*,* $TiO_2 = 1.0$ *g* dm^{-3}*,* $[KBrO_3]_0 = 30.0$ *mmol* dm^{-3}*,* $[H_2O_2]_0 = 30.0$ *mmol* dm^{-3}*,* $[(NH_4)_2S_2O_8]_0 = 30.0$ *mmol* dm^{-3}*, initial pH was 7.0, UV radiation intensity was 1950* $\mu W\ cm^{-2}$*, temperature was 25 ± 0.5°C*

Electron acceptors such as hydrogen peroxide, potassium bromate and ammonium persulfate were added into the solution in order to enhance the decolorization [3–5]. All the additives showed a beneficial effect on the decolorization of the dye, whereas $S_2O_8^{2-}$ have been found to enhance the decolorization of pollutant remarkably. The efficiency of $TiO_2/UV/H_2O_2$ process is comparable to $TiO_2/UV/KBrO_3$ process. TiO_2-based photocatalysts also offer the advantages of high physical and chemical stability, low cost, easy availability, low toxicity, and excellent photoactivity [6].

In order to confirm the behavior of RB 19 decolorization by $TiO_2/UV/KBrO_3$, $TiO_2/UV/H_2O_2$ and $TiO_2/UV/(NH_4)_2S_2O_8$ processes in different practical water samples under best conditions, we chose three kinds of water samples as experimental matrixes: (1) Lab deionized water (DW) as the simulation wastewater treatment effluent, (2) surface water (SW) collected from the Nišava River (pH 7.2, Ca^+ = 79 mg dm^{-3}, Mg^+ = 21 mg dm^{-3}, Na^+ = 13.42 mg dm^{-3}, Cl^- = 69 mg dm^{-3}, SO_4^{2-} = 35 mg dm^{-3}, HCO_3^- = 240 mg dm^{-3}), and (3) dyebath effluent water (DEW) collected from a local cotton dyeing. Dyebath effluent contained 0.050 g dm^{-3} of dye RB 19. Assisting chemicals were also present in reactive dyebath effluent: 40 g dm^{-3} NaCl (electrolyte, aggregation of dye onto fabric), 13 g dm^{-3} Na_2CO_3 (pH buffer), 0.51 g dm^{-3} NaOH (produces covalent bonds between dyestuff and fabric), 0.79 g dm^{-3} acetic acid (neutralization), 0.50 g dm^{-3} alkylphenol polyglycol ether (detergent, washing out of unfixed dyestuff). For preparing a model effluent, dyebath effluent wastewater was diluted to get a new solution with 50.0 mg dm^{-3} of RB 19. RB 19 was spiked in surface water after the water samples filtration with the initial concentration 50 mg dm^{-3}. Figure 2 shows the removal efficiency of RB 19 obtained by $TiO_2/UV/KBrO_3$, $TiO_2/UV/H_2O_2$ and $TiO_2/UV/(NH_4)_2S_2O_8$ processes. Each process was carried out in all three matrixes: DW, SW and DEW.

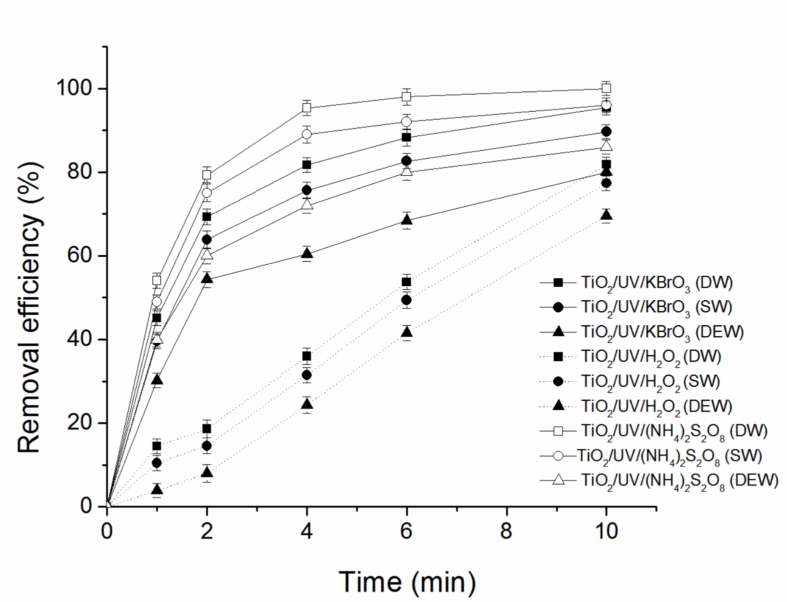

Figure 2 *The removal of RB 19 by different oxidation processes:* $TiO_2/UV/KBrO_3$ *(pH = 7.0,* $[RB19]_0$ *= 50.0 mg* dm^{-3}*,* TiO_2 *= 1.0 g* dm^{-3}*,* $[KBrO_3]_0$ *= 30.0 mmol* dm^{-3}*, UV intensity 1950 μW* cm^{-2}*),* $TiO_2/UV/H_2O_2$ *(pH= 7.0,* $[RB19]_0$ *= 50.0 mg* dm^{-3}*,* TiO_2 *= 1.0 g* dm^{-3}*,* $[H_2O_2]_0$ *= 30.0 mmol* dm^{-3}*, UV intensity 1950 μW* cm^{-2}*) and* $TiO_2/UV/(NH_4)_2S_2O_8$ *(pH= 7.0,* $[RB19]_0$ *= 50.0 mg* dm^{-3}*,* TiO_2 *= 1.0 g* dm^{-3}*,* $[(NH_4)_2S_2O_8]_0$ *=30.0 mmol* dm^{-3}*, UV intensity 1950 μW* cm^{-2}*)*

As shown in Figure 2, in the surface water and dyebath effluent the removal efficiency of RB 19 was lower than that in the deionized water because of the interference of complex constituents in the surface water and dyebath effluent.

CONCLUSION

The decolorization of the Reactive Blue 19 solutions examined strongly depends on the electron acceptors. From the economical point of view, the $TiO_2/UV/(NH_4)_2S_2O_8$ process emerges as the most attractive oxidation system for reactive dye effluents in terms of complete decolorization (100.00% in less than 10 min) very closely followed by the $TiO_2/UV/KBrO_3$ process (96.44% after 10 min) and $TiO_2/UV/H_2O_2$ process (87.79% after 10 min). All three oxidation processes were carried out in three matrixes (lab deionized water, surface water collected from the Nišava River and dyebath effluent water from a local cotton dyeing). In the surface water and dyebath effluent, the removal efficiency of Reactive Blue 19 was lower than that in the deionized water because of the interference of complex constituents in the surface water and dyebath effluent.

ACKNOWLEDGEMENT

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A NOVEL STAINLESS STEEL/Bi_2O_3 ELECTRODE FOR ELECTROCHEMICAL DEGRADATION OF TEXTILE DYE

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Abstract

Stainless steel/Bi_2O_3 electrode was synthesized by galvanostatic electrodeposition on stainless steel substrate and calcination at 500°C. Characterization by SEM, EDX, XRD and TGA revealed that the anode surface was fully covered with pure α-Bi_2O_3, which formed inhomogeneous coat. This electrode was used for electrochemical degradation of a textile dye Reactive Orange 4 (RO 4) in the presence of H_2O_2. The optimization of decolorization parameters (applied current density, H_2O_2 and Na_2SO_4 concentration) was done.

Keywords: stainless steel/Bi_2O_3, dye, degradation, parameters

INTRODUCTION

Wastewater originating from textile and other industries contain synthetic organic dyes, which presents a serious environmental problem, due to high resistance of those dyes towards standard physico-chemical removal procedures. Electrochemical degradation of textile dyes has many advantages, such as high efficiency, environmental compatibility, versatility and safety. Electrochemical oxidation of the dyes is usually accomplished by hydroxyl radical •OH, a strong oxidant, electrogenerated by water decomposition at the anode, which can lead to a complete mineralization of a dye. The anodic material is very important; certain materials based on metal oxide coats make very good anodes, due to their high surface area and excellent mechanical and chemical resistance even at high current densities [1,2]. Electrochemical stability and catalysis behaviour makes Bi_2O_3 an interesting material for the application in electrochemical oxidation of various organic pollutants [3,4]. In this work, stainless steel/Bi_2O_3 electrode was synthesized by galvanostatic electrodeposition on stainless steel substrate, followed by calcination, and used as anode for electrochemical degradation of the textile dye Reactive Orange 4.

MATERIALS AND METHODS

The electrode was prepared by electrodeposition from 0.3 mol dm^{-3} Bi (III) solution in 1 M HNO_3 at constant current density of 10 mA cm^{-2} during 120 minutes at 20 ± 0.5°C in the two electrode cell with a stainless steel sheet as a substrate (cathode) and a Pt sheet as auxillary electrode (anode). All electrochemical experiments were performed using Amel 510 DC potentiostat (Materials Mates, Italy) controlled by VoltaScope software package. After the deposition, the stainless steel sheet covered with deposited coat was washed with water, dried at 50°C for 12 h, calcined at 500°C for 90 minutes in a furnace in the air and used as anode for electrochemical degradation of RO 4. It was examined by SEM, EDX (Hitachi SU8030), XRD (Siemens D500) and TGA (Q5000, TA Instruments, USA). Dye degradation was done under galvanostatic conditions in one compartment two-electrode cell, with synthesized anode and Pt sheet as the cathode. The working dye solutions were prepared by diluting the stock solutions, which were prepared by dissolving the required amount of powdered dye in deionized water. The required amount of H_2O_2 and Na_2SO_4 were added to the working dye solutions. Dye concentrations were determined spectrophotometrically (UV-1650 PC, Shimadzu, Japan) at 497 nm.

RESULTS AND DISCUSSION

Characterization of the electrode

XRD pattern of the synthesized electrode shows a series of sharp, narrow diffraction peaks with characteristic 2θ values at: 27.4°, 33.3° and 46.3°, corresponding to (120), (200) and (041) reflection, respectively, of a highly crystalline monoclinic α-Bi_2O_3 at the stainless steel surface (Figure 1). No trace of any other Bi_2O_3 phase was detected.

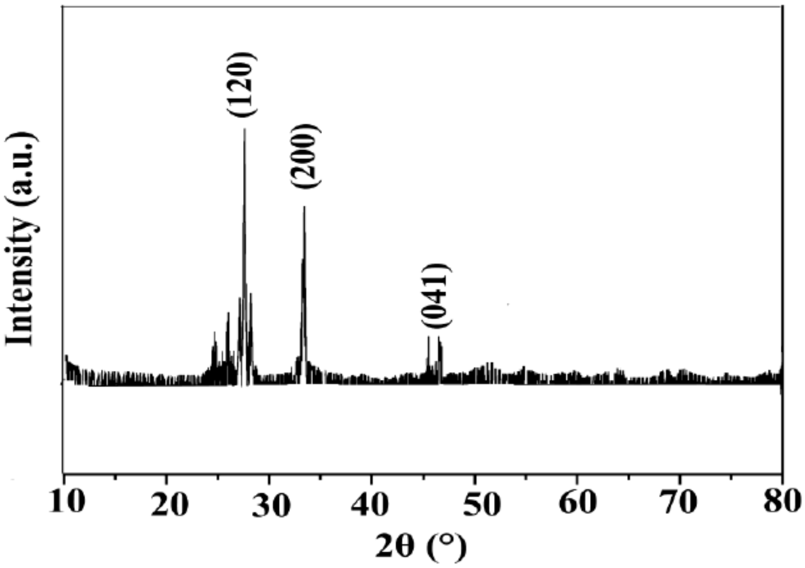

Figure 1 *XRD pattern of the obtained electrode*

Electrode surface is mostly composed of oval and worm-like particles, with some of them closely packed, most of them seemingly sintered, forming the larger aggregates (Figure 2). The particles of undefined shapes and different sizes are also spotted in places, as well as the large pores and holes with different shapes and sizes between particles and particle aggregates. Though the surface does not seem very compact, it is mechanically stable.

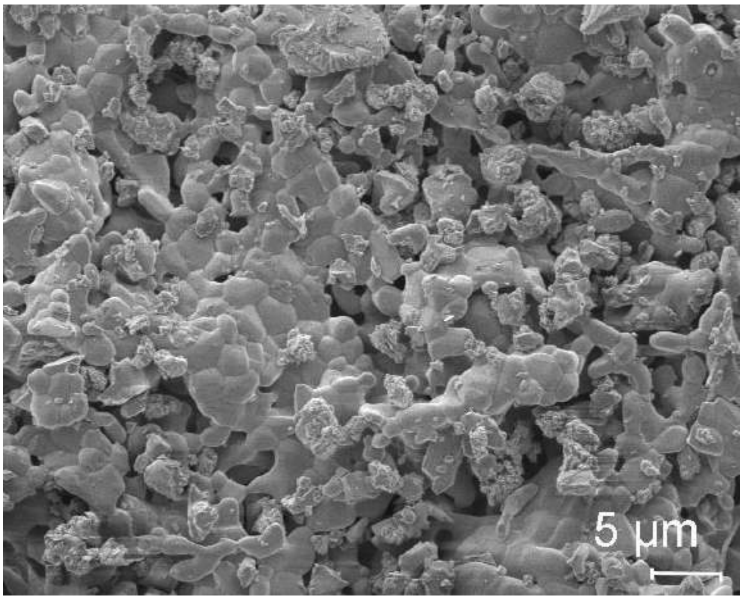

Figure 2 *Surface morphology of the synthesized stainless steel/Bi_2O_3 electrode*

EDX shows that weight ratios of Bi and O on the surface are 88.05% and 11.95%, respectively, close to their theoretical weight ratios in Bi_2O_3 of 89.70% and 10.30%, respectively, meaning that the coat posses little higher O-content. It might be adsorbed oxygen or moisture as well.

The obtained Bi_2O_3 coat was peeled of the surface and heated from room temperature to 600 °C at a heating rate of 10°C /minute (Figure 3). No significant change of its weight was observed within the given temperature interval, indicating its chemical stability under these conditions. Total weight loss was 1.97% and it might be attributed to a slight loss of oxygen.

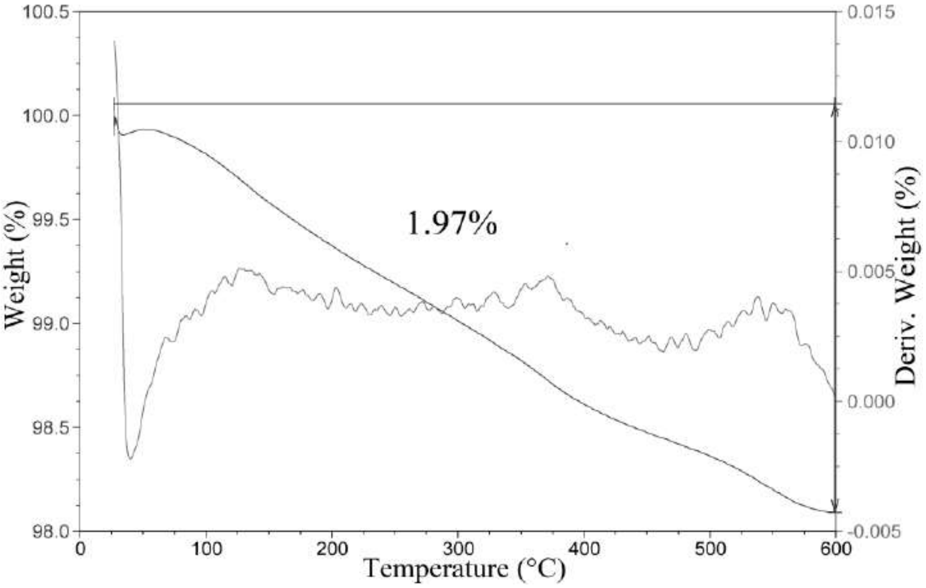

Figure 3 *TG data for deposited Bi_2O_3*

Dye degradation

RO 4 does not react with H_2O_2. Its sorption on stainless steel/Bi_2O_3 anode is negligible. Its electrochemical degradation without H_2O_2 is slow. In the presence of H_2O_2, fast electrochemical decolorization under the applied electric current at the stainless steel/Bi_2O_3 anode is observed.

The applied current density (*j*) affects the dye degradation rate (Figure 4). Total decolorization was achieved at all of the applied current densities, but decolorization time decreases with the increase of *j*. That decease is more notable for the lower *j* values; the increase of *j* from 40 mA cm^{-2} to 50 mA cm^{-2} dos not bring any significant decrease in decolorization time, meaning that the process has reached its limit current density, so it was assumed that the optimal current density for the process was 40 mA cm^{-2}.

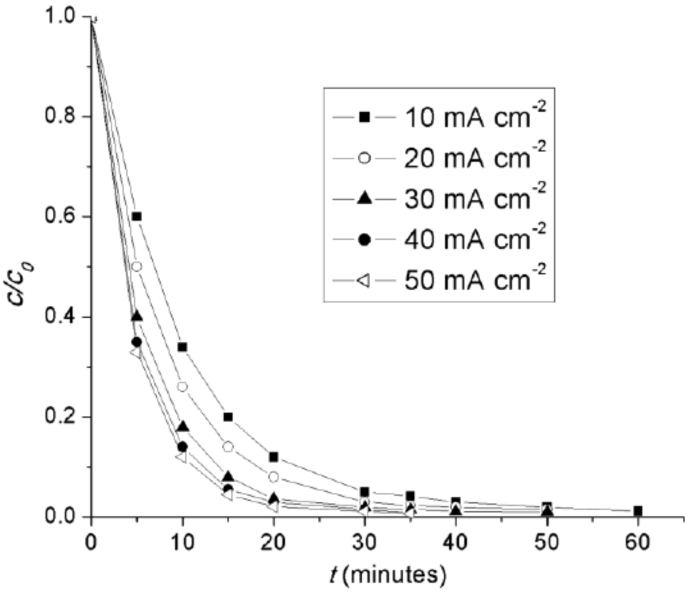

Figure 4 *Effect of current density on the decolorization time of RO 4 at stainless steel/Bi_2O_3 anode (c_{0dye} = 0.08 mmol dm^{-3}, c_0 (H_2O_2) = 10 mmol dm^{-3}, c_0 (Na_2SO_4) = 10 mmol dm^{-3})*

Initial H_2O_2 concentration has a significant effect on the decolorization time (Figure 5), since it is a source of •OH radical, which is generated by decomposition of H_2O_2 at the anode at high potential. And which oxidizes the dye. Decolorization time decreases as the H_2O_2 concentration increases up to 10 mmol dm^{-3}, as expected. However, an increase of the H_2O_2 concentration up to 20 mmol dm^{-3} causes a slight increase of the decolorization time. The reason is probably the loss of some •OH radicals due to the scavenging effect, which occurs at relatively high H_2O_2 concentration; when electrogenerated •OH radicals start to react with the excess H_2O_2 and produce hydroperoxyl radicals, HO_2•, which are much les reactive than •OH radicals [5]. Thus, the process is the most efficient with 10 mmol dm^{-3} H_2O_2, which is assumed to be the optimal H_2O_2 concentration.

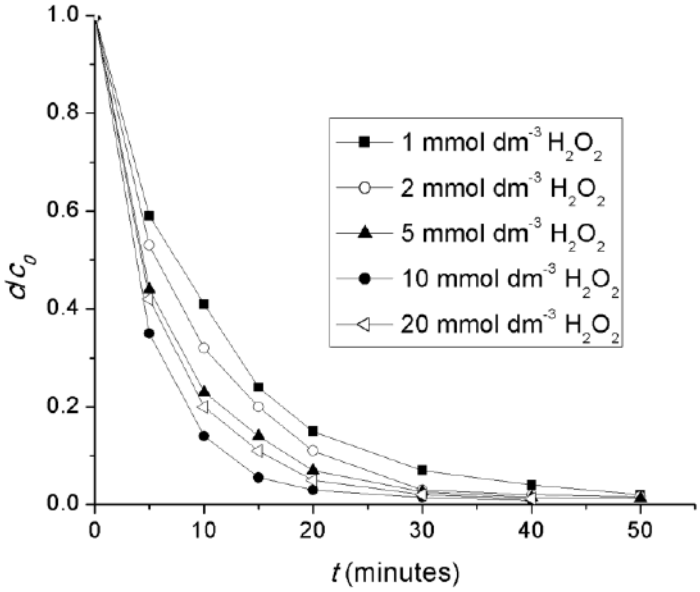

Figure 5 *Effect of H_2O_2 initial concentration on the decolorization time of RO 4 at stainless steel/Bi_2O_3 anode (c_{0dye} = 0.08 mmol dm^{-3}, j =40 mA cm^{-2}, c_0 (Na_2SO_4) = 10 mmol dm^{-3})*

Na_2SO_4, which is added to the dye solutions in order to increase electrical conductivity, also affects the decolorization time as well (Figure 6). As the Na_2SO_4 concentration increases from 1 to 10 mmol dm^{-3}, the dye decolorization time decreases, but when its concentration increased from 10 to 20 mmol dm^{-3}, decolorization time increased compared to that in the presence of 10 mmol dm^{-3} Na_2SO_4, i.e., decolorization efficacy decreases. This decrease occurred because SO_4^{2-} anions are also able to react with the electrogenerated •OH radicals, and competition between the dye and the SO_4^{2-} anions with the respect to •OH radicals may occur as well [5]. Thus, the optimal Na_2SO_4 concentration in the investigated system is assumed to be 10 mmol dm^{-3}.

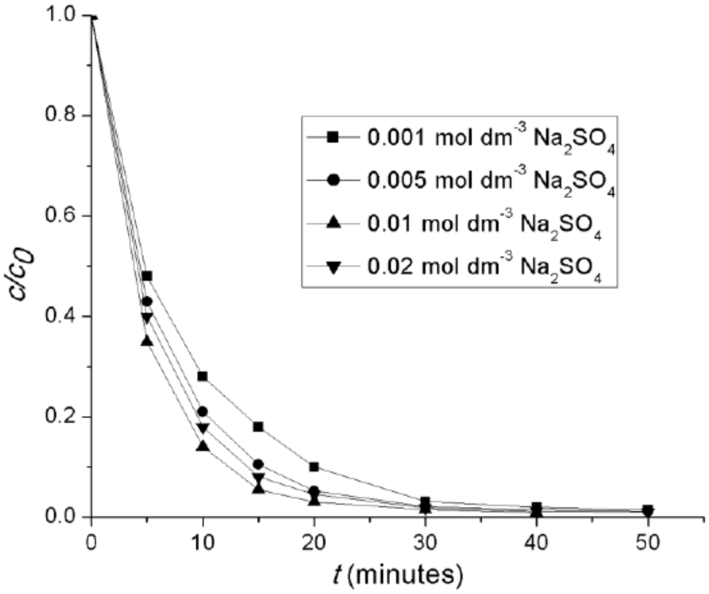

Figure 6 *Effect of Na_2SO_4 initial concentration on the decolorization time of RO 4 at stainless steel/Bi_2O_3 anode (c_{0dye} = 0.08 mmol dm^{-3}, j =40 mA cm^{-2}, c_0 (H_2O_2) = 10 mmol dm^{-3})*

CONCLUSION

Stainless steel/Bi_2O_3 electrode was synthesized by galvanostatic electrodeposition on stainless steel from Bi (III) acidic solution, fallowed by calcination at 500°C. The anode surface was covered with inhomogeneous, mechanically stable coat of pure α-Bi_2O_3. The obtained Bi_2O_3 was chemically stable to the heating up to 500°C. The synthesized electrode was used as the anode for electrochemical oxidative degradation of textile dye RO 4. Decolorization time decreases as the current density and concentration of H_2O_2 and Na_2SO_4 increase, but only up to certain value of each of these parameters; decolorization time is the lowest for the current density of 40 mA cm^{-2} and H_2O_2 and Na_2SO_4 concentrations of 10 mmol dm^{-3}. These values are taken as the optimal ones, with which the complete decolorization proceeds in about 35 minutes. Increase of current density above 40 mA cm^{-2} does not significantly affect the decolorization time, and increase of H_2O_2 and Na_2SO_4 concentrations above 10 mmol dm^{-3} causes the increase of decolorization time.

ACKNOWLEDGEMENT

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ISOTHERMAL TITRATION CALORIMETRY STUDY OF As(III) BINDING TO HUMIC ACIDS

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Abstract

Part of Cu post flotation tailings of Copper Mine Bor were reclaimed by reconstructing the topsoil with arable soils and revegetation in 1991. Humic acids were isolated from these Technosols and binding of arsenic present at high concentration, to selected humic acid was studied by Isothermal Titration Calorimetry (ITC). Same binding experiment was performed with the standard IHSS soil humic acid and results obtained were compared. From the results presented in this study it can be concluded that ITC technique can be successfully used to get quantitative insight into interaction energies between metal ions and soil humic acids. Humic acids investigated are of different type and origin having various characteristics, influencing so differences in As(III) binding. Row ITC data obtained can be used to determine thermodynamic parameters associated to the As(III)-humic acid complexation process applying relevant theoretical models. Theoretical treatment applied could even distinguish various humic acid reactive groups. Additionally, to explain results obtained using chosen theoretical MNIS model and calculate thermodynamic parameters pointing to nature of binding process, additional pH-metric (potentiometric) titration must be performed. As at the location studied arsenic as very toxic metal is present at extremely high concentrations influencing environment contamination, this study is of great environmental significance.

Keywords: Cu Post Flotation Tailings; Technosol Humic Acids; As(III) Binding; Isothermal Titration Microcalorimertry

INTRODUCTION

One of the largest mines in Serbia is the Copper Mining and Smelting Combine Bor. Besides other mine wastes, post-flotation tailings (PFT) dumps as a result of copper ore processing were formed. The PFT dump "Polje 2" was definitively abandoned in 1987. In addition to degradation of large land areas, these mine wastes are sources of pollution to the surrounding environment. In order to restore the function of a portion of PFT dumps, reclamation measures were implemented. In 1991, an area of about 16 ha was reclaimed by reconstructing the topsoil with natural arable soil, an average depth of 40 cm. The soil was taken from the southern part of the town of Bor where the residential area expanded. One part of the reclaimed area was planted with grass and the other with trees. Previous investigations of reclaimed PFT 20 years after remediation [1] have shown that A horizon (about 45 cm deep) was formed on the soil surface by reclamation process, mixing of natural arable soils with tailings. Most of these soils are characterized by degraded structure, low humus content, predominantly low pH, high As and Cu concentrations, and low soil microbial activity. According to WRB 2007 [2], these soils are classified as RSG Technosols.

Humic substances (HSs) are the most important organic components present in water, soil, and sediments and have significant environmental functions. They are recognized for their role in controlling both the fate of environmental pollutants and the biogeochemistry of organic C in the global ecosystem [3]. Humic substances affect the soil and water properties through their participation in dynamic processes where their constituent molecules interact with other molecules or ions (complexation/decomplexation), solid surfaces (adsorption/desorption), and among themselves (aggregation/deaggregation) [4]. Their roles in removal of heavy metals from soil and water, inhibition of free radicals formation by metal catalysis, reduction, and stabilization of metal nanoparticles are among the most important [5].

To get quantitative insight into interaction energies between As(III) ion and humic acids and to determine thermodynamic parameters associated to the metal-humic acid complexation process, Isothermal Titration Calorimetry technique was used [6,7].

MATERIALS AND METHODS

Humic acid samples

Two various humic acids were investigated in this study. The first (T1HA) was isolated from soil sample taken at a 0-25 cm depth [8,9] from the A horizon of Technosols (T) on reclaimed Cu PFT "Polje 2", Bor - Serbia. Selected T1 soil sample was classified as a silt loam. T1HA was isolated from soil using a modified IHSS method (HA gel was dried at 35°C, powdered, and sieved using a 0.05-mm sieve) [10]. Results obtained for Technosol humic acid (T1 HA) were compared to well characterized standard IHSS humic acid isolated from Elliott Soil (ESHA), which is silt loam, silty clay loam or loam, moderately acid to neutral [11].

Stock humic acid suspensions of T1HA and ESHA (2 g/l) were prepared in 0.01 M KOH and stored at 4^{o}C. Working HA suspensions (0.8 g/l) were prepared before each titration by mixing stock suspensions and 0.1 M KNO_3 solution (1:1.5). Initial pH of working HA suspensions was adjusted to 5.

Preparation of As(III) solutions

As(III) solutions were prepared using sodiumhydroxoarsenate (III) ($NaAsO_2$) (Merck) in 0.1 M KNO_3. Two concentrations were used in titration experiments: 5 and 10 mmol As/l.

Isothermal Titration Calorimetry

Termal events were monitored by the Thermal Activity Monitor (227, LKB Bromma, Sweden) using a perfussion cell (227-401/402, Sweden) as measuring device. Titrations were performed using Radiometer Automatic Titrator (ABU 80, Denmark). Prior to titration experiments, measuring cell of the perfussion system was filled with 2.5 ml of HA suspension, thermally equilibrated in four steps and calibrated (10 µW range) using both static and dynamic calibration procedure. Working temperature was 298.15K. Titration experiments started after the stable base line was obtained.

Titrant (As(III) solution) was added in 30 µl portions at every 20 minutes for experiments investigating binding at various pH values, and at every 30 minutes in experiments comparing As(III)-HA binding for two humic acids studied. Titration speed was 50 µl/min in both cases. For each titration, the output signal, power (µW) versus time (min), was recorded by the TAM assistant software and thermograms were obtained. Software used for titration control and data acquisition, as well as software for termogram peak area determination, was developed in the laboratory.

RESULTS AND DISCUSSION

ITC thermograms representing heat changes upon As(III) complexation with ESHA and T1HA at different pH values are presented in Figures 1 to 6.

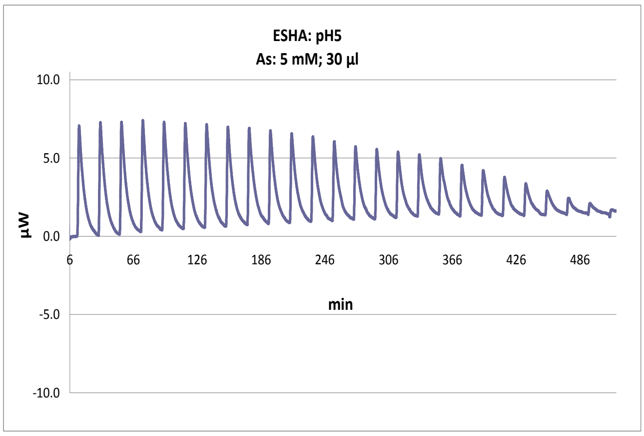

Figure 1 *Reaction heat change of binding ESHA and As(III) at pH5*

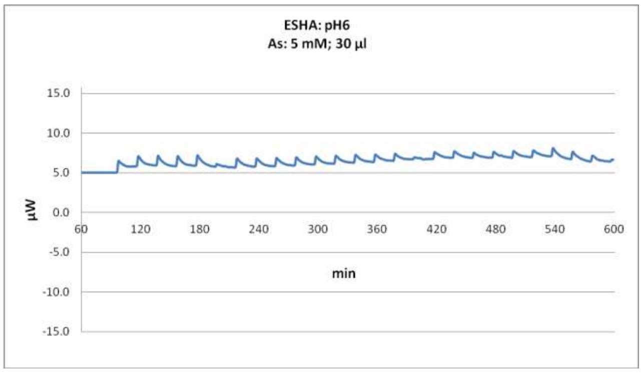

Figure 2 *Reaction heat change of binding ESHA and As(III) at pH6*

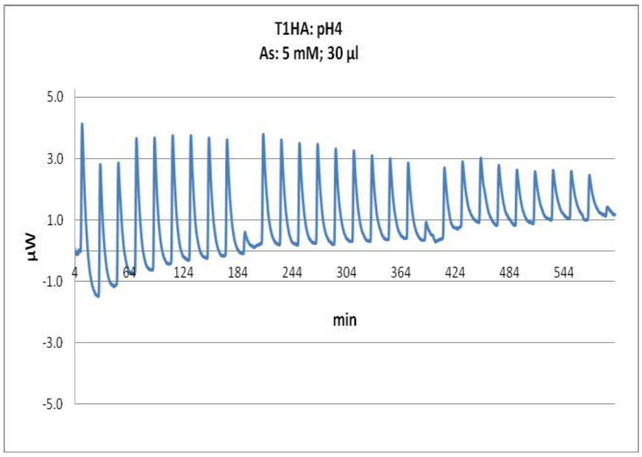

Figure 3 *Reaction heat change of binding T1HA and As(III) at pH4*

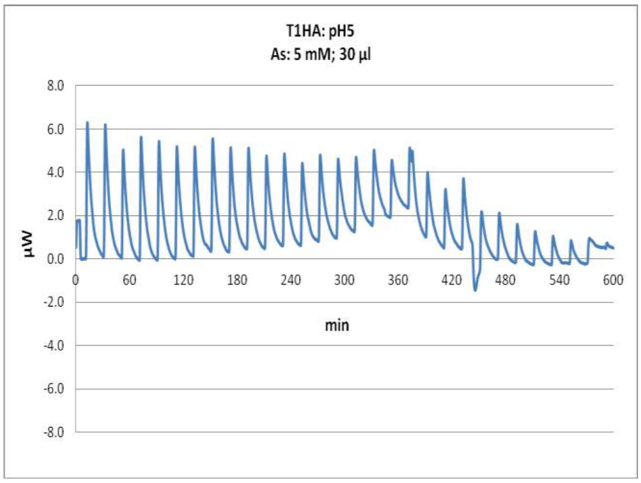

Figure 4 *Reaction heat change of binding T1HA and As(III) at pH5*

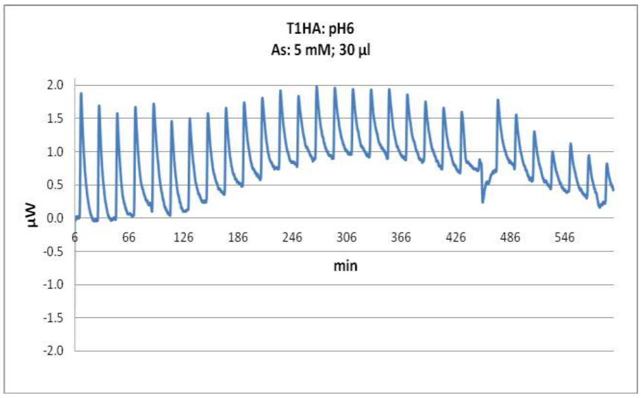

Figure 5 *Reaction heat change of binding T1HA and As(III) at pH6*

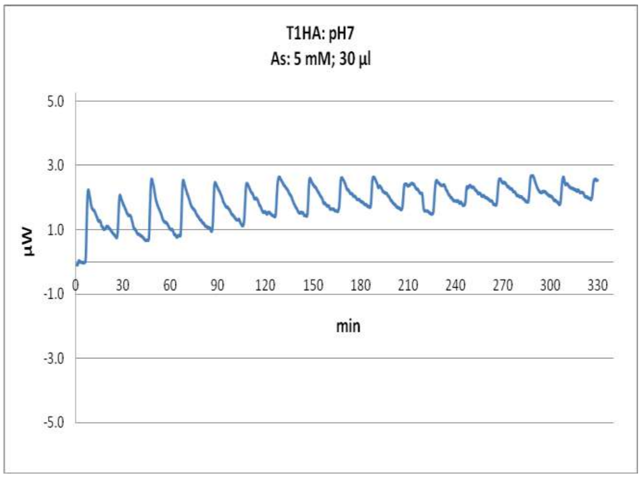

Figure 6 *Reaction heat change of binding T1HA and As(III) at pH7*

From results presented in Figures 1-6 revealing positive sign of heat effects, it is obvious that binding of As(III) to both humic acids studied is exothermic process. Each thermogram peak represents one titrant injection. Peak areas represent heat evolved for the given titrant injection. Based on the peak area calculated for each single injection, cumulative heat reaction and As(III) concentration for every injection was calculated and their dependence is presented in Figure 7.

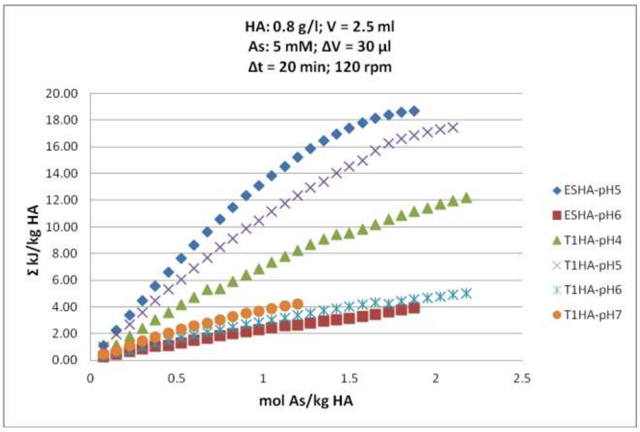

Figure 7 *Cumulative reaction heat versus As(III) concentration for T1HA and ESHA at various pH values*

It is obvious from Figure 7 that heat changes are highest at pH5, but more pronounced for ESHA. At pH higher than 5 are much lower for both humic acids studied and do not differ significantly. Additionally, it can be seen that heat change values for T1HA are significantly lower at pH4 than at pH5. At higher As(III) concentration (10 mM) (Fig.ure 8) difference in heat effects changes are more pronounced in comparison to lower concentration (Figure 7). As for lower As(III) concentration, heat effects are more pronounced for ESHA at higher concentration.

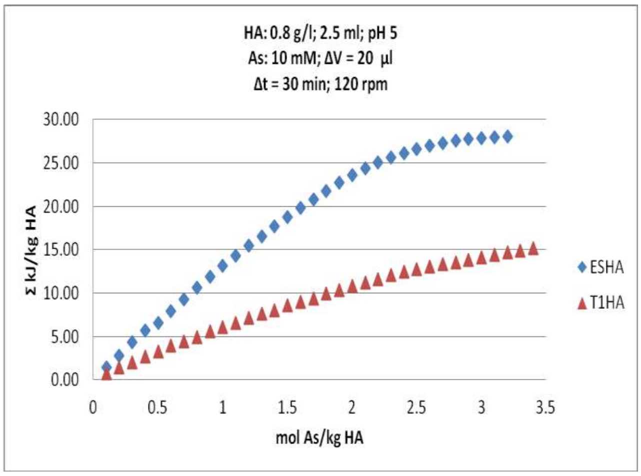

Figure 8 *Cumulative reaction heat versus As(III) concentration for T1HA and ESHA at pH5*

CONCLUSION

From the results presented it can be concluded that ITC technique can be successfully used to get quantitative insight into interaction energies between metal ions and soil humic acids. Nevertheless, it is evident that optimisation of ITC measuring parameters is necessary to improve measurement uncertainty. Humic acids investigated are of different type and origin having various characteristics, influencing so differences in As(III) binding. Row ITC data obtained can be used to determine thermodynamic parameters associated to the metal-humic acid complexation process applying relevant theoretical models. Theoretical treatment applied could even distinguish various humic acid reactive groups. Additionally, to explain results obtained using chosen theoretical MNIS model and calculate thermodynamic parameters pointing to nature of binding process, additional pH-metric (potentiometric) titration must be performed.

As at the location studied arsenic as very toxic metal is present at extremely high concentrations influencing environment contamination, future investigations will be focused to investigation of As binding to humic acids.

ACKNOWLEDGEMENT

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DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) CONTENT IN FOOD AND HEY IN PLJEVLJA MUNICIPALITY, MONTENEGRO

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Abstract

This paper aimed to investigate the content of polycyclic aromatic hydrocarbons (PAHs) in three types of food (cheese, apples, potatoes) in municipality Pljevlja, north part of Montenegro. We also examined the content of these substances in hay, as a representative of livestock feed. All four types of samples were taken from locations: Thermal power plant (TE Pljevlja) and Zinc and lead mine (Šuplja stijena, Montenegro). The analysis examined the presence and concentration of fourteen polycyclic aromatic hydrocarbons. The obtained results showed the following: almost all samples contained naphthalene and acenaphtene (most were found in samples near the Thermal power plant), and the highest concentration of benzo[a]pyrene was found in the potato sample also at the site around the Thermal power plant.

Keywords: PAHs, food, contamination, thermal plant, mine

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are highly teratogenic, persistent carcinogens and they are widespread in the environment. They can occur either during biological processes or through human activities. Natural sources of PAHs are forest or brush fires, volcanic activity, hydrothermal processes and anthropogenic sources are car emissions or cigarette smoke, thermal processing of food (roasting, frying, grilling), drying or smoking food. They are strongly adsorbed to the organic fraction of soils and therefore they do not usually penetrate deeper in soil layers. Once they reach the soil, the PAHs there remain because they are, as very non-polar, insoluble in water, and thus cannot be further mobilized through the soil. After deposition in the soil, they can further accumulate in plants, and through the food chain they can reach the human body. Determination of PAHs content in food is very important especially in terms of food safety and health reasons. Food can be contaminated by PAHs from environmental sources and from the way of preparing food in the household. In 2007, the European Food Safety Authority (EFSA) proposes benzo[a]pyrene as a good indicator of food pollution of PAHs [1]. The European Commission set maximum levels for benzo[a]pyrene and PAHs in 2011. According to this legislation, maximum level of benzo[a]pyrene in food is 6.0 μg/kg, and sum of PAHs is 35.0 μg/kg [2]. Based on the results of analyses of over 10,000 samples, EFSA reported this kind of exposure distribution to these substances by foods [3]. Thus, dietary exposure to PAHs from vegetables and nuts is 14%, fruits 5 % and cheese 1 %. The maximum exposure is from seafood products (19%) and meat products (12%).

In this paper we have examined the presence and concentration of fourteen polycyclic aromatic hydrocarbons which are shown in table 1. According to International Agency for Research on Cancer (IARC), all substances are classified in four groups: 1 – carcinogenic to humans; 2A-probably carcinogenic to humans; 2B – possibly carcinogenic to humans, 3 – not carcinogenic to humans [4].

Table 1 *PAHs, their structures, psysical constants and carcinogenicity*

Name	Abbreviation	M (g/mol)	Carcinogenicity group (IARC)
Naphtalene[1]	NPH	128	2B
Acenaphtalene	ACY	152	N.A.
Fluorene	FLR	166	3
Phenanthrene	PHE	178	3
Anthracene	ANT	178	3
Fluoranhtene	FA	202	3
Pyrene	PYR	202	3
Benzo[*a*]anthracene	BaA	228	2B
Chrysene	CHR	228	2B
Benzo[*b*]fluoranthene	BbFA	252	2B
Benzo[*k*]fluoranthene	BkFA	252	2B
Benzo[*a*]pyrene	BaP	252	1
Dibenzo[*ah*]anthracene	DBahA	278	2A
Benzo[*ghi*]perylene	BghiP	276	3

N.A. – not available

MATERIALS AND METHODS

Materials and Sampling

Samples were taken from agricultural households near Pljevlja in period September-November 2019. The households are located near two sources of pollution, Thermal power plant (TE Pljevlja) and Zinc and lead mine (Šuplja stijena, Montenegro). Samples 1, 2, 3, 4, 6, 7 and 11 are located near Thermal power plant. Sample 5 is located between Thermal power

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[1] According to a number of authors, naphthalene is not considered a typical PAH but is rather labelled as “specific PAH“. However, since it is a significant environmental pollutant and belongs to the group of potentially carcinogenic agents, and it can cause the breakdown of red blood cells, naphtalene is included in the group of the most commonly analyzed PAHs.

plant and surface Coal mine. Samples 8, 9 and 10 were collected from households near Zinc and lead mine. Apples and potatoes were sampled directly from the indicated locations. The hay was taken from the agricultural households where it was located, but it was mowed and dried to the specified sites. The cheese was obtained from cows that consumed hay, which was mowed at the indicated sites and as such was sampled.

For PAHs analysis samples were homogenized in blender, weighed (2g for cheese and hay; 10g for apples and potato) and prepared by QuEChERS method [5]. In first part of preparation 10 ml of distilled water was added for cheese and hay samples, homogenized by vortex (this step is not necessary for apple and potato samples). For sample extraction QuEChERS 1 was used (4 g anhydrous magnesium sulphate; 1 g of sodium chloride; 1 g trisodium citrate dihydrate; 0.5 g disodium hydrogen citrate sesquihydrate). For clean up step QuEChERS 2 was used (900 mg anhydrous magnesium sulphate; 150 mg PSA; 15mg GCB). After preparation samples were analysed by High-Performance Liquid Chromatography (HPLC) with fluorescence detector.

RESULTS AND DISCUSSION

Total contents for the PAHs measured in this study are listed below. Figure 1 and 2 show a diagram of PAHs ratio concentrations in potato and apple samples, respectively: FLR, ANT, FA, PYR, BaA, CHR, BkFA, DBahA and BghiP were below the detection limits of the instrument for potato samples.

As observed from the measurement results presented in the Figure 1, acenaphtalene (ACY) was present in potato samples from all 11 locations. The highest concentration of this PAH is at location 5, between the Thermal power plant and Coal mine, as well as at location 11, in the vicinity of the Pljevlja Thermal power plant. No carcinogenicity group was assigned to this hydrocarbon. Slightly elevated naphthalene concentrations were found at locations 4 and 8. It is similar with concentration of benzo[b]fluoranthene (BbFA) at location 6. However, we found a worryingly high concentration of benzo[a]pyrene in the potato sample at site 6 (Thermal power plant surrounding). Based the EU Regulations, the maximum allowable concentration of this PAH is 6 µg/kg. Also note that this compound belongs to class 1 carcinogenic agents (table 1) [4] and considered as environmental indicator for PAHs contamination.

According to EU regulation No 835/2011 [2], maximum levels of PAHs in food was calculated from the sum of the concentrations of PAHs. The range of these concentrations, depending on the type of food, is 10.0 - 35.0 µg/kg. An increased concentration of the sum of the PAHs was found in the potato sample at location number 6 and it was 8.39 µg/kg, but it is still significantly lower than the upper limit. The lowest concentration of total PAHs was found in the sample from the site 1. PHE, ANT, PYR, BbFA, BkFA and DBahA were below the detection limits of the instrument.

Higher concentrations of naphthalene (NPH) were found in the examined apple samples in the vicinity of the Thermal power plant compared to the potato samples taken from the same locations, Figure 2. However, except for the sample from sites 1 and 2, these concentrations are relatively low. Acenaphtalene (ACY) was found in samples from almost all sites, but its concentration is highest at site 3. Benzo[a]anthracene (BaA) was found in moderate concentrations at all locations around the Zinc and lead mines, as well as at most locations around the Thermal power plant while concentrations of benzo[a]pyrene are quite low in most locations. The highest concentration of total PAHs was found in the sample from the locality 1 and it was 7.35 µg/kg, and the lowest in the sample from the site 11 (both sites are in the vicinity of the Thermal power plant).

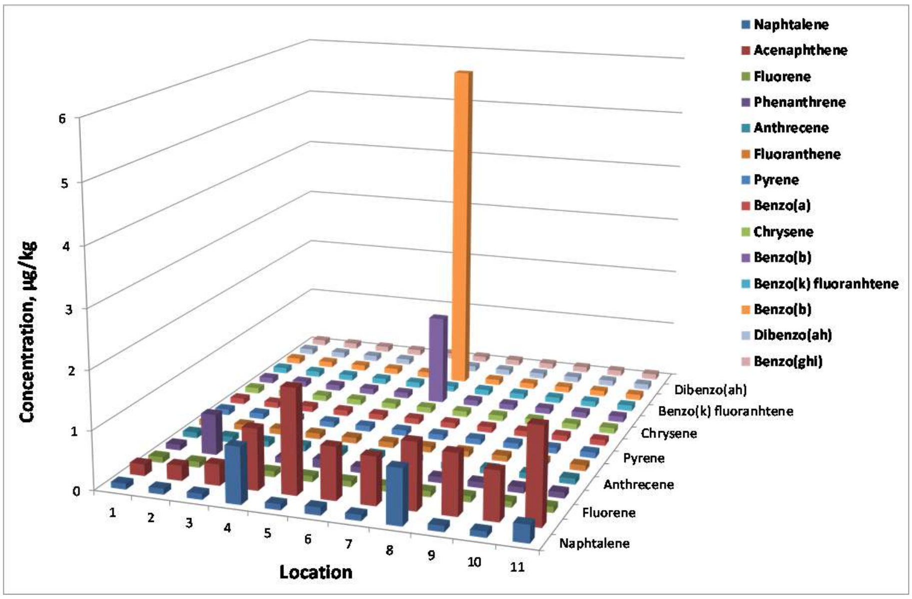

Figure 1 *Comparison of PAHs concentrations in potato samples from different sites*

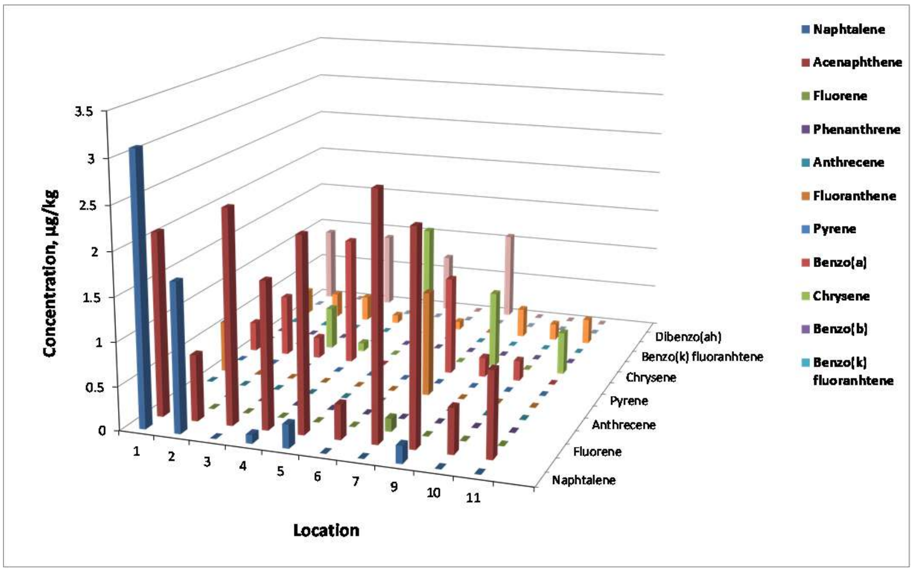

Figure 2 *Comparison of PAHs concentrations in apple samples from different sites*

In Figure 3 and 4 are shown PAHs concentrations in cheese and hay samples on different locations, respectively. According to EU regulation No 835/2011 [4], the maximum allowed concentration of PAHs in milk and milk products is 1.0 µg/kg. The highest concentration of naphthalene (NPH) was measured in the cheese sample number 4, while acenaphtalene (ACY) was present in increased (and unallowed) concentrations in almost all remaining samples tested. The concentration of total found PAHs is highest in the cheese sample from location number 4 (2.45 µg/kg) while in other samples it is lower, but still higher than maximum allowed concentrations from the point of view of food safety. Based on these analyses and according to this regulation we conclude that only cheese from location 3 is safe for human consumption. All remaining analysed PAHs were below the limit of detection.

In order to examine the impact of cows' food consumption on transporting PAHs into the products derived from these cows, we examined PAH contents in the hay, at the locations where the cows were fed and collected the same hay. The relationships between the concentrations of the measured substances are presented graphically in Figure 4.

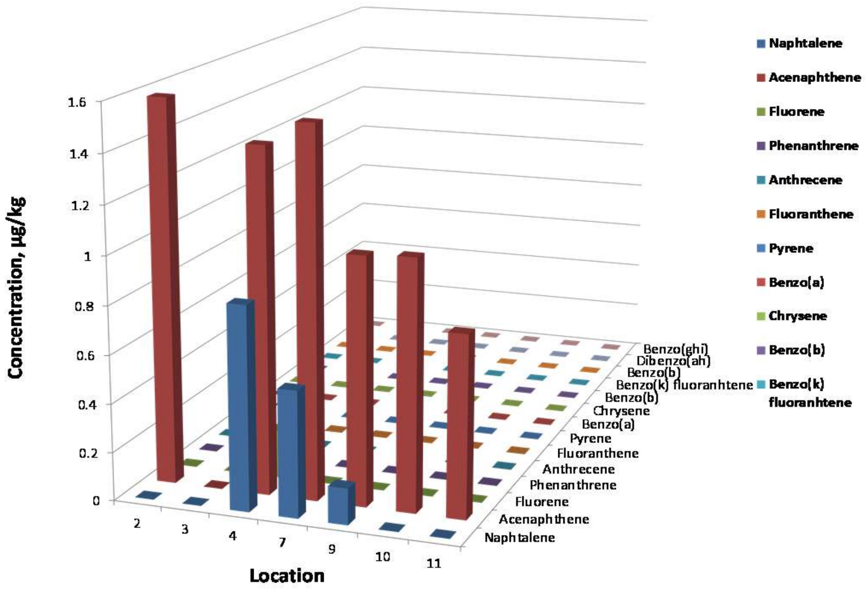

Figure 3 *Comparison of PAH concentrations in cheese samples from different sites*

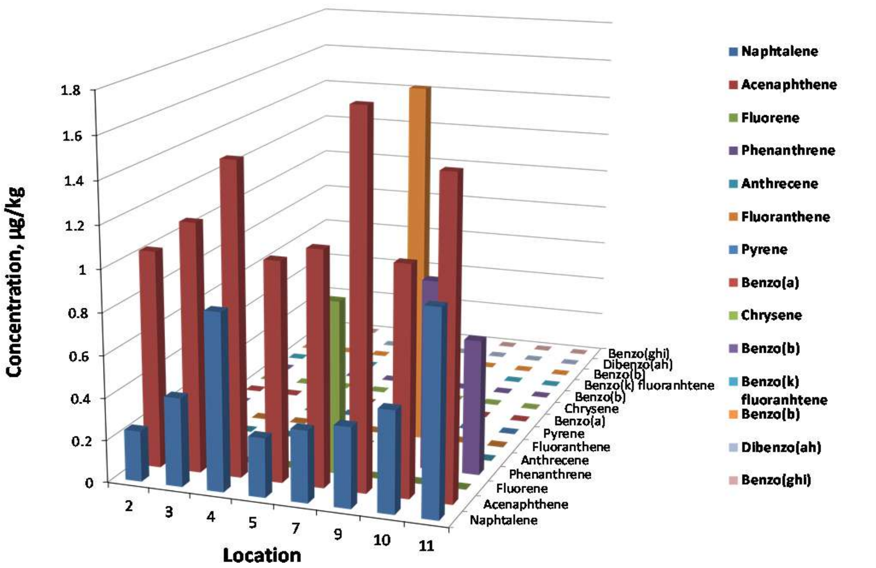

Figure 4 *Comparison of PAH concentrations in hay samples from different sites*

ANT, PYR, BaA, BbFA, BkFA, BaP, DBahA and BghiP were below the limit of detection. Here again, the concentration of naphthalene is highest in the sample from locality number 4 but also from locality number 11. Acenaphtalene (ACY) was found in all samples at relatively high concentrations, given that it is food for livestock. Fluoranhtene (FA) was found in enlarged concentration in sample number 9. The concentration of total found PAHs is highest in the hay sample from location number 9 and the lowest in sample number 2.

CONCLUSION

The results of our investigation have shown that the pollutants are transported by air to plants for human consumption. In most cases, according to the analysis of total PAHs in the tested food, we can conclude that a greater amount of these compounds are emitted from the Thermal power plant than from the Zinc and lead mines.

We could not find a direct dependence of the concentration of PAHs in cheese relative to their concentration in the hay sample consumed by the cows. Analysing the content of PAH in the cheese, we have shown that these pollutants can be incorporated into the food chain in a non-metabolized form. Based on the content of individual or even total PAHs in the samples obtained from the indicated locations, we can estimate the degree of pollution of both the food itself and the environment.

ACKNOWLEDGEMENT

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CORROSION BEHAVIOUR OF ZA27 AND ZA27/EGGSHELL COMPOSITE IN SCOTCH BONNET PEPPER FLUID

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Abstract

This study investigated the corrosion behavior of ZA27 and ZA27/Eggshell Composite in pepper fluids. The objective of the study is to know the corrosion behavior such as corrosion rates, corrosion potentials and pitting potentials of ZA27 and ZA27/Eggshell composite in pepper fluids. ZA27 and ZA27/Eggshell composites were prepared in the laboratory. The prepared alloy and composite were then tested for corrosion behavior in pepper fluids by potentiodynamic method. The result of the study showed that corrosion behavior of ZA27 and ZA27/Eggshell composite is dependent on the particular pepper fluid environment.

Keywords: metal matrix composites, ZA27, eggshell, particulate reinforcement

INTRODUCTION

The term “corrosion” is generally applied to a reaction involving oxygen. However, in the world of chemistry, the term “Oxidation” does not only apply to a reaction with oxygen. An element is “Oxidized as opposed to being “reduced”, when it gives up electrons and to form a compound. For example, sodium converts to sodium chloride in the presence of chlorine in what is referred to as an “Oxidative” reaction [1]. The importance of corrosion is widespread, and goes beyond huge financial loss due to engineering material loss. Corrosion control treatment is necessary to reduce the leaching of biologically toxic metals such as lead and cadmium [2]. Corrosion control treatment also affects consumers’ perceptions of the quality of drinks by reducing metallic tastes, water color and odors [2]. Hence, the need for corrosion studies for better understanding of corrosion.

Zinc-Aluminum (ZA) alloys are alloys with Zinc as the base metal, with higher concentrations of Aluminum when compared to traditional Zinc alloys. These alloys have proven themselves in a wide variety of demanding applications. They are alloy materials that offer designers and casting specifiers viable, cost-effective alternatives for their component requirements. Specifically, compared to Aluminum, the Zinc-Aluminum alloys are harder and stronger, machine more easily, have superior pressure tightness, and have substantially better wear and bearing characteristics. The alloys 8 and 12 are not subject to incentive sparking. The alloys become viable choices when Aluminum is inadequate.

While many studies have reported investigations on ZA27 alloy [3–5], only Adedayo and Abdulsalam [6] and Adedayo [7] have published research efforts to characterize

ZA27/Eggshell composite. The work of Adedayo and Abdusalam [6] dwelled on engineering management of chicken eggshell for improvement of properties of ZA27 alloy. In their work, 20% of 600 microns particles of eggshell were added to ZA27 through casting. The result of their study showed that strength of ZA27 alloy is improved with addition of 20% of eggshell.

In this present work, the corrosion responses of ZA27 and ZA27/Eggshell composite in pepper fluids are being studied. Although, peppers are important food spice, only scanty technical information is available on industrial processing of pepper, and on effect of processing equipment materials on the pepper paste. There are no information on chemical characteristics of ZA27 and ZA27/Eggshell composite in pepper fluids. Hence the need for this present study to provide useful information for engineering management of pepper processing plants. The study will equally provide vital information useful for evaluating implication of food contact of ZA27 and ZA27/Eggshell composite.

MATERIALS AND METHODS

The study materials are ZA27 and ZA27/Eggshell composite rods produced in the laboratory by melting ZA27 alloy. A volume of about 850ml of the molten alloy was bailed out, and 170 ml of prepared eggshell sieved to 600 microns was added to the molten alloy and stirred vigorously. Previous researches published have used particulate sizes of a few microns, however current trend is exploring particulate sizes between 100 to 850 microns [5–7]. The mixture was in sand mold into rods with 15mm diameter and 200mm in length. A control sample which had no eggshell content was also prepared.

The electrochemical responses of ZA27 alloy and ZA27/eggshell composite in pepper fluid were evaluated by potentiodynamic method. The pepper fluid was obtained from scotch bonnet pepper, by squeezing the fluid out of the pepper fruits ground to paste by a blender. The ZA27 and ZA27/Eggshell composite samples used for the potentiodynamic analysis were metallographically prepared and polished. The polished samples were then mounted in Bakelite with connected flexible conducting wires for potentiodynamics analysis. The prepared samples were made the working electrodes, and the counter electrode is platinum. The reference electrode is Ag/AgCl. A scan rate of ~ 1mv/s was used with open circuit potential (OCP) for 600s. The polarization curve was studied with potentiostat equipped with VERSASTAT 4 software. The entire electrochemical test were performed at room-temperature.

RESULTS AND DISCUSSION

The results of the electrochemical corrosion of the test samples by potentiodynamic method are presented as potentiodynamic polarization curves in the Figures 1 and 2, while Table 1 presents corrosion rates and potentials of ZA27 and composite in the pepper fluid. Figures 1a and 2a present the potentiodynamic polarization curve of the specimens in the pepper fluid while Figures 1b and 2b show the microstructures of the samples after they were exposed to pepper fluid through potentiodynamic analysis.

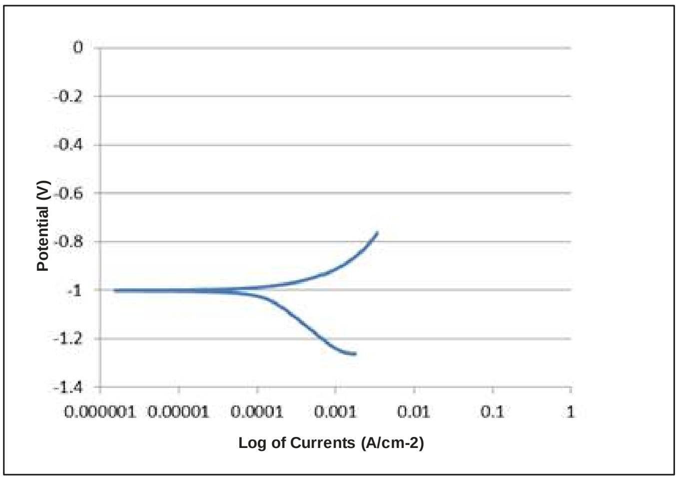

Figure 1a *Polarization curve of ZA27 in Scotch bonnet Pepper fluid*

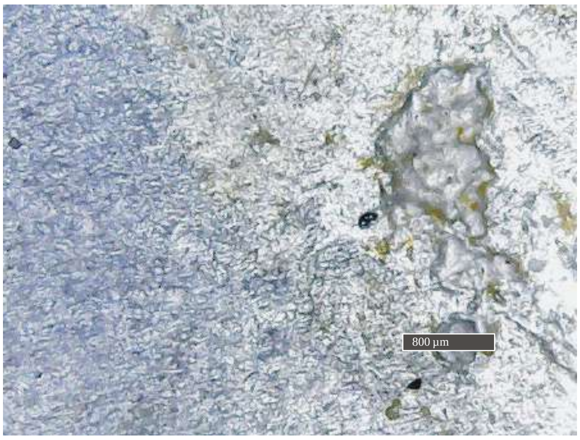

Figure 1b *Microstructure of ZA27 exposed to Scotch Bonnet Pepper fluid through potentiodynamic test*

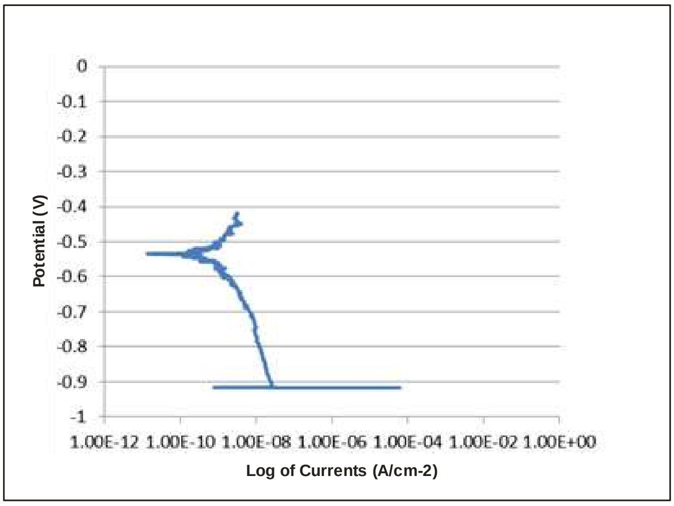

Figure 2a *Polarization curve of ZA27-Eggshall composite in Scotch bonnet pepper fluid*

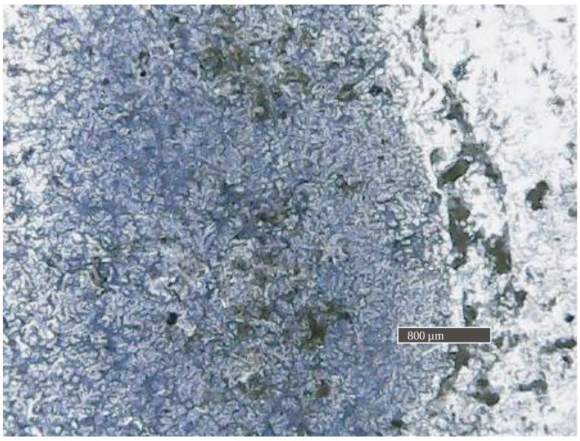

Figure 2b *Microstructure of ZA27- Eggshell composite exposed to Scotch Bonnet Pepper fluid through potentiodynamic test*

Table 1 *Corrosion rates and potentials of ZA27 and composite in pepper fluids*

Sample	E_{corr}	Corrosion Rate
ZA27	-1.005 V	1.872 mmpy
ZA27/Eggshell	-0.543149 V	$2.34 \cdot 10^{-5}$ mmpy

In Figure 1a, the potentiodynamic polarization curve of ZA27 in Scotch Bonnet fluid is presented. The polarization curve has both anodic and cathodic domains [3]. The cathodic domain includes potentials below the corrosion potential (E_{corr}), where current density determined by the cathodic reaction shows a continuous increase in the current density of the cathodic branch as the potential decreases [4]. The polarization curve is significantly active corrosion behavior, where current density increased with applied voltage. Corrosion potential for this system of pepper fluid and ZA27 is -1.005V and corrosion rate is 1.872 mmpy. The microstructure of the ZA27 sample immersed in scotch bonnet presented in Figure 1b revealed the presence of some intergranular corrosion, which suggests the susceptibility of ZA27 alloy to intergranular corrosion in scotch bonnet. In Figure 2a, the polarization curve of ZA27/Eggshell composite in Scotch Bonnet Pepper fluid is presented. The E_{corr} for the system is – 0.543149 V, and the corrosion rate is $2.34 \cdot 10^{-5}$ mmpy. The curve is active, but weakly passivating with some pitting potentials at about -0.45 mV. Presence of pits is confirmed in the microstructure of the sample presented in Figure 2b. Comparing the performance of ZA27 and ZA27/Eggshell in the pepper fluid, it is evident that the ZA27/Eggshell composite show lower corrosion rates and therefore exhibit better corrosion resistance. This suggests that introducing eggshell into ZA27 alloy to improve corrosion resistance should be encouraged.

CONCLUSION

ZA27 alloy generally exhibits good corrosion resistance in pepper fluids. However, comparing the performance of ZA27 and ZA27/Eggshell in the pepper fluid, it is evident that the ZA27/Eggshell composite show lower corrosion rates and therefore exhibit better corrosion resistance. This suggests that introducing eggshell into ZA27 alloy to improve corrosion resistance should be encouraged. The use of ZA27 as a material for producing grinders in processing pepper fruits to paste is recommended. The use of eggshell particles as reinforcement composite particulates in ZA27 alloy materials for producing pepper grinding product is also recommended.

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CORROSION BEHAVIOUR OF ZA27 AND ZA27/EGGSHELL COMPOSITE IN SIMULATED SEA WATER

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Abstract

This study investigated the corrosion behavior of ZA27 and ZA27/Eggshell Composite in simulated sea water. The objective of the study is to know the behavior, corrosion rates, corrosion potentials and pitting potentials of ZA27 and ZA27/Eggshell composite in simulated sea water. ZA27 and ZA27/Eggshell composites were prepared in the laboratory, the prepared alloy and composite were then tested for corrosion behavior in simulated sea water by potentiodynamic method. The result of the study showed that ZA27/Eggshell composite had better corrosion resistance; therefore the choice of ZA27/Eggshell composite is preferred for sea water or simulated sea water environment.

Keywords: Metal matrix composites, ZA27, eggshell, particulate reinforcement, Zinc

INTRODUCTION

Zinc Aluminium (ZA) alloys are a new family of zinc casting alloys that have been found useful in a wide variety of demanding applications. The most common alloys available in this family are the alloys designated as ZA8, ZA12 and ZA27. The alloys are designated 8, 12, and 27 to indicate their approximate aluminium content. Both tensile strength and compressive strength of the alloy have been studied elaborately. These ZA alloys are not subject to incentive sparking, and they become viable choices when Aluminum is inadequate [1].

Although some studies have been carried out to investigate the corrosion behaviours of alloys and effects of particulate reinforcement on properties of alloys [2–4], however, the literature has reported only Adedayo and Abdulsalam [5] and Adedayo [6] to studied and characterize ZA27/Eggshell composite. The investigations made by Adedayo and Abdusalam, [5] focused on managing chicken eggshell to improve engineering properties of ZA27 alloy. The study showed that 20% of 600 microns particles of eggshell added to ZA27 through casting improved strength of ZA27 alloy.

In this particular study, the corrosion responses of ZA27 and ZA27/Eggshell composite in simulated sea water are being studied. Only scanty technical information is available on effects of eggshell as particulate reinforce in alloys on corrosion behavior of alloys in Sea water. There are no information on chemical characteristics of ZA27/Eggshell composite in Sea water. Hence the need for this present study to provide useful information for engineering application of ZA27 in marine environment.

MATERIALS AND METHODS

The study materials are ZA27 and ZA27/Eggshell composite rods produced by melting zinc scrap with 27% Aluminum metals obtained from Aluminum cables. About 3 Kg of Zinc metal scrap was melted in a lift-out crucible furnace, after which about 0.82 Kg of Aluminum was dissolved in the molten zinc metal. A volume of about 850 ml of the molten alloy was bailed out, and 170 ml of prepared eggshell sieved to 600 microns was added to the molten alloy and stirred vigorously. Previous researches published have used particulate sizes of a few microns, however current trend is exploring particulate sizes between 100 to 850 microns [4-6].The mixture of molten metal alloy and eggshell produced was then quickly poured into a prepared sand mold and cast into rods with 15mm diameter and 200 mm in length. A control sample which had no eggshell content was also prepared by casting in sand molds. Produced cast rods were then machined on a lathe machine into test pieces of 10 mm diameter and 10 mm length. High Speed Steel (hss) cutting tool was used, with a cutting speed of 305 revolutions per minute. Micrometer screw gauge and vernier callipers were used for measuring the dimensions of the machined samples**.** The electrochemical responses of ZA27 alloy and ZA27/eggshell composite in simulated sea water were evaluated by potentiodynamic method. The ZA27 and ZA27/Eggshell composite samples used for the potentiodynamic test were metallographically prepared by grinding successively with abrasive papers of 60p, 120p and 220p before they were polished. The polished samples were then mounted in Bakelite with connected flexible conducting wires before they were immersed in simulated sea water for potentiodynamics test. The prepared samples were made the working electrodes, and the counter electrode is platinum. The reference electrode is Ag/AgCl. A scan rate of ~ 1mv/s was used with open circuit potential (OCP) for 600s. The polarization curve was studied with potentiostat equipped with VERSASTAT 4 software. The entire electrochemical test were performed at room-temperature.

RESULTS AND DISCUSSION

The results of the electrochemical corrosion of the test samples by potentiodynamic method are presented as potentiodynamic polarization curves in Figures 1 and 2, while Table 1 presents corrosion potentials and rates of ZA27 and ZA27/Eggshell composites in simulated sea water.

In Figure 1a, the polarization curve of ZA27 in simulated sea water is presented. The polarization curve has both cathodic and anodic branches [2]. The cathodic domain includes potentials below the corrosion potential (E_{corr}), where current density determined by the cathodic reaction shows a continuous increase in the current density of the cathodic branch as the potential decreases [3]. The anodic branch shows a spontaneously passive behavior with few pitting potentials. The micrograph of the sample presented in Figure 1b revealed few pits randomly distributed in the micrograph, confirming presence of pits as indicated by the polarization curve of Figure 1a. The micrograph also reveals areas of white patches which are adhesions to the surface of the sample as a result of immersion of the sample in simulated sea water for potentiodynamic test. The corrosion potential for the system is -11.868 mV and the corrosion rate is $7.2655e^{-07}$ mmpy.

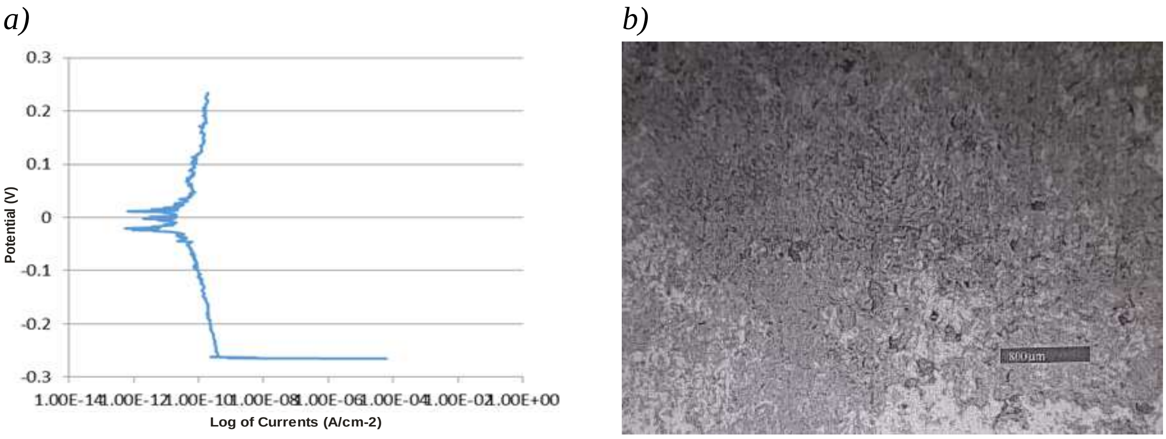

Figure 1 *a) Polarization curves of ZA27 in simulated sea water; b) Microstructure of ZA27 in Simulated sea water*

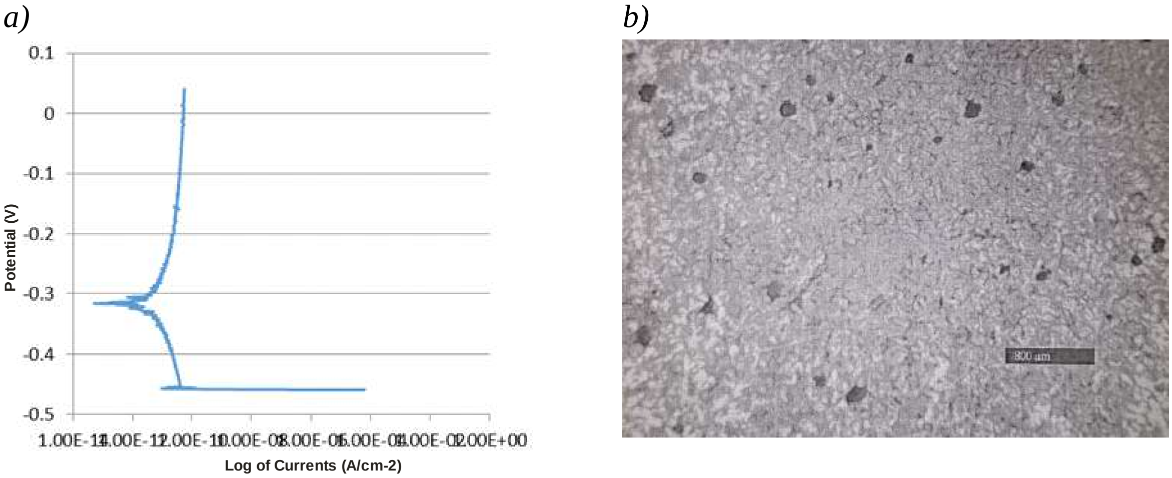

Figure 2 *a) Polarization curves of ZA27/Eggshell composite in simulated sea water; b) Microstructure of ZA27/Eggshell composite in simulated sea water*

In Figure 2a, the polarization curve of ZA27/Eggshell composite in simulated sea water is presented. The polarization curve has both anodic and cathodic branches. The anodic branch shows a spontaneously passive corrosion behavior. The micrograph of the sample is presented in Figure 2b. The Ecorr for the system is -339.925 mV and the corrosion rate is 5.6874e-08 mmpy.

Table 1 *Corrosion potentials and rates of ZA27 and ZA27/Eggshell composites in simulated sea water*

Sample	Corrosion potential	Corrosion rates
ZA27 in Simulated sea water	-0.011868 V	$7.2685 \cdot 10^{-7}$ mmpy
ZA27/Eggshell in Simulated sea water	-0.339925 V	$5. \cdot 10^{-8}$ mmpy

CONCLUSION

The study has shown that ZA27 alloy material has good corrosion resistant property. Introducing eggshell into the matrix improves the corrosion resistance ability of the alloy material in sea water/Simulated sea water environment. ZA27/Eggshell composite had improved corrosion resistance, therefore the choice of ZA27/Eggshell composite is preferred for sea water or simulated sea water environment.

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MODIFIED FLY ASH AS A NEW ADSORBENT FOR Cu^{2+} REMOVAL FROM AQUATIC SOLUTIONS

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Abstract

Given the fact that copper is the one of the metals of great industrial application, there are numerous opportunities for environmental pollution with this metal. Considering the importance of water for human health, today a special attention is paid to the removal of copper ions from wastewater before being discharged into environment. The aim of this paper was to investigate the fly ash, the waste material from coal fired power station as adsorbent for Cu^{2+} *removal from aquatic solution. Fly ash, supplied from coal fired power station Pljevlja in Montenegro, was modified by alkali activation process and used for the adsorption test. The paper emphasizes the influence of solid / liquid ratio, pH of solution, initial copper concentration in solution and temperature on the removal efficiency of* Cu^{2+} *from aquatic solution. It has been shown that increase the pH in the range of 3-5, initial concentration from 20-100 ppm and solid/liquid ratio from 0.4-0.8 lead to the increase of copper removal efficiency from aquatic solution. Moreover the increase of temperature from 20-45* $^{\circ}C$ *is favorable from the stand point of* Cu^{2+} *removal from solutions.*

Keywords: copper, fly ash, adsorption, aquatic solution

INTRODUCTION

The copper is one of the essential micronutrient influencing a different metabolic process in a human body, but when it exceeds some limits the copper exposes the toxic effect on the human health. Long term copper intake leads to nose, mouth and eyes irritation and causes stomach diseases and ultimately can lead to fatal liver and kidney damage. Chronic copper poisoning leads to Wilson's disease [1]. So the World Health Organization set the value of 0.05 mg L^{-1} as the maximally allowed Cu concentration in a drinking water [2].

The water contamination by Cu is a result of different anthropological activity (metal processing, mine industry, agriculture etc.). Due to the rapid industrialization there is a potential dangerous of water contamination by Cu. So, a great attention is paid to the wastewater treatment before being discharged in the environment.

There are numerous methods for a Cu removal from wastewater [3] but adsorption is recognized as a relatively cheap and easy feasible method for a metal removal from wastewater. The active carbon is mainly in a use as a commercial adsorbent but in pass decade the numerous by-product from industrial sector are proposed as a possible adsorbent for a heavy metals removal from wastewater.

Thus the aim of this study was to investigate the use of fly ash (the by-product of coal combustion in coal fired power stations) as novel low-cost adsorbent for Cu^{2+} removal from aquatic solution.

MATERIALS AND METHODS

Fly ash supplied from coal fired power station Pljevlja in Montenegro was used for adsorbent preparation. Its chemical composition is given in the Table 1.

Table 1 *Chemical composition of fly ash*

Component	%
SiO_2	49.45
Fe_2O_3	5.23
Al_2O_3	21.77
TiO	0.66
CaO	13.34
Na_2O	0.46
ZnO	4.5·10-3
MgO	1.29
MnO	0.02
P_2O_5	0.24
K_2O	1.40
Loss of ignition	4.35

Fly ash modified by alkali activation was used as a sorbent for adsorption tests. Alkali activation was carried out by mixing of fly ash with alkali activator in a solid to liquid ratio of 1.2 to 1. The mixture of 10 M NaOH and commercial water glass (commercial Na silicate solution: Na_2O = 8.5%, SiO_2 = 28.5%, density of 1.39 kg/m^3) was used as an alkali activator. These two solutions were mixed in a mass ratio of 1.5. The paste obtained by mixing of fly ash and alkali activator was casted in a closed plastic mould and cured for 48 h at 65° C. After that time, the samples were allowed to cool, removed from moulds and left to stay for additional 28 days at ambient temperature before being powdered to the size below 63 µm.

Such prepared sorbent was washed with distilled water until the neutral pH value was obtained. Subsequently, the wet adsorbents were dried at 105°C. A set of adsorption tests was performed in a batch conditions at 25, 35 and 45 °C by mixing sorbent with solution containing 20-120 mg L^{-1} of Cu^{2+} ions at pH between 3 and 5 and solid to liquid ratio of 0.4-0.8 for a period of 60 min. All the experiments were carried out in triplicate and the average values of the results are taken into account. Copper sulfate pentahydrate ($CuSO_4·5H_2O$) and deionized water were used for the preparation of copper containing solution.

Upon completion of adsorption tests, the solutions were filtered and analyzed for the concentration of Cu^{2+} by using inductively coupled plasma optical emission spectrometry (ICP-OES). Removal efficiency of Cu^{2+} ions (RE) from aquatic solutions was determined using equations Eq.1.

$$RE = \frac{(C_o - C_t)}{C_o} \cdot 100;\% \tag{1}$$

where C_o and C_t are initial and final concentrations of Cu^{2+} in solutions.

RESULTS AND DISCUSSION

Influence of pH of solution

The results of investigation of pH of solution on the removal efficiency of Cu^{2+} from aquatic solution are given in the Figure 1. It is evident that increase of pH of solution from 3 to 5 lead to the increase of removal efficiency from 38.8% to 74. 3% e.g. the higher removal efficiency was achieved in slightly acid solution than in a strong acid solution. This can be explained by the competition of Cu^{2+} and H^+ ions to adsorb on the active site of sorbent. The increase of pH of solution lead to the decrease of H^+ ions concentration and increase the concentration of Cu^{2+} ions adsorbed [4]. Since the maximal removal efficiency was achieved at the pH of 5, this pH value was chosen as an optimal for further experiment.

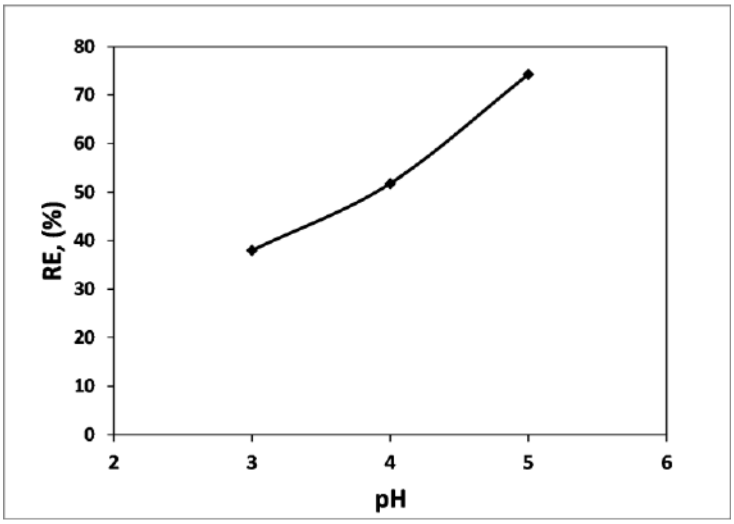

Figure 1 *Influence of pH of solution on the efficiency of* Cu^{2+} *removal from aquatic solutions*

Influence of initial solution concentration and sorbent dosage

Investigation of the influence of initial Cu^{2+} concentration on the efficiency of Cu^{2+} removal from aquatic solution was carried out in the range of 20-120 mg L^{-1} and the results are given in the Figure 2a. The removal efficiency of Cu^{2+} ions from aquatic solution increases from 39.7% to 74.3% with the increase of initial Cu^{2+} concentration from 20 to 100 mg L^{-1}. Further increase of initial metal concentration in the solution up to 120 mg L^{-1} did not changed the removal efficiency considerably ant thus the value of initial Cu^{2+} concentration was chosen as an optimal for the rest of experiments. The increase of metal removal efficiency with the increase of initial metal concentration in a solution can be explained by the increase of amount of Cu ions adsorbed on the available active site on the adsorbent surface. At the initial Cu concentration of 100 mg L^{-1}, all available active sites on the sorbent surface were occupied, so the further increase of initial concentration to the value of 120 mg L^{-1} had no influence on the removal efficiency of Cu^{2+} ions from solution.

Since the availability of active sites on the sorbent surface depend on the amount of sorbent used for the adsorption tests, the influence of sorbent dosage on the metal removal efficiency was investigated in the range of solid to liquid ratio of 0.4 to 0.8 and the results are given in the Figure 2b. The results indicate that increase of adsorbent dosage in investigated range lead to the increase of removal efficiency from 44.2% (at solid to liquid ratio of 0.4) to 74.3 % (at solid to liquid ratio of 0.8).

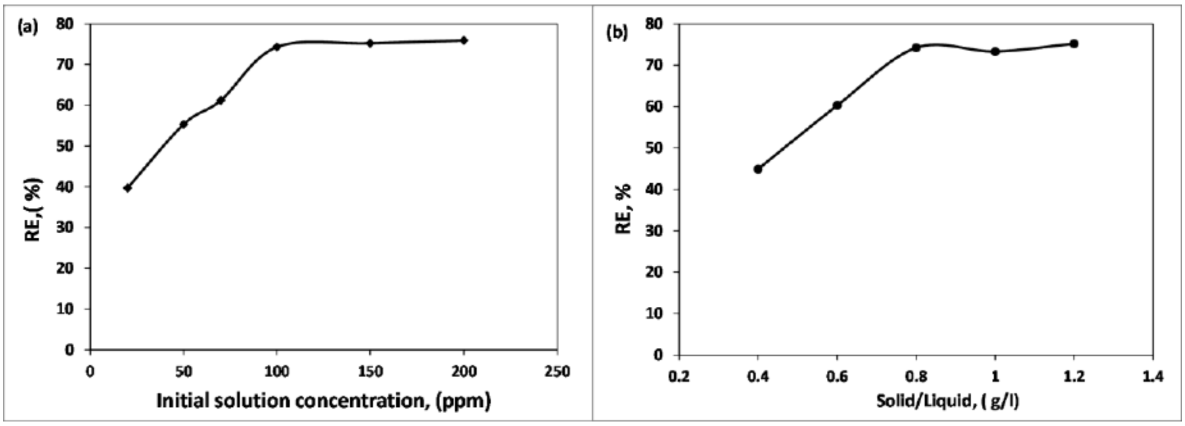

Figure 2 *a) Influence of initial solution concentration and b) sorbent dosage on the efficiency of Cu^{2+} removal from aquatic solutions*

Influence of time and temperature

Figure 3 presents the results obtained by the investigation of time and temperature of adsorption test. The results obtained have shown that the adsorption of Cu^{2+} on the fly ash based adsorbent occur in a relatively short time and the maximal removal efficiency was achieved after 10 min and practically did not changed with the further prolongation of adsorption process. This means that equilibrium of Cu^{2+} adsorption was achieved within the first 10 min. Since the adsorption process involves a several steps including the diffusion of metal ions to the sorbent surface, influence of temperature of adsorption was needed to be investigated. The results obtained indicate theta increase of temperature from 25 to 45 °C is favorable for the adsorption of Cu^{2+} process.

The removal efficiency was increased from 61.4% at 20 °C to 74.3% at 45 °C after 10 min of test which can be explained by the increase of diffusion of metal ions to the sorbent surface [5].

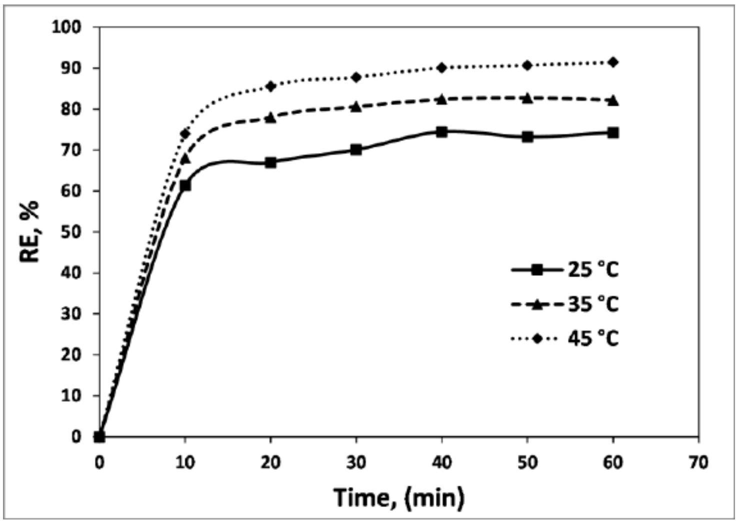

Figure 3 *Influence of time and temperature on the efficiency of* Cu^{2+} *removal from aquatic solutions*

CONCLUSION

Based on the results obtained in this study the following conclusions can be drown:

- The removal efficiency of Cu^{2+} ions from aquatic solutions increase in the pH range of 3-5.
- Increase of initial metal concentration in the range of 20-100 mg L^{-1} and sorbent dosage in the range of 0.4-0.8g L^{-1} lead to the increase of Cu^{2+} ions removal efficiency.
- Cu^{2+} adsorption on fly ash modified by alkali activation is a relatively fast process and equilibrium was achieved within 10 min.
- The metal removal efficiency increases with the increase of temperature in the range of 25-45 °C.

ACKNOWLEDGEMENT

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HYDROTHERMAL CARBONIZATION–GREEN PROCESS FOR CARBON MATERIAL PREPARATION

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Abstract

A hydrothermal carbonization process of simple sugar or low value biomass–plane tree seed, can be transformed into an efficient form of carbonaceous material. Elemental analysis of the obtained samples suggests that the hydrothermal carbonization is useful technique for making carbon-rich substances. Low porous carbonaceous materials were produced by means of the hydrothermal carbonization of fructose at 140 and plane tree seed at temperatures in the 200–260°C range. The materials so formed from fructose are composed of agglomerates of carbonaceous microspheres (size ~2–5 µm), as evidenced by SEM. The combination of the results of the elemental analysis with that obtained by infrared spectroscopic technique has allowed us to assume that the material surface possesses oxygen functionality groups (i.e. hydroxyl, carbonyl, carboxylic…).

Keywords: hydrothermal carbonization process, fructose, plane tree seed, carbonaceous material

INTRODUCTION

Green chemistry, also called sustainable chemistry, has been focused on the designing of products and processes that minimize or eliminate the use and generation of hazardous substances and on the environmental impact of chemistry. The main principles that cover such concepts are: the use of renewable material feedstock and energy sources, the design technological approaches for preventing pollution, the use of safe, environmentally friendly substances, including solvents, whenever possible, the design of energy efficient processes, avoiding the production of waste, etc. [1].

Carbon materials can be made with a wide range of structures, compositions and properties, depending on the nature of the organic precursor and process parameters [2–5]. So, carbon has a wide variety of allotropes, from crystalline (diamond and graphite) to amorphous (carbon black, active carbon, glassy carbon, etc.) as well as the nanostructured forms of crystalline carbon (fullerenes, nanotubes, nanodiamond, and graphene) [6,7].

Hydrothermal carbonization (HTC) process is a technique to turn simple sugars or waste biomass as renewable material into black soil, peat, brown carbon and carbonaceous materials, all in water [8–10]. This thermal treatment is under autogenous pressure at temperatures in the 150–350°C range [11].

HTC of low value biomass is a tool for the sequestration of atmospheric CO_2. Biomass is the biggest carbon converter, with the highest efficiency to bind CO_2 from the atmosphere. This is due to microbial decomposition of biomass that liberates exactly the amount of CO_2 formerly bound in the plant material [12].

Carbon materials obtained by HTC can be made with a wide range of carbon nanostructured and nanaporous properties that provides attractive opportunities for various applications: environmental protection, energy-storage and conversion, in catalysis, for sensor, etc. Due to these properties there are various applications in green chemistry. In that sense, HTC can be seen as much more than just a technique for making carbon-rich substances.

MATERIALS AND METHODS

All samples have been prepared by hydrothermal carbonization of different precursors varying the row material and process parameters.

Fructose and plane tree seed were used as a raw material for carbonaceous material preparation. Fructose (analytical purity, Centrohem, Stara Pazova, Serbia), was dissolved in 0.1 M HNO_3 solution (40 mL) to form 0.5 M (F1), 1 M (F2) and 3 M (F3) fructose solution. Collected plane tree fruits were cut open to take the inside seed that consist from bristles and achene. The seed was washed than dried in an oven and finally milled in coffee mill. Plane tree seed (2 g: PTS1 and PTS4, or 5 g: PTS2 and PTS3) were dispersed in about 50 ml of water. All samples were mixed with magnetic stirrer at room temperature for about 15 min.

These solutions or mixtures were put in a reactor and closed. After that reactor was sealed and placed in the dryer and then temperature is adjusted at various temperatures (t) from 140 to 260^{o}C and maintained (τ) from 3 to 70 hours. The samples are marked depending on the process parameters, as follows: F1, F2 and F3: t=140^{o}C, τ=3 h; PTS1: t=260^{o}C, τ=5.5 h; PTS2: t=260^{o}C, τ=19 h; PTS3: t=260^{o}C, τ=25 h, and PTS4: t=200^{o}C, τ=70 h.

After hydrothermal carbonization, the precipitate was collected by filtration and then washed repeatedly with distilled water and ethanol. Samples denoted with F were carbonized in tube oven up to 800^{o}C under an inert atmosphere. After carbonization samples were labeled as FC.

The resulting samples were characterized by, nitrogen adsorption/desorption isotherms measurements, (EA) elemental analysis by Vario EL III analyser, (XRD) analysis, scanning electron (SEM) and Fourier transform infrared spectroscopy (FTIR).

RESULTS AND DISCUSSION

The percentages of carbon retained in the final solid product obtained by elemental analysis are listed in Table 1. As should be seen, after HTC all samples show increase in carbon content. For the samples obtained from the fructose drastic increase in carbon content as well as and for specific surface area (S) can be seen after carbonization process.

It can be seen that, depending on the operational conditions, the carbon present in the PTS retained in the hydrochar products is in the 55–60 wt.% range.

Table 1 *Chemical elemental analysis and surface area for samples obtained by HTC*

Sample	C (wt.%)	O (wt.%)	H (wt.%)	N (wt.%)	S (m^2/g)
Fructose	40	53	7	-	-
F1	60.61	34.91	4.48		
F2	60.64	34.86	4.50	-	103
F3	59.87	35.55	4.58	-	48
F3C	91.51	7.65	0.43	-	173
PTS	45.82	47.85	4.63	1.70	-
PTS1	55.06	41.58	2.75	0.61	-
PTS2	54.70	40.17	0.92	0.92	-
PTS3	59.73	34.87	4.89	0.51	-
PTS4	57.46	34.46	6.44	1.64	-

Figure 1, shows results of the XRD analysis of the PTS samples. As can be seen the all sample has amorphous structure.

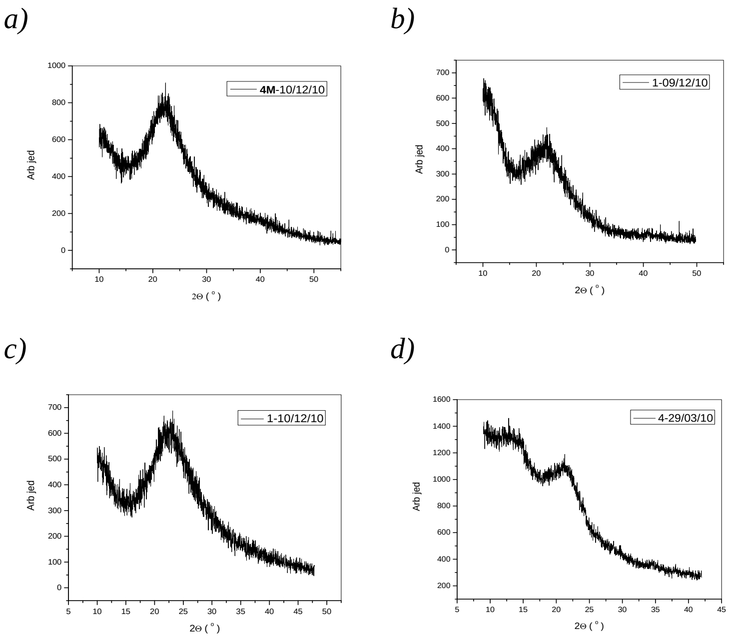

Figure 1 *XRD analysis of the PTS samples a) PTS1; b) PTS2; c) PTS3; d) PTS4*

SEM analysis shows that the microspheres formed during HTC process of fructose persists and after carbonization process (Figure 2).

Figure 3 shows results of the of FTIR analysis. There are some present some functional groups on the surface of the samples, and they are very similar for both samples.

Comparing results from EA analysis (Table 1) with results of FTIR (Figure 3) it become obvious presence of oxygen.

a) bar=10 μm *b) bar=10 μm*

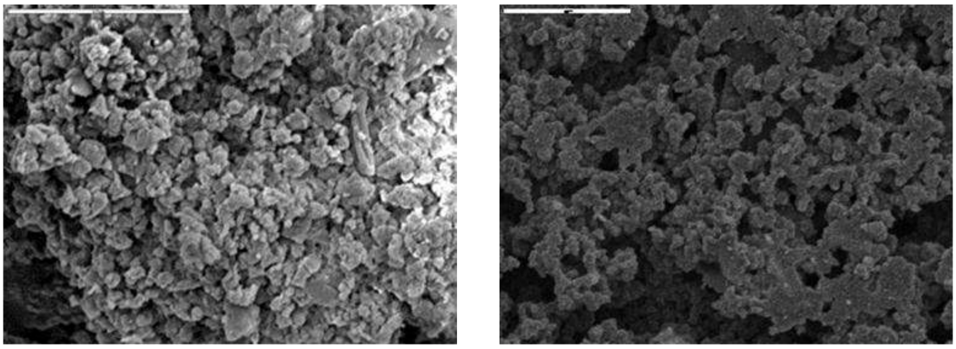

Figure 2 *SEM micrographs of sample F3 a) before carbonization; b) after carbonization*

a) F2 *b) PTS*

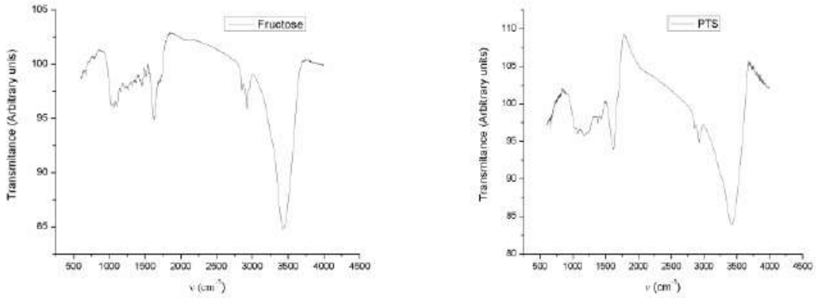

Figure 3 *FTIR analysis of samples obtained by HTC from a) Fructose; b) plane tree seed*

CONCLUSION

Hydrothermal carbonization process is efficient and green process for making carbon reach substances from simple sugar and biowaste material such as plane tree seed. Simple sugar like fructose can change to hydrochar at low temperature such as 140°C. It is quite natural that the carbonization process increases carbon content and improves porosity in this material.

Presence of oxygen functional groups on the surface of materials after HTC process is confirmed by FTIR analysis.

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THE APPLICATION OF PENCIL GRAPHITE ELECTRODE IN ELECTROANALYSIS

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Abstract

Different methods including ultraviolet (UV) spectroscopy, liquid chromatography, capillary electrophoresis and electrochemical methods are used to analyze the target compounds in various mediums. In comparison with others, electrochemical methods are more sensitive, simpler and faster and have been widely used for determination of electroactive compounds. In recent years, graphite pencil electrodes as working electrodes have been used in the analysis of inorganic and organic compounds. This working electrode is available, cost effective and has good reproducibility and sensitivity for low concentration of analyte. Additionally, graphite pencil electrodes are easy to modify. The surface of graphite pencil electrode could be improved by using modifiers or electrochemical pretreatment.

Keywords: electrochemical methods, pencil graphite electrode, modified pencil graphite electrode, electrochemical pretreatment

INTRODUCTION

Electrochemical methods are widely used in various areas including corrosion processes, adsorption processes on surfaces, reaction mechanisms, kinetics of electron transfer processes and for determination of compounds in different mediums [1–4]. In comparison to the ultraviolet (UV) spectroscopy, liquid chromatography and capillary electrophoresis, electrochemical methods are simpler, more economical, faster and more sensitive to reach the lower limit of detection [5].

The most common methods used in electroanalytics are cyclic voltammetry, differential pulse voltammetry, square wave voltammetry and adsorptive stripping voltammetry. Voltammetry is an electrochemical method in which different working electrodes are used including glassy carbon electrode (GCE), carbon paste electrode (CPE), platinum, graphite pencil electrode (GPE) and boron doped diamond electrode (BDDE) in order to determine target compound [6,7].

APPLICATION OF GRAPHITE PENCIL ELECTRODE

Graphite pencil electrode belongs to the graphitic electrodes and has properties such as good conductivity, high surface area, cost effectiveness and easily availability [8]. It is a nanocomposite containing graphite as the main component and clay. The content of these compounds determines hardness of graphite pencil. As the content of graphite is greater, the pencil is softer [9].

Some researcher groups reported that graphite pencil electrodes have better properties than other carbon-based electrodes. In the paper by Gowda *et al.* [10] was observed that GPE has larger surface area (0.255 cm2) than CPE (0.0951 cm2). Thus, GPE was successfully used for determination of paclitaxel without any preconcentration. Furthermore, Dilgin *et al.* [11] compared the properties of GPE and GCE for determination of acyclovir in Britton-Robinson buffer at pH 4. Based on the obtained cyclic volatmmograms, the peak current was significantly improved when GPE was used in comparison to the GCE. This behaviour can be attributed to the presence of clay that generates a porous structure and a high specific surface area of the pencil graphite [12].

Tavares *et al.* [13] investigated the influence of the softness of graphite on voltammetric response by cyclic voltammetry in a $K_4[Fe(CN)_6]$ solution. They observed that harder graphite shows higher peak current than softer graphite. This behaviour could be explained by the presence of polarized chemical groups in softer graphite. Additionally, greater sensitivity and reproducibility is found for harder graphite pencil electrodes. Also, Skrzypczyńska *et al.* [9] investigated the effects of the hardness of graphite pencil electrode on the voltammetric signal of pentachlorphenol. In this research 2B, 5B and 8B pencil graphites were used. The sensitivity of the electrodes was correlated with the hardness of the pencil graphites and follows the order: 2B < 5B < 8B. Limit of detection of used electrodes was 0.277 mmol/L, 0.189 mmol/L and 0.098 mmol/L for 2B, 5B and 8B, respectively.

The pencil graphite electrode was investigated for determination of different compounds in pharmaceuticals and certain results are summarized in Table 1.

Table 1 *The electroanalytical application of pencil graphite electrode in pharmaceuticals*

Compound	Technique	Experimental conditions	LOD[e]	Reference
Acetaminophen	CV[a]	Mcllvaine buffer (pH 6)	/[f]	[14]
Acetylsalicylic acid	SWV[b]	Britton-Robinson buffer (pH 1.81)	167 ng/mL	[15]
Vitamin B6 Vitamin B1	DPV[c]	0.2 M NaOH	2.81 µg/L 5.34 µg/L	[16]
Paclitaxel	DPV[c]	Phosphate buffer	0.00246 µg/L	[17]
Niclosamide	DPV[c]	Britton-Robinson buffer (pH 7)	0.015 µg/L	[18]
Eugenol	DPV[c]	Britton-Robinson buffer (pH 2)	0.085 µg/L	[19]

***Table 1** continued*

Acyclovir	DPV[c]	Britton-Robinson buffer (pH 4)	0.3 µg/L	[11]
Chlorpromazine	CV[a] DPV[c]	Phosphate buffer (pH 7)	0.003 µg/L	[20]
Nalbuphine Hydrochloride	DPV[c]	Britton-Robinson buffer (pH 6)	6.38 µmol/L	[21]
Itraconazole	As-DPV[d]	Britton-Robinson buffer (pH 2)	9.1 ng/L	[22]

[a] CV – cyclic voltammetry; [b] SWV – square wave voltammetry; [c] DPV – differential pulse voltammetry; [d] As-DPV – anodic stripping differential pulse voltammetry; [e] LOD – limit of detection; [f] / – no data.

Based on the results shown in Table 1, it can be said that the graphite pen electrode has been successfully applied to determine the pharmaceutical compounds under different conditions.

PRETREATMENT OF GRAPHITE PENCIL ELECTRODE

Graphite pencil electrodes are easy to modify in order to enhance their sensitivity [23]. The surface of graphite pencil electrode could be improved by using modifiers or electrochemical pretreatment. During electrochemical pretreatment some functional groups containing oxygen such as carboxylic, carbonyl or phenolic could be formed on the surface. Because of that, the current response of the analyte is enhanced. Electrochemical pretreatment of electrode surface is suitable because it is very simple and less time-consuming than treatment with some complex material [8].

Ozcan and Sahin [24] investigated the possibility of application of electrochemically treated GPE to determine uric acid in urine and blood serum. The GPE was treated in the mixture of lithium perchlorate and sodium carbonate solutions. They reported that the mixture of $LiClO_4$ and Na_2CO_3 showed synergistic effect on the electrochemical treatment of GPE that led to the higher response of uric acid. According to the obtained results, it was concluded that electrochemically treated GPE could be applied in determination of uric acid in biological samples. Further, Alipour *et al.* [25] electrochemically treated pencil graphite electrode in phosphate buffer solution at 1.80V for five minutes. Such prepared electrode was used for determination of morphine. Electrochemically treated GPE showed well defined two anodic peaks at about 0.35 V and 0.8 V respectively in comparison to only one peak at 0.5 V with untreated GPE. The detection limit of morphine in biological samples with electrochemically treated GPE was 0.26 µM.

Koyun and Sahin [26] in their research used modified pencil graphite electrode with poly(L-cysteine) for determination of Sunset Yellow in food and beverage samples.

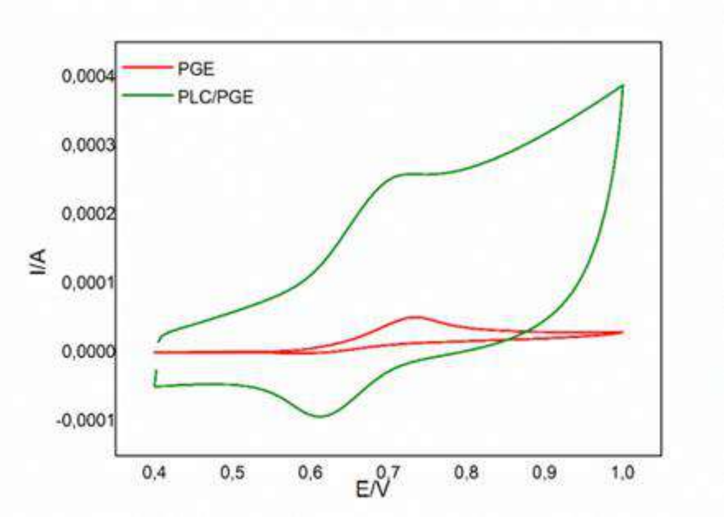

Figure 1 *Cyclic voltammograms of phosphate buffer solution (0.1 M, pH 7) containing 1 mM Sunset Yellow at the bare PGE and modified PGE, scan rate 100 mV/s [26]*

The obtained results using cyclic voltammetry (Figure 1) reveals that peak current of Sunset Yellow is enhanced on modified GPE in comparison on bare GPE. Also, the surface morphology obtained by scanning electron microscopy (SEM) (Figure 2) indicates that modified GPE has rough surface and sphere-like structures in comparison to the bare GPE. It is assumed that the polymerization of L-cycteine on the GPE is occurred and the rough surface is responsible for the improved electrochemical behaviour.

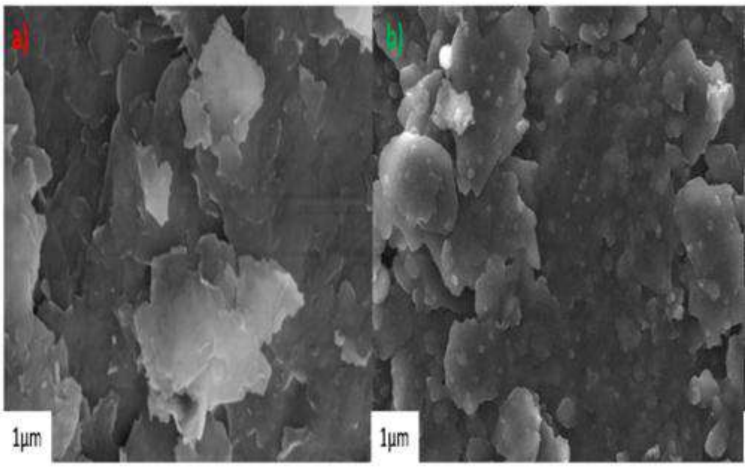

Figure 2 *Scanning electron microscopy micrographs of the a) bare GPE and b) modified GPE [26]*

Pattar and Nandibewoor [27] used polyaniline and polypyrrole as modifiers for graphite pencil electrode. Such prepared electrode was used for detection of 2-thiouracil in pharmaceuticals and human biological fluids. According to the obtained results, the electro-oxidation of 2-thiouracil was irreversible, diffusion controlled process. By comparing the intensity of peak current on a cyclic voltammogram for bare graphite pencil electrode and modified ones, it is observed that the peak intensity is enhanced using modified electrodes. It is presumed that modified electrodes have larger surface area than bare graphite electrode.

CONCLUSION

The applicability of electrochemical methods is diverse. They can be used in investigation of corrosion processes, reaction mechanisms and kinetics of electron transfer processes as well as for the determination of compounds in different medium. Among the various electrodes used in these methods, pencil graphite electrode stands out due to its sensitivity, conductivity and easy availability. The pencil graphite electrode was used in determining of various compounds such as metal ions, phenolic and pharmaceutical compounds. The hardness of the pencil graphite electrodes has effect on the voltammetric response. Additionally, the graphite pencil electrodes are easy to modify. Therefore, the research groups performed electrochemical treatment of the pencil graphite electrodes or treated them using some modifiers. Based on the obtained results, it is concluded that the analyte peak current on the modified GPE is enhanced in comparison to the bare GPE.

ACKNOWLEDGEMENT

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RECOVERY OF METALS FROM SPENT LITHIUM ION BATTERIES

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Abstract

With the development of portable electric appliances and electric vehicles, there came a rise in the production of lithium-ion batteries, and, consequently, an increase in the number of spent batteries. Recycling of spent batteries, from the point of view of the environmental protection, economy and health, is inevitable. Due to the high content of valuable and polluting metals such as Cu, Co, Li, Ni, Mn, etc. it is necessary to do metal valorization when many methods can be applied. The most widely used methods are: solvent extraction, chemical precipitation, and various electrochemical processes. However, in recent times, work has been done on the development of new and more efficient methods and technologies for the separation of metals from used batteries. Such methods would have great merit for minimal environmental pollution.

Keywords: Lithium-ion batteries, valorisation, recycling

INTRODUCTION

The essential division of batteries can arrange them into two fundamental classifications: primary batteries and secondary batteries. Lithium-ion batteries (LIBs) are categorized as secondary batteries. LIBs are composed of: cathode, anode, electrolyte and separator. Pure carbon is utilized as the anode whereas the cathode material is made out of $LiMeO_2$ (Me = Co, Ni, Mn, Fe ...) and, lastly, lithium salts are dissolved in the electrolyte solution. LIBs also contain various organic solvents such as: ethylene carbonate (EC), dimethyl carbonate (DMC), propylene carbonate (PC), diethyl carbonate (DEC) and ethylmethyl carbonate (EMC) [1–3].

In 2000, the global LIB production reached 500 million units and practically 4.6 billion in 2010 [4]. In 2014, however, the production of the LIBs in China has come to 5,287 billion units [3].

The general reusing process incorporates two essential categories: physical and chemical procedures. Physical procedures can be frequently linked with the pre-treatment forms, for example, pounding, sieving and the separation of materials to remove the cathode materials from the case, collector and anode active materials. On the other hand, the chemical procedures can be summed up as pyrometallurgy, biometallurgy and hydrometallurgy. Pyrometallurgical forms are regularly joined by high gas emissions and have high energy consumption, so they require rigid air filtration measures and costly gear investments. By utilizing these procedures, nickel, cobalt, and copper can be recuperated adequately, while lithium and aluminium can be lost in the slag [5]. In any case, pre-treatment of utilized LIBs is not required in such procedures, and their higher energy consumption, high equipment investment, and natural contamination can impede their application. The biometallurgy procedure brings numerous advantages, for example, high productivity, minimal effort and the utilization of a simple apparatus. The long treatment time frame and the troublesome incubation of microbes limit the popularization of this procedure. Consequently, the most well established process is the hydrometallurgy. The hydrometallurgy procedure frequently began with the acid leaching, utilizing the diluted H_2SO_4, HNO_3, HCl, or even mixed acid to dissolve the cathode material.

PRETREATMENT OF Li–ION BATTERIES

As indicated by Figure 1, three basic routes are in the recycling process. Route 1 represents reusing or recuperation process, which consists of pre-treatment (sometimes the discharging process is also regarded as a pretreatment process), pyrometallurgical process, and hydrometallurgical process. Route 2 is the fixing procedure. Route 3 presents the reusing procedure, which is mainly based on reusing Cu, Al foil, and plastic that could be straightforwardly reused after disassembling the elements. The accomplishment of the Route 3 relies upon the productivity of the disassembly procedure to a great extent. As for route 2, the advantage of it is shorting the recycling route to decrease the loss of valuable metals or materials and increase the profile of technologies. Moreover, the strategies for reuse and fixing are frequently disregarded even though these procedures could be extremely advantageous and reasonable in terms of expenses because of their short and effective flows.

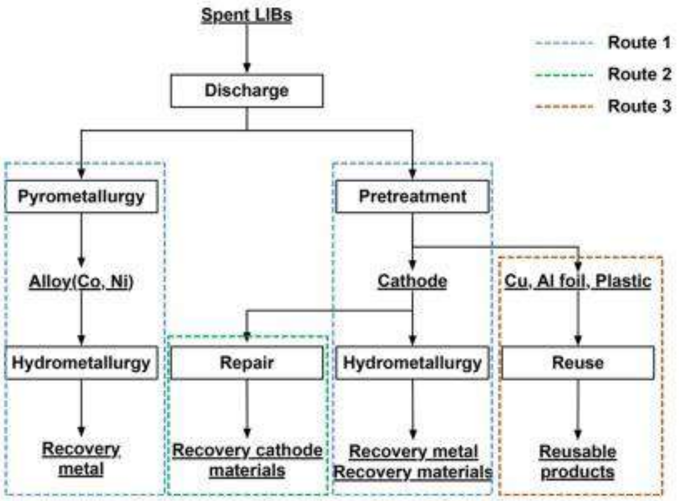

Figure 1 *General flow sheet of spent LIB treatment processes [5]*

Spent LIBs generally contain 5%–20% cobalt (Co), 5%–10% nickel (Ni), 5%–7% lithium (Li), 5%–10% different metals (copper (Cu), aluminium (Al), iron (Fe), etc., 15% natural mixtures, and 7% plastic [6].

Pyrometallurgical process

The pyrometallurgical procedure is one part of the extractive metallurgies that is implemented in order to remove minerals and concentrates with thermal treatment through physical and synthetic changes that enhance the recuperation of valuable metals. Pyrometallurgical techniques have been generally researched in retrieving Zn, Ni, Cd, and other significant metals from used Zn−Mn dry batteries or Ni−Cd batteries. Generally speaking, smelt slags were utilized in pyrometallurgical strategies to isolate metals in which some metals end up in the slag and target metals transform into alloy.

When conducting a typical pyrometallurgical process, Li will end up in the slag stage, which must be additionally removed. Carbothermal reduction methods as a pyrometallurgical method to recycle Li and other metals have received attention in recent years. In this procedure, the blended utilized LIBs can be transformed to metal oxide, pure metal, or lithium carbonate. In one stage, lithium carbonate is filtered by water, while the graphite in the draining slag consumes and leaves metal oxide as the last residue. In the following step, pure metal, graphite, and lithium carbonate are additionally isolated by wet magnetic separation. In any case, the pyrometallurgical advances are also currently facing difficulties in reducing energy consumption and meeting the rigorous requirements for the treatment equipment.

Biometallurgical process

Bioleaching is a rising interdisciplinary procedure that incorporates biology, chemistry and metallurgy. The success of the biometallurgical procedure basically relies upon the capacity of microorganisms to transform the insoluble strong compounds into dissolvable and extractable structures.

Hydrometallurgical process

The hydrometallurgical technique is widely used to recover significant metals from spent LIBs. In the beginning, Co and Li are dissolved by acid leaching or biological leaching. At that point metals in the solution can be recouped by means of a chemical or an electrochemical deposition. Co and Li can likewise be isolated by organic solvent extraction, and afterwards be recovered by electrolysis or chemical precipitation. It has numerous advantages when compared to the pyrometallurgical procedure, for example, because of high extraction effectiveness, low energy consumption, minimal dangerous gas discharge, and low expenses. It has a tremendous potential and can therefore be widely used in the industrial realization. In any case, little flexibility for the removal of crude materials can be a real challenge.

Leaching

In order for the spent LIBs to be reused, the cathode materials are usually dissolved in leaching reagents followed by separation and extraction as the fundamental stages, which are just like other metallurgical procedures. In the development phases of the research, inorganic acid reagents, for example, HCl, HNO_3, and H_2SO_4 were generally utilized as leaching agents and demonstrated to be plausible and effective, but they likewise had a few downsides. The chemical reaction (1) of utilizing HCl can be described as:

$$8HCl + 2LiCoO_2 \rightarrow 2CoCl_2 + Cl_2\uparrow + 2LiCl + 5H_2O \quad (1)$$

The leaching efficiency of Co without reductants follows the order of $HCl>HNO_3 \approx H_2SO_4$. The generally high reducibility level of HCl predominantly adds to this diverse leaching performance. In this manner, the leaching efficiency of most reagents would be unsatisfying unless H_2O_2 or different reductants are included. The mechanism for the decrease response can be described as (taking $LiCoO_2$ for instance) following reaction (2):

$$3H_2SO_4 + 2LiCoO_2 + 2H_2O_2 \rightarrow Li_2SO_4 + 5H_2O + 3/2O_2\uparrow + 2CoSO_4 \quad (2)$$

With increasing in reductant concentrations, the leaching efficiency and reaction rate would first increase accordingly and then reach a plateau at which leaching efficiency and reaction rate would not vary appreciably.

RECOVERY OF METALS FROM LEACHATE

The leachate that can be obtained upon acid leaching generally contains many metal ions. One of the fundamental focuses for the reusing procedure is to get pure metal or metal compounds. In any case, the coexistence of different metal ions in the leachate will unavoidably smother the reusing of pure metal or metal compounds. Likewise, the overlap of the pH range for the precipitation of various metals makes the endeavour to obtain pure metals from a single step precipitation insufficient. Consequently, the leaching solution must be subjected to various stages of separation and extraction, e.g., solvent extraction, selective precipitation, and an electrochemical method to accomplish acceptable degrees of purity.

Solvent Extraction

Solvent extraction is otherwise known as a liquid−liquid extraction technique that incorporates the diverse relative solubility’s of compounds in two immiscible fluids to isolate them from one another. Despite the fact that it is facing the difficulties in isolating compounds with similar functional groups, it stays well-grounded and is broadly applied in the extraction of tungsten and molybdenum, copper from minerals, nuclear reprocessing, and the production of fine organic compounds.

In one study, Kang *et al.* [7] proposed a procedure that includes acid leaching, precipitation, and extraction that yielded an estimated 92% of Co recouped. In this proposed procedure, subsequent to leaching with 2M H_2SO_4 and 6 vol.% H_2O_2, Co is specifically separated from the purified aqueous phase through equilibrating with 50% saponified 0.4M Cyanex 272 at an equilibrium pH~6. Therefore, following the removal of the stacked organic stage with 2M H_2SO_4, a solution of 96 g/L Co remains after the procedure, from which pure pigment−grade cobalt sulphate can be recovered by utilizing evaporation/recrystallization.

Nayl *et al.* [8] extracted and isolated Mn(II), Co(II), Ni(II) and Li(I) from the leach liquor in used LIBs. Precipitates of Mn(II), Co(II), Ni(II) and Li(I) with more than 99% of purity could be acquired under the researched conditions (20% Acorga M5640 in kerosene with agitation for 5 min at 30°C at an equal stage proportion of unity).

Solvent extraction can provide metals with high levels of purity and efficiency, and is generally conducted at room temperature within a short timeframe. Nonetheless, this procedure likewise has a few downsides, for example, complex activities and significant expenses for solvents. Therefore, future research efforts should be focused on the improvement of economical solvents as well as the cyclic use of solvents.

Selective precipitation

The selective precipitation is a single chemical procedure that has been widely researched and applied in separating metals from complex systems of compounds. At times, it is difficult to precipitate just a single ion from the solution.

There is an overlap between stable areas of $Co(OH)_2$ and $Ni(OH)_2$, and it is so enormous to the point that Ni^{2+} and Co^{2+} are likely to be co−precipitated by means of a neutralization reaction. However, the stable areas of Ni^{2+} and $Co(OH)_3$ have a significantly smaller overlap. Hence, one potential methodology is to transform Co^{2+} to Co^{3+} to accomplish a selective precipitation of Co^{3+} in this small area. This procedure was demonstrated to be possible and effective by Joulié *et al.* [9]. With NaClO as the oxidant, the recovery efficiencies of Co and Ni were both almost 100%. The reaction mechanism can be expressed as following reactions (3,4):

$$Co^{2+} + ClO^{-} + 2H_3O^{+} \rightarrow 2Co^{3+} + Cl^{-} + 3H_2O \qquad (3)$$

$$Co^{3+} + 6OH^{-} \rightarrow Co_2O_3 + 3H_2O \qquad (4)$$

Kim *et al.* [10] researched a hydrothermal re-lithiation strategy utilizing a concentrated LiOH solution at 200°C with no scraping methods to recover LCO cathodes and their results indicated that in spite of the fact that the acquired and recovered LCO had some electrochemically inactive polluting impurities, it was still able to accomplish a starting discharge capacity of 144.0 mAh/g and a capacity retention of 92.2% after 40 cycles.

Electrochemical method

In comparison to other hydrometallurgical procedures for reusing metals from spent LIBs, the electrochemical method can yield the cobalt compound of the highest level of purity since it does not include different substances and hence avoids the introduction of other impurities in the system.

Myoung *et al.* [11] applied an electrochemical deposition and a suitable thermal treatment to extract cobalt oxide from Co (III) of waste $LiCoO_2$ cathodes. Under relevant pH conditions, island-shaped cobalt hydroxide is precipitated in the titanium substrate and the thermal treatment of the cobalt hydroxide brings about the creation of cobalt oxide.

Freitas *et al.* [12] recovered cobalt from spent LIBs by utilizing electrochemical techniques and initiate a series of discussions about the electrochemical deposition of cobalt, the difference in pH value in the electrochemical reaction and the impact of pH on the development of crystals.

CONCLUSION

The general reusing of spent LIBs includes methodical engineering comprising of a source control, a handling control, and a treatment. By increasing ecological awareness, a great deal of consideration will be given to the improvement of green and basic reusing strategies. Moreover, in the long run, the essential way for the spent LIBs to be reused lies in the choice of recently developed materials, for example, cathodes, anodes, and electrolytes, just as well as battery designs. Therefore, efforts must be focused on the use of abundant and nontoxic materials so that whatever developments are made will not create new environmental problems. With simpler battery designs facilitating better treatment of spent LIBs.

ACKNOWLEDGEMENT

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APPLICATION OF SIMULATION METHODS AND ANALYSIS OF THE INFLUENCE OF PRECIPITATION REGIME ON TURBIDITY OF KARST AQUIFER: A CASE STUDY OF KARST ZLOT'S SPRING (BOR, SERBIA)

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Abstract

Water resources from karst aquifers are becoming more and more important sources of fresh and quality drinking water. Efflux and the quality of karst aquifers depends mostly of the pluviographic regime, as well as on the regime of surface water that sink. For these reasons, it is necessary to monitor the quality parameters of karst aquifers, but the pluviographic regime of the area should also be observed. Monitoring of the spring is basic for establishing an adequate simulation model. Long-term monitoring of those parameters enables the application of simulation models through dependence between quantity precipitation and characteristic parameters of water quality. Establishment of a simulation model for dependence between precipitation, water level and turbidity, will make the management of the water system in the city of Bor more secure. Based on the weather forecast, the occurence time of turbidity on the source will be known, which will allow timely response and disconnection of the source from the water supply system.

Keywords: karst aquifers, water quality, turbidity, regression models

INTRODUCTION

Karst aquifers have a special importance in the water supply because the water resources of this area require minimal processing in order to obtain good quality drinking water [1]. The biggest problem with karst aquifers is the decrease or increase in water levels during long periods without rain or long rainy periods. The response of karst aquifers to precipitation is often rapid, and the change in certain parameters of quantity and quality is sudden (ie. leakage, groundwater level, turbidity, total number of bacteria, suspended sediment). If the anthropogenic factor is not present on a basin that drains a particular well, the flow regime and the quality of karst aquifers depend on the pluviographic regime and the regimes of formed surface sinking streams. On the other hand, the regimes of formed surface sinking streams that nourish the karst are also conditioned by the pluviographic regime of the given area. Under the influence of precipitation the karst groundwater begins to move extremely fast, causing the surrounding terrain to flush out and the formation of turbid water consisting of suspended and colloidal particles.

The karst aquifer is characterized by a turbidity in water that occurs abruptly, rarely exceeding 20 Nephelometric Turbidity Units (NTUs) and rapidly decreasing to 2 -3 NTUs. Turbidity 2 -3 NTU can be detain in the water for up to ten days, and such water is already hygienically defective water, to which a certain technological procedure must be applied.

Quality and safe management with wells, in the water supply process, includes knowledge of the input parameters that cause turbidity, such as the size of the dispersed particles, the amount of precipitation, the ambient temperature and the water temperature, the number and thickness of the aquifer layers through which the groundwater passes to the springs [2].

The aim of this paper will be to point out the importance of monitoring parameters of water quality at the spring, and to present the results of the conducted analyzes, as well as the results of simulation models on the waters of karst Zlot`s spring which are used for water supply in the city of Bor. A characteristic of the Zlot`s spring is that after a period of sudden snow or intense rainfall occurs turbid water. The turbidity at the Zlot`s spring reaches values up to 20 NTU. Spring water quickly and abruptly turbid to higher NTU values, decreases rapidly to 1-2 NTU values, but takes days or weeks to fall below 1 NTU. The subject of this paper will be based on the prediction of increased water turbidity depending on precipitation. The application of simulation methods can predict the effects of precipitation, as the bigest factor, on the occurrence of turbidity of spring water [3]. Establishing an adequate simulation model during water system management will be more accurate. Based on the forecast, the occurrence time of turbidity at the spring will be known, which will allow timely response and exclusion of the spring from the water supply system.

MATERIALS AND METHODS

Study Area

The study area is the Zlot`s spring located in the basin of river Beljevina, 11 km southwest of Bor. The Zlot`s spring consists of 4 captive sources: Gaura Mare, Gaura Mika, Rnić and Mejlanović. The flow regime of captive springs and the river itself is extremely complex. The flow regime is primarily influenced by the geological and hydrogeological diversity of the river basin.

Climatic data used in the research were taken from the database of the Republic Hydrometeorological Service of Serbia [4]. Data of daily precipitation was taken from the nearest meteorological station Crni Vrh. The flow and water level of the river Beljevina is measured at the station "Seliste", which was built a decade ago by the Republic Hydrometeorological Service of Serbia. The water level of the river Beljevina is recorded at the same time every day.

Methods of Analysis

Continuous monitoring of turbidity at Zlot`s spring was started in 2010. For this purpose, Portable Turbidimeter (Eutech TN 100) was used to measure turbidity in raw water samples. A samples of raw water were taken every two hours. According to The Official Gazette on the Hygienic Safety of Drinking Water [5], the maximum permissible turbidity value is 1 NTU. When the turbidity was higher than 1 NTU, sample for measurement of the turbidity was taken by the hour. Water samples were analyzed from each captured spring individually. Samples with higher turbidity than 1 NTU are excluded from the water supply system. Turbidity was determined immediately after sampling, so that three turbidity measurements were made on the basis of one sample, and a mean value was adopted for the reference value of turbidity for the investigeted sample.

RESULTS AND DISCUSSION

Regression models were used for simulation of parameters for quality of karst aquifer water such as turbidity, precipitation and water level. Autoregression (AR), cross-regression (CR) and autocross-regression (ACR) models were used to simulate turbidity at the karst source. The AR model was applied to obtain the correlation coefficient of the measured and calculated turbidity values, applying equation (1) [6]:

$$TDS_i=a+b_1\cdot TDS_{i-1}+b_2\cdot TDS_{i-2}+ b_2\cdot TDS_{i-2} + +b_{10}\cdot TDS_{i-10} \qquad (1)$$

where TDS_i is water turbidity at time “*i*”, the independently variable TDS_{i-1}, TDS_{i-2}, .TDS_{i-k}, were analyzed parameter of water turbidity for 1, 2, ... k days and a, b are the parameters of the model.

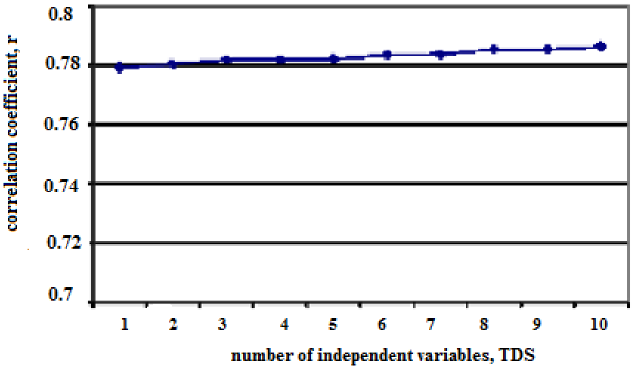

Figure 1 *Correlation coefficient obtained by autoregressive method depending on the time shift expressed in days*

The correlations between the observed and calculated TDS values using equation (1) are given in Figure 1 and Table 1.

Table 1 *Correlation coefficients obtained by regression method*

Time shift (day)	TDS-TDS	TDS-P	TDS-H
1	0.779109	0.366334	0.637869
2	0.780128	0.423894	0.678277
3	0.781625	0.447547	0.71283
4	0.781628	0.459245	0.728664
5	0.781875	0.464304	0.742501
6	0.783336	0.464355	0.751948
7	0.783529	0.464401	0.753945
8	0.785223	0.464427	0.755461
9	0.785227	0.464501	0.756107
10	0.786202	0.464541	0.757202

*P – precipitation, H-water level

CR model for simulation of turbidity obtained via measured amount of precipitation was based on following equation [6]:

$$TDS_i=a+b_1{\cdot}P_{i-1}+b_2{\cdot}P_{i-2}+\ldots+b_{10}{\cdot}P_{i-10} \tag{2}$$

where the dependent variable TDS_i in time "*i*" and the known independent variable amount of precipitation P_{i-1}, P_{i-2}, ... P_{i-k}, for 1, 2, .. .k days.

The correlation between TDS and P using equation (2) is given in Table 1 and Figure 2.

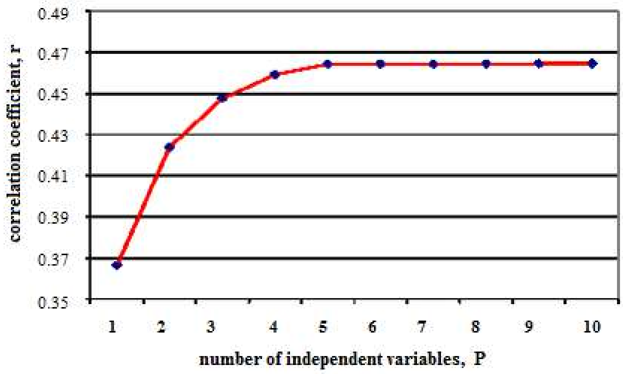

Figure 2 *Correlation coefficient obtained by cross-regression method depending on the time shift expressed in days*

From Figure 2 it can be concluded that the inclusion of 4 or 5 independently variables (in this case precipitation with a shift of up to 5 days) is sufficient. Subsequently, the inclusion of independent variables does not increase the quality of the regression equation, that is, we do not get any better simulations by including new variables. This can be proved by the regression equation, which will most likely show that they are insignificant in the equation, so they should not be included in the equation (more than 5 terms).

The simulation of turbidity at the expense of the water level of the river Beljevina is performed according to the same principle as for precipitation, using the following equation [6]:

$$TDS_i=a+b_1{\cdot}H_{i-1}+b_2{\cdot}H_{i-2}+\ldots+b_{10}{\cdot}H_{i-10} \tag{3}$$

where: H is water level.

From Figure 4 it is concluded that the inclusion of 5 or 6 independent variables (in this case the water level with a shift of up to 6 days) is sufficient.

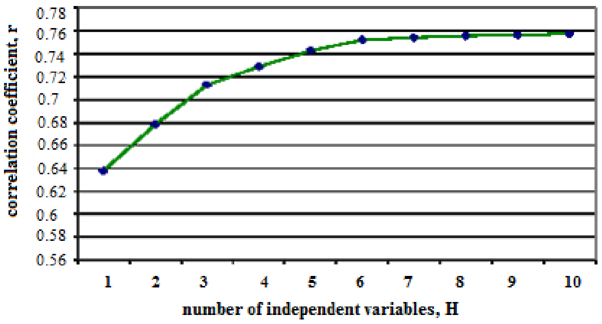

Figure 3 *Correlation coefficient obtained by cross-regression method depending on the time shift expressed in days*

Based on the above, an equation with 6 displacements is set, considering that there is a dependence for these displacements. The turbidity of the Zlot`s spring is simulated using known independent variables such as precipitation, water levels and turbidity registered in the given profile of the previous days. Based on the presented results, the following equation of multiple linear regression was formed:

$$TDS_i = a + b_1{\cdot}TDS_{i-1} + b_2{\cdot}P_{i-1} + b_3{\cdot}P_{i-2} + b_4{\cdot}P_{i-3} + b_5{\cdot}P_{i-4} + b_6{\cdot}H_{i-1} \tag{4}$$

where are: TDS_i and TDS_{i-1} turbidity of the Zlot`s spring at the moment "*i*" and "*i-1*", then P_{i-1}, P_{i-2}, P_{i-3}, P_{i-4}, daily precipitation amounts recorded at the meteorological station Crni Vrh in at the time *i -1, i -2, i -3* i *i-4* and H_{i-1} is water level of the river Beljevina in the profile of Selište at the moment *i-1*. Parameters a, b_1, b_2, b_3, b_4, b_5 and b_6 are dimensionless parameters of the above equation, which are obtained by the method of least squares and whose values are presented in Table 2.

Table 2 *Multiple linear regression coefficients*

a	b_1	b_2	b_3	b_4	b_5	b_6
-0.63678	0.63380	0.07620	-0.00986	-0.00626	-0.00640	0.01841

Using the values of the obtained parameters, the calculation of the turbidity value can be done on the basis of the observed values of precipitation, water level and turbidity of the Zlot`s spring. The previous analysis of the influence of precipitation on the water level of the river Beljevina in the Selište profile, as well as on the turbidity of the waters of the captured springs of the Zlot`s spring, indicates the fact that there is a good correlation between precipitation and the considered variables.

CONCLUSION

The defined equation of multiple linear regression enables the prediction of turbidity values in a certain moment at the Zlot`s spring, based on previously measured values of precipitation, water level and turbidity. In this way, opportunities are created for the management of the company for the distribution of drinking water to realize its strategic plan, to deliver hygienically safe drinking water, in sufficient quantity, at any time through a set of preventive procedures.

From an ethical point of view, the significance of this work is also very important. Water with increased turbidity contains a certain type of bacteria that can cause gastroenteritis. On the other hand, since turbidity entails an increased concentration of organic and inorganic substances, it is necessary to maintain a higher concentration of residual disinfectant in water, in this case chlorine, which increases the possibility of trihalomethane formation in the reaction of residual chlorine and present natural organic matter. It is very important to know that trihalomethanes are carcinogenic and extremely harmful to human health.

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DISPOSAL OF FLYING ASH FROM THERMAL POWER PLANTS

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Abstract

The problem of fly ash as a by-product of thermal power plants is an actual issue. This ash is extremely hazardous to the environment. It contains particles of extremely small diameter that are easily carried by the wind, and have many toxic elements and heavy metals. The scattered particles reach the water and soil, thus causing environmental contamination. Multiple solutions have been offered to remedy this serious problem, which relates not only to the environment (land, air and water) but also significantly affects the health of people living close to the thermal power plants. Remediation of ultra-fine particles spread by aeolian erosion reduces the potential for water and soil contamination as well as crops used by the population for nutrition, and thus for acute and chronic diseases found to be caused by fly ash pollution. The use of elemental sulfur, which is a secondary product of the oil refining process, in order to bind fly ash, manages waste, thus solving two environmental problems.

Keywords: environment, fly ash, heavy metals, solid waste, risk, pollutants, contamination, waste management, protection.

INTRODUCTION

Now days, it is virtually impossible to imagine a life without electricity. The primary energy sources used in power generation are coal, oil, natural gas and fossil fuels. When low-calorie coal types are used in the production of electricity, many environmental pollutants are produced as a result of their combustion. Their combustion produces solid waste as well as harmful gases that lead to significant pollution of water, land and air. One of the biggest problems facing both employees in thermal power plants and, even more importantly, people living near the thermal power plant is fly ash [1].

In most existing thermal power plant installations, ash that has not reacted in the coal combustion process is carried to special landfills where it is deposited. At the exit of the thermal power plant, ash is soaking with water. At the landfill, the water level should be constantly above the ash level to prevent ash spreading [2]. To make an ash watering system more effective, it must be constant, adapted to the weather conditions. Water has to be applied over a larger area than the surface of the ejected ash. This requires a large amount of water, which significantly complicates the ash moistening process without being a permanent solution [3]. In practice, adequate wetting is practically impossible to achieve because the quantities of ash that emerge from the thermal power plant daily are extremely high. Data show that about 35 million tons of coal, mainly lignite, is used in power plants in Serbia annually [4,5]. This type of coal has a lower heat output of 6000-8000 kJ/kg, average moisture content of 45-53% and ash of 10-23%. Daily consumption of coal is from 17000 to 19000 tons per unit of power plant ("Nikola Tesla" thermal power plant, Obrenovac), whereby a significant amount of ash remains by burning coal in thermal power plants, producing every kilowatt of electricity. The landfills where ash is deposited have a total area of approximately 1639 hectares. Between 1974 and today, between 250 and 300 million tons of ash and slag have been disposed. Ash is one of the most common pollutants in the workplace and the environment, polluting land, water and air.

MATERIALS AND METHODS

In this study, the possibility of using elemental sulfur to bond fly ash was investigated. To be used for this purpose, it is necessary to modify the elemental sulfur, which is a secondary product of the oil refining process, with dicyclopentadiene to a chain crystal structure. The process of homogenization and binding of ultrafine ash particles with sulfur would be carried out in the reactor at temperatures of 150ºC to 170ºC by injecting sulfur in an amount of 15% to 22% with intensive mixing of the components. As the ash leaving the thermal power plant is already at the high temperature required for the sulfur agro-metering process, no additional heating of the system is necessary. The ash is fed to the corresponding reactor with a rotary mixer at the exit point from the existing plant. At these temperatures, elemental sulfur enters the molten state boundary, and plays the role of filler and binder. The ash particles get coated, and increase the dimensions and weight. Analyzes show that the particle content of less than 63 μm decreases from 17.5% to 7% (with 15% sulfur added) and 1% (with 22% sulfur added). During the cooling process of the obtained product (after homogenization and agglomeration), a product is obtained that can be deposited much more easily into the landfill without additional use of the wetting system used so far to prevent the fly ash from scattering. The resulting ash-sulfur agglomerate cannot be dispersed by the wind due to the size and weight of the particles. Sulfur that coats the ash prevents heavy metals from leaching from the ash and thus reduces water and soil pollution. This procedure is a permanent solution to the problem of the deposition of ash from thermal power plants, and the problem of environmental pollution also.

RESULTS AND DISCUSSION

The bonding of ultra-fine ash particles with elemental sulfur solves three current problems. This implies a drastic reduction in the amount of fly ash spread by aerosol erosion over the wider area of the thermal power plant. This has a direct impact on reducing the respiratory diseases of the surrounding population, as well as reducing pollution of water and land on which food crops are cultivated. Reducing the intake of heavy metals into the body would significantly reduce the number of patients with malignant diseases. Statistics show that over 50% of the population has respiratory problems, and that almost 2/3 of school and preschool children have similar problems, which can be directly linked to the impact of ash dump. In addition to the complex effects of air pollution factors, other food and drinking factors are also important, as the areas around power plants are mostly populated by agrarian populations, and many households use both drinking water and the food they produce at these locations. Considering the statistical data on the number of patients with respiratory diseases in these regions, environmental pollution in the ash dumps reaches the level of ecological catastrophe. Chemical analysis of ash reveals the presence of heavy metals (Zn, Cr, Cd, Sr, Pb, Co, and Ni) that through the diet indirectly enter the human body and increase the number of cancerous diseases. Remediation of fly ash has therefore become a burning problem from an environmental point of view.

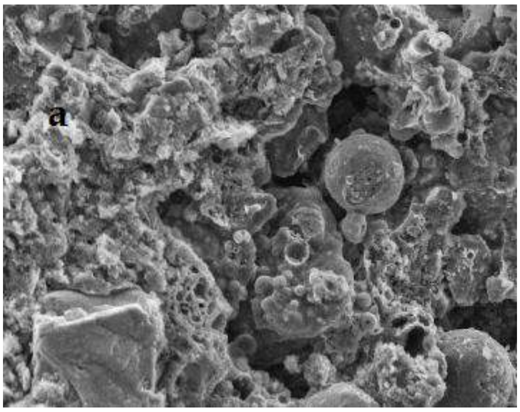

***Figure 1** SEM micrographs original fly ash*

Using sulfur, which is a co-product in the oil refining process, reduces the sulfur landfill, which without that threatens to become a serious environmental problem. Elemental sulfur is a product of oil refining process and a result of desulphurisation of the resulting petroleum products. It is a ballast material and also threatens to become a serious environmental problem. In the future, the amount of sulfur obtained and deposited in this way will be increasing with us, with the tightening of domestic regulations on the sulfur content of petroleum products and the approximation of those regulations to EU norms. In recent years, the world has been intensively working on finding effective ways to rationally consume rapidly increasing amounts of elemental secondary sulfur. This technological solution enables the use of elemental sulfur, which is a by-product of the petroleum refining process, as a binder of fly ash particles of less than 63 μm and reduces the amount of these ultrafine particles from 17.5% to 1%. This would allow its permanent binding to soil and thus suppressing aeolian erosion of deposited ash. Implementing suitable technical solutions shown in this article, it could effectively solve both environmental problems in one place.

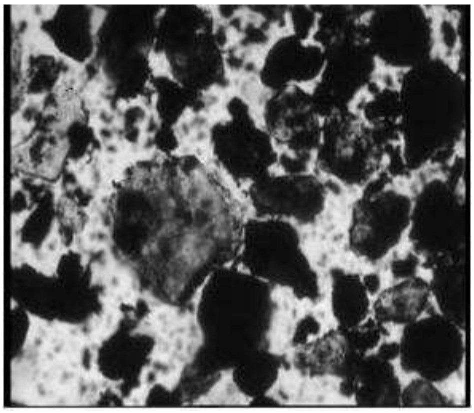

***Figure 2** SEM of a sample of fly ash bound with sulfur*

CONCLUSION

Repairing fly ash problems by bonding to elemental sulfur, it is not necessary to make drastic changes to the existing equipment within the thermal power plant. As the ash temperature at the outlet of the reactor is at the appropriate level required for the sulfur bonding process, it is sufficient to associate the outlet system with a mixer in which to agglomerate. Some solutions even require sintering of the material, which requires the investment of large material assets and new facilities. After sulfur-coated agglomeration, the resulting product is transported to already existing by-products landfills. It is not necessary to use water used in large quantities for the purpose of wetting fine ash particles, which thus far prevents the ash from spreading around the environment and affects the pollution of surrounding soil and water due to the presence of heavy metals in the ash. By wetting system, it would be necessary to ensure that the water level is always above the ash level, which is difficult to achieve under current conditions. Ash binding to sulfur completely replaces the use of water, which significantly reduces material investment, as a problem of summer high temperatures. Elemental sulfur that would be used as a binder for ash agglomeration is available without investment because it is a secondary product in the oil refining industry, and as such is a disposal problem, so this technological solution would practically solve the problem of its disposal as well. Ash after agglomeration can still be used in the construction industry and in the road construction process.

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EFFECTS OF ALLELOPATHY ON THE SPREAD OF INVASIVE SPECIES *Aster Lanceolatus* WILLD. COMPLEX

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Abstract

Aster lanceolatus Willd. *complex is an invasive plant in many European countries. There are several traits that may contribute to the invasiveness success of this species. One of them could be the presence of allelopathic compounds in soil. Therefore, this study set out to assess the allelopathic potential of the topsoil from A. lanceolatus growing sites on bioassay species (Lactuca sativa* L.*). Four localities were selected, and the soil sandwich method was applied. Percentage of seed germination, length of radicles and hypocotyls of bioassay species were recorded. The soil collected from the invaded sites significantly inhibited the germination of L. sativa seeds on three localities. However, the soil from invaded sites promoted elongation of the hypocotyl. Similarly, radicle growth was significantly promoted in treatments with soil from the invaded sites on one locality. From the present study, it can be concluded that allelochemicals are present in the soil infested with this plant and that allelopathy could be an important mechanism that promotes the spread of A. lanceolatus. Further research is needed to investigate types of allelochemicals present in the A. lanceolatus tissue and the mechanisms of their influences.*

Keywords: *Aster lanceolatus* Willd. complex, invasive plants, allelopathy, bioassay

INTRODUCTION

Invasive plants reduce species richness, change habitat and ecosystem functioning, affecting ecosystem services and human well-being [1,2]. Unremitting climate changes affect the plants and the ones that will survive will be those that are capable to evolve or to quickly adapt to changes, migrate and colonize areas that suit them better. Invasive plants have these abilities and it is reasonable to anticipate that they will pose an even greater threat to biodiversity and economy [3].

Aster lanceolatus Willd. complex is a herbaceous perennial, native to North America. This species is considered invasive in many European countries and in many Lists of invasive species it is marked as highly invasive. Previous research showed that *A. lanceolatus* has the ability to influence soil properties [4,5]. It usually grows in the pioneer communities of variable floristic composition [6]. In Serbia, *A. lanceolatus* has become the dominant plant on wet habitats and in some urban areas, reducing floristic species diversity [7]. Its spread is conditioned by species biology and reinforced by climate change, anthropogenic impacts and competitive interrelationships [8].

A great number of studies examined which traits are especially important in terms of climate change and invasion successes and try to predict how invasive species will behave in new conditions. Responses of plants to global changes will be species-specific, with potential influences on community structure [9]. Also, much of the current literature on plant invasion pays particular attention to competition for limited resources and the release of allelochemicals as two main mechanisms contributing to invasion success [10]. Allelochemicals can be excreted into the soil as exudates from living plants or by plant residues and they can inhibit seed germination and plant growth [11,12]. The chemical composition of plant residue, especially the content of secondary metabolites affects the soil organisms and has an important role in the mineralization and absorption of soil nutrients by plants [13]. Biochemical changes in soil may be the result of allelopathic impacts of invasive plants on natural vegetation and by replacing natural vegetation, and by changing species composition, invasive plants alter soil properties and form mono-stands [14–16].

It is noticed that plants exposed to increased CO_2 have increased concentration of carbohydrates, which induced an increase in the concentration of secondary compounds in the leaves which are potential allelopathic substances and thus hinder the allelopathic potential of species [17]. Changes in temperature, precipitation, and climatic variability will presumably have an indirect influence on allelopathy by altering rates of decomposition [18].

It is of great importance to determent traits that contribute to the spread and the formation of dense, monospecific stands of *A. lanceolatus*. Laboratory bioassays can be used to assess the impact of allelochemicals and to eliminate the various interferences through the controlled conditions in which the research takes place [19]. The purpose of this study is to evaluate the allelopathic effect of the topsoil from *A. lanceolatus* growing sites on bioassay species.

MATERIALS AND METHODS

To compare the allelopathic potential of topsoil from invaded and adjacent uninvaded plots on receptor plants, four localities were selected: Beočin, Beška, Kumodraž, and Sremski Karlovci. At each site, several 1 m^2 plots were selected in invaded patches and adjacent uninvaded patches with native vegetation. In each plot, five soil samples 10 x 10 cm, at a depth of 10 cm were collected. Roots and rhizomes were removed from the soil. These five soil samples were air-dried, sieved (< 2 mm) and 200 g of each sample were mixed up to a single sample for each plot.

Lettuce (*Lactuca sativa* L.) seeds were used as the receptor plant in the bioassay. This plant was selected because it has rapid germination and high sensitivity to bioactive substances [20].

Soil sandwich method was applied to compare the allelopathic potential of the soil in invaded and uninvaded sites. Into 9 cm Petri dishes, containing 3 g of soil, 5 ml of agar (0.75%), cooled at 42 ^{o}C, was added [21,22]. After solidification, 3.2 ml of agar was added to the soil-agar layer. 15 *L. sativa* seeds were sown in one Petri dish at 20 ºC (±2) and a 16h photoperiod was applied. Treatments were replicated three times with soil from invaded and three times with soil from uninvaded sites. Percentage of seed germination, length of radicles and hypocotyls of bioassay species were recorded after 3 days.

For all investigated parameters, one-way analysis of variance (ANOVA) followed by Fisher's LSD test ($P < 0.05$) was applied. Germination percentage values were arcsine transformed before being subjected to a one-way analysis of variance. All statistical analyses were carried out using STATGRAPHICS Centurion XVI (Statpoint Technologies, Inc., Warrenton, VA, USA).

RESULTS AND DISCUSSION

Plants that through the production of secondary metabolites have a negative impact on other plants are considered allelopathic [23]. Bioassays can be used to identify the presence of phytotoxic compounds in plant tissue or soil. Comparison of topsoil of invaded and adjacent uninvaded plots with native vegetation will show the impact of invasive plants on some soil properties [24,25]. Also, comparing growth parameters of bioassay species in soil in which the donor plant has been grown in the same soil where the plant has not been grown can indicate the presents of allelochemicals [26].

Except for volatile compounds, most compounds produced by the plants are likely to flow into the soil [27]. According to some authors, soil-free bioassays carried out under controlled conditions, such as Petri dishes, probably overestimate the effect of allelopathy since the soil can significantly neutralize the effects of secondary metabolites [13,26]. To prove the existence of the allelopathic compounds, it is important to evaluate the plant growth activity of soils. Also, agar usage in bioassays provides the transfer of water-soluble chemicals from soil to bioassay species [28].

The soil collected from the invaded sites on all localities significantly inhibited the germination of *L. sativa* seeds, except in treatment with soil from locality Beška (Figure 1). The highest reduction was noticed in treatment with soil from invaded sites from locality Sremski Karlovci.

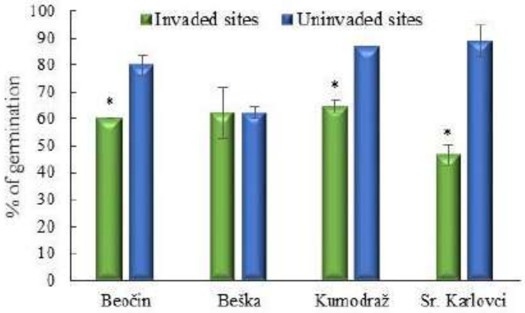

Figure 1 *L. sativa germination percentage in soil bioassay. Bars represent means ± SE. Asterisk above the bars indicates a significant difference among invaded and uninvaded sites on a given locality at* $p<0.005$

The soil from invaded sites promoted elongation of the hypocotyl (Figure 2). Although hypocotyl length was higher in treatment with soil from invaded sites on the other three localities, those differences were statistically significant only at locality Kumodraž. Soil collected from invaded sites on locality Beška significantly promoted radicle growth (Figure 3). Radicle elongation was noticed in the treatment with soil from invaded sites on locality Sremski Karlovci but without significant differences. The length of radicle decreased in treatment with soil from invaded patches on the other two localities, but without significance (Figure 3).

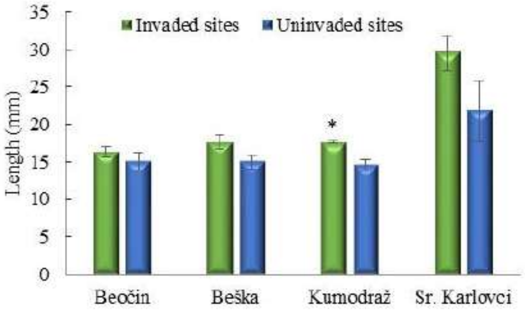

Figure 2 *Hypocotyl growth of L. sativa in soil bioassay. Bars represent means ± SE. Asterisk above the bars indicates a significant difference among invaded and uninvaded sites on a given locality at p<0.005*

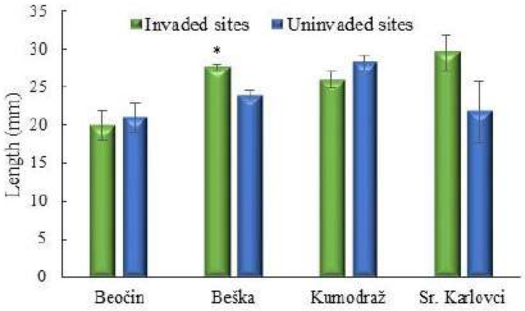

Figure 3 *Radicle growth of L. sativa in soil bioassay. Bars represent means ± SE. Asterisk above the bars indicates a significant difference among invaded and uninvaded sites on a given locality at p<0.005*

In accordance with the present results, previous studie [29] have demonstrated that aqueous extracts obtained from different vegetative organs of *A. lanceolatus* have an inhibitory effect on seed germination and seedling growth of the test species. Inhibition of seed germination of test species in soil bioassay may be the result of allelochemical stress and is a confirmation that the secondary metabolites produced by *A. lanceolatus* are released and accumulated in the soil beneath [30]. Cell division and elongation which are essential for growth are known to be inhibited by allelochemicals [31].

Community composition can be changed by the influence of allelopathic plants [26,27]. It is anticipated that plants will produce greater levels of chemicals under a changing environment which will affect the way plants interact with one another through the processes of competition and allelopathy [9]. It has been suggested that a low concentration of some allelochemicals can inhibit the development of some species, while in higher concentration they may have a stimulative effect on the growth of other species [32]. Initially, these substances can have little impact on community vegetation, but they can have long- term effects [26]. Moreover, over time these substances could increase their concentration in soil [26], and thus their impact on adjacent plants. *A. lanceolatus* is herbaceous perennial and these plants release exudates into the soil over several growing seasons. The results of this study could explain the invasive success and the existence of monodominant stands of this invasive species.

Even though allelopathic inhibition is a separate process from the competition, allelopathic plants can take advantage of this process by excluding other potential competitors [30]. However, separating allelopathy and competition can be difficult since these processes can influence each other [26]. Many phytotoxic compounds were extracted and isolated from plants and their residues [28]. Dias *et al.* [33] found that aromatic water of *A. lanceolatus* inhibited germination and hypocotyl growth of *L. sativa*. Non-native species with allelopathic substances become more competitive in new communities compared to native plants which are vulnerable to new allelochemicals. *Asteretum lanceolati* community in Serbia is characterized by the presents of a large number of invasive species [7]. The results of this research provide further support for the hypothesis that *A. lanceolatus* inhibit the development of indigenous flora, which creates empty space on the site and causes increased nutrient availability that triggers an increase in the number of invasive species in the community.

CONCLUSION

From the present study, it can be concluded that allelochemicals are present in the soil infested with this plant. Components of an ecosystem are closely interlinked and factors that change one component often have an indirect impact on the other. Responses of plants to global changes will be species-specific, potentially shifting plant community structure. Results of this study showed that soil collected from sites infested with *A. lanceolatus* inhibited the germination of *L. sativa* seeds, while it promoted elongation of hypocotyl and radicle of test species. Therefore, the results of this study should be confirmed and supplemented by additional experiments in natural conditions to determine the exact role of allelochemicals in the spread of this invasive species. Also, further research will investigate the types of allelochemicals present in the *A. lanceolatus* tissue as well as the mechanisms of the influences of these compounds.

ACKNOWLEDGEMENT

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CHANGES IN THE DISTRIBUTION OF *Vaccinium* L. GENUS IN RELATION TO THE SOIL ACIDIFICATION SCENARIO

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Abstract

In the hilly and mountainous regions on the territory of Serbia, three species of Vaccinium genus are described: V. myrtillus, V. uliginosum and V. vitis-idaea. As these species present one of the most important biological and economic resources of every country, conservation of their population is very important. Soil acidification is one of the major threats to floristic diversity. In this paper the possible changes in the cover of the Vaccinium species at selected localities, in relation to the scenario of soil acidification, is presented. The investigations are performed in selected mountainous and hilly regions of Serbia: Stara planina Mt., Kopaonik Mt., Vlasina, Kamena Gora and Divčibare. In order to investigate the cover changes of selected species VSD model was used. In addition to changes in cover of Vaccinium species, the changes of cover of the most common characteristic species were also observed. Based on obtained results, it could conclude that soli acidification will not condition decreasing of Vaccinium sp. populations at investigated localities.

Keywords: *Vaccinium* sp., VSD model, distribution prediction

INTRODUCTION

The species of the *Vaccinium* genus include deciduous or evergreen shrubs which belong to Ericaceae family. They are widespread in the mountainous regions of central Europe and in the boreal and sub-arctic regions of northern Europe, particularly on the ground floor of coniferous forests. In the hilly and mountainous regions on the territory of Serbia, three species of this genus are described: V. *myrtillus*, *V. uliginosum* and *V. vitis-idaea*. These species are one of the most important biological and economic resources of every country. Namely, *Vaccinium* species are medicinal plants and their berries are edible and in many countries they are traditionally harvested. Harvesting is very popular in the poor countries, as well as, in developed countries such as Finland, Sweden, Norway as well as Russia [1]. Finland, Sweden, Norway and Russia are the countries where the fruits of *V. myrtillus* and *V. vitis-idaea* are harvested in largest quantities, relative to other species [1–3]. In many countries harvesting of *Vaccinium* species is unsustainable. The unsustainable harvesting is one of the threats to *Vaccinium* species conservation. Also, soil acidification presents one of the major threats to floristic diversity. Soil acidification is a natural process that can either be accelerated by certain human activities [4]. This process caused reduction of the soil pH that is conditioned by nitrogen, sulfur or carbon deposition. Soil acidification affects decrease of floristic diversity. Some investigations [5,6] point out that nitrogen and sulphur deposition in the soil causes changes in populations of *Vaccinium* sp.

In accordance with the importance of *Vaccinium* sp. conservation in Serbia, the goal of this investigation was determined. The main aim of this paper was to determine the possible changes in the cover of the *Vaccinium* species at selected localities, in relation to the scenario of soil acidification, using the VSD model. Obtained results could be useful for future monitoring and harvesting of *Vaccinium* species.

MATERIALS AND METHODS

Phytocoenological investigations

In order to predict the possible changes of the species cover at the selected localities (Table 1), analysis of certain plant communities were done. Phyotcoenological investigation has been performed in period from 2009 to 2012. For the analysis, those plant communities in which *Vaccinium* sp. have high presence degree were chosen.

Table 1 *Selected species at the studied localities for the VSD model*

Localities	**GPS coordinates**	**Species**
Kopren (Mt Stara planina)	N 43°19′56.88″ E 22°47′48.43″	*Vaccinium myrtillus, V. vitis-idaea, Erica carnea, Juniperus communis, Luzula multiflora, Thymus sp.*
Srebrnac (Mt Kopaonik)	N 43°18′59.04″ E 20°50′06.19″	*Vaccinium myrtillus, V. uliginosum, Juniperus communis, Calamogrostis arundinacea, Nardus stricta, Thymus sp.*
Kamena Gora	N 43°17′15.01″ E 19°33′53.88″	*Picea abies, Luzula sylvatica, Oxalis acetosella, Vaccinium myrtillus*
Divčibare	N 44°07′49.12″ E 20°00′55.42″	*Pinus nigra, P. sylvestris, Erica carnea, Daphne blagayana, Vaccinium myrtillus, Avenella flexuosa*
Vlasina	N 42°47'40.20" E 22°22'50.70"	*Bruckenthalia spiculifolia, Vaccinium myrtillus, V. vitis-idaea, V. uliginosum, Avenella flexuosa, Calamogrostis arundinacea*

VSD/Veg model

The VSD (Very Simple Dynamic Soil Acidification Model) model was applied to analyze the acidification process at selected localities. This model is used in order to calculate critical sulfur (S) and nitrogen (N) loads in ecosystems [7].

In order to simulate the spread of certain plant species, within selected habitats over time, based on the input data on abiotic factors (climate and edaphic factors), Veg-model was used. Veg-model is incorporated into the VSD model. The model then calculates the relative surface of the studied habitat that the certain species could occupy, depending on its ability to survive under appropriate habitat conditions. For the simulation of plant species spread, the model does not include a complete list of species found in the area, but includes the edificators and the most common characteristic species. The model performs the simulation of species spread based on the ecological characteristics of the species and the change in abiotic factors which occurs during the selected time [8].

The localities encompassed by this investigation are presented in the Table 1. Also, the Table 1 shows species selected by Veg-model.

RESULTS AND DISCUSSION

Anthropogenic acid deposition–induced soil acidification is one of the major threats to biodiversity, ecosystem functioning and services [9]. As already mentioned, soil acidification implies a decreasing of the soil pH value.

By the VSD model, for the given conditions, for each locality, the trend of the ratio of pH and C/N (carbon to nitrogen ratio) was analyzed for the period from 1960 to 2100, in the soil layer up to 20 cm. Also, for each locality, species that occur with the highest cover in phytocenoses were isolated in order to analyze changes in the cover of these species, and especially species of the genus *Vaccinium,* in the community over time.

Nordin *et al.* [5] found that under certain conditions, related to soil load with nitrogen, population of *Vaccinium myrtilus* и *V. vitus-idaea* would be reduced. At the other hand, Coudun and Gégout [6] concluded that cover of *Vaccinium myrtilus* could be increased up 50 %, when the environmental conditions are such that the pH value of the soil is <4, the C/N ratio is > 30 and the air temperature is <6°C. So, depending on the change in pH and C/N in the soil, changes in the structure of the plant community may occur over time.

At Divčibare, the model has been monitored the changes in the cover of the following species: *Pinus nigra*, *P. sylvestris*, *Erica carnea*, *Daphne blagayana*, *Avenella flexuosa* and *Vaccinium myrtillus*. It can be observed that the model does not predict changes in cover for *Vaccinium myrtillus* and *Erica carnea*. For the other species monitored in the model, significant changes in coverage occurred between 1960 and 2004 (Figure 1).

Figure 1 *Chages of characteristics species cover over time at Divčibare*

From 2010 to 2100 the cover of *Daphne blagayana* and *Avenella flexuosa* will increase, while the cover of *Pinus nigra*, *P. sylvestris* and *Abies alba* will decrease. However, these changes are not significant (Figure 1).

The cover of *Picea abies*, *Luzula sylvatica*, *Oxalis acetosella*, and *Vaccinium myrtillus* has been monitored at Kamena Gora. Figure 2 shows that by 2010 the cover of *Oxalis acetosella* is changing, increasing and decreasing, but compared to 1960 the cover of this species in 2010 is smaller. From 2010 until the target year, its cover will remain unchanged. The cover of *Picea abies* and *Luzula sylvatica* species has been increasing from 2002, with a more pronounced increase in *Luzula sylvatica*. The cover of *Vaccinium myrtillus* grows from 2005.

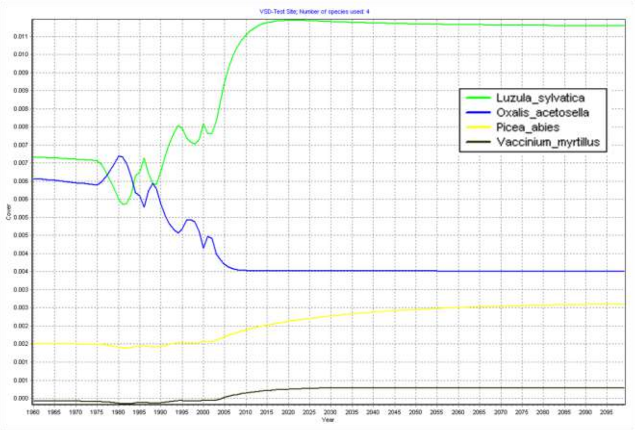

Figure 2 *Chages of characteristics species cover over time at Kamena Gora*

At Srebrnac (Mt Kopaonik) *V. myrtillus*, *V. uliginosum*, *Juniperus communis*, *Calamagrostis arundinacea*, *Nardus stricta* and *Thymus sp*. have been monitored (Figure 3).

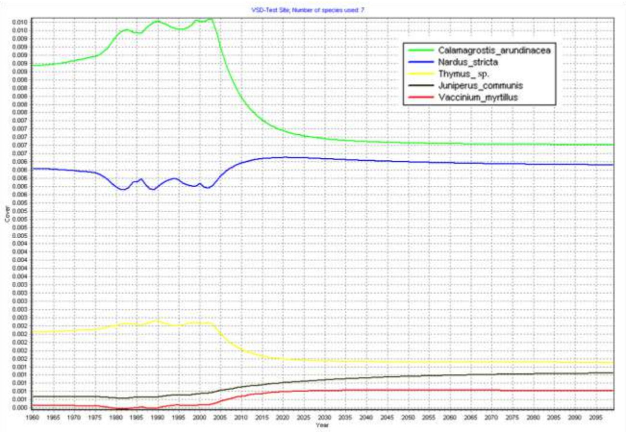

Figure 3 *Chages of characteristics species cover over time at Srebrnac (Mt Kopaonik)*

The largest changes in species cover are recorded for the species *Calamagrostis arundinacea* whose cover declines sharply from 2003 to 2025, followed by a slight declining of cover to the target year. The cover of *Nardus stricta* oscillates between 1975 and 2015, after which it will remain stable until 2100. From 2005 to 2015 cover of the species *Thymus sp.* declines, and after that period it remain unchanged until the target year. Changes in the cover of *V. myrtillus* and *Juniperus communis* have the same trend. Their cover increases gradually from 2000 to 2035, and further, by 2100 it will be stable. However, the model does not predict any changes for *V. uliginosum* at this locality (Figure 3).

By VSD model, the cover of *Bruckenthalia spiculifolia*, *Vaccinium myrtillus, V. vitis-idaea, V. uliginosum*, *Avenella flecuosa* and *Calamagrostis arundinacea* has been monitored at Vlasina (Figure 4).

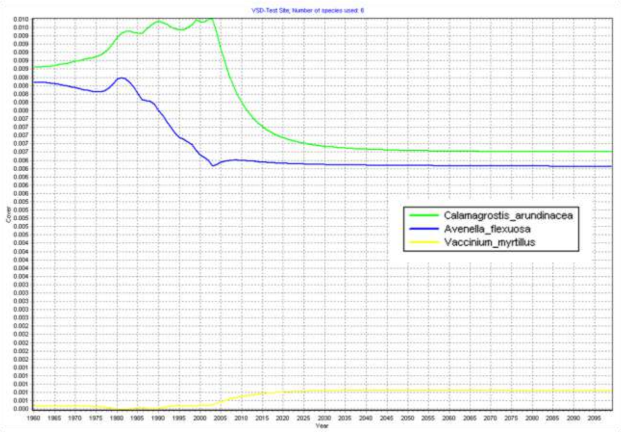

***Figure 4** Chages of characteristics species cover over time at Vlasina*

The model does not register cover changes for *V. vitis-idaea*, *V. uliginosum* and *Erica carnea*. The trend of changing *Calamogrostis arundinacea* cover at Vlasina is the same as at Srebrnac (Mt Kopaonik). The coverage of *Avenella flecuosa* decreased between 1976 and 2003. Furthermore, cover this species remains stable over time. The model predicts an increase of *Vaccinium myrtillus* cover from 2000 to 2015, followed by a stable period.

At Kopren (Mt Stara planina) the changes of the cover of following species has been monitored: *V. myrtillus*, *V. vitis-idaea*, *Bruckenthalia spiculifolia*, *Juniperus communis, Luzula multiflora* and *Thymus sp*. (Figure 5). According to the model the cover of *Thymus sp.* will decline sharply from 2003 to 2020, and after it will gradually stabilize. From 2004, the cover of *Vaccinium myrtillus* and *Juniperus communis* increase by 2030 for *V. myrtillus*, respectively until 2090 for *Juniperus communis*, and after that period stabilization will begin (Figure 5).

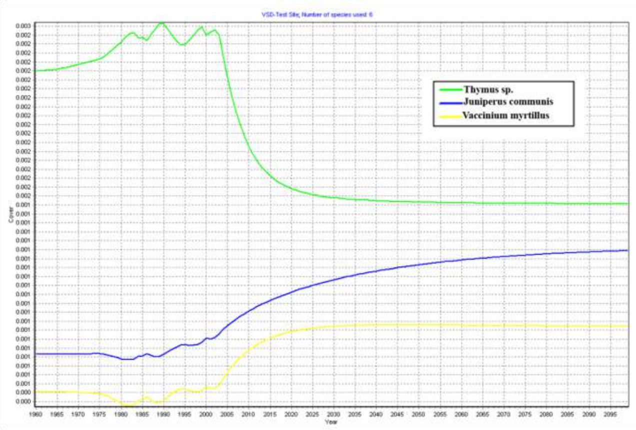

***Figure 5** Chages of characteristics species cover over time at Kopren (Mt Stara planina)*

CONCLUSION

VSD model does not detect changes of cover in *Vaccinium uliginosum* and *V. vitis-idaea* at studied localities. Also, the VSD model does not predict change of *V. myrtillus* cover at Divčibare. At other localities, the model predicts the increasing abundance of *V. myrtillus*. This change is most pronounced at Kopren (Mt Stara planina). Based on obtained results it could be concluded that soli acidification will not condition decreasing of *Vaccinium sp*. populations.

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ADSORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING ACTIVATED CARBON PREPARED FROM HAZELNUT SHELL

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Abstract

The discharge of colored wastewater from different industries into natural streams has caused many significant problems such as increasing the toxicity and chemical oxygen demand (COD). In addition to all the contaminants found in industrial wastewater, dyes are the most undesirable for toxicological and aesthetic reasons. This work describes the adsorption process of one of the most dominant dye in textile and paper industry, methylene blue (MB) from aqueous solutions with activated carbon prepared from hazelnut shell (HSAC). In Serbia hazelnut shells represent an agricultural waste that is generated during the production of hazelnuts and in most cases it's not used for any purpose, usually just disposed on landfill or burned in furnaces. The adsorption process is generally known as effective and complementary to conventional treatments in the removal of dyes compounds. Adsorption studies were performed on powdered HSAC, in ambient temperature, on pH value between 2–9 and with different masses of adsorbent (50 – 1500 mg). The results show that HSAC can be applied in the process of adsorption for the purpose of removing MB from aqueous solution.

Keywords: methylene blue, adsorption, activated carbon, pH value

INTRODUCTION

The visual pollution has a significant impact on residential and tourist areas and it is related to different sources with negative effects on the living environment. Industrial pollution and production are synchronously connected and in developing countries with less environmental regulations with weaker environmental standards, can turn them "pollution havens" for developed countries [1]. Wastewater production has substantially increased due to rapid industrial development, which is ultimately responsible for the degradation of water quality [2].

Dyes are the first indicator of pollutants in wastewater and they are used in many industries such as, paper, carpets, plastics, cosmetics, graphic and textiles in order to color their products and can be classified as natural and synthetic which are complex organic molecules having groups such as azo, carbonyl, methine, nitro, quinoid, etc [3]. Large amounts of complex dye wastewaters are generated as a result of use of too much water during coloring processes, particularly in textile industry [4].

The discharge of colored wastewater from these industries into natural streams has caused many significant problems such as increasing the toxicity and chemical oxygen demand

(COD) of the effluent, and also reducing light penetration, which has a derogatory effect on photosynthetic phenomena [5].

Most of the dyes are resistant to photo-oxidation and non-biodegradable in nature and some of conventional treatment methods such as biological and coagulation/flocculation are generally unsuccessful for the removal of wastewater containing dyes [6]. There are advantages and disadvantages of various methods of dye removal from wastewaters, many physicochemical methods have been tested, but only process of adsorption is considered to be superior to other techniques and it has fascinated the researchers owing to its accuracy, easy operation, insensitivity to toxic substances and ability to treat concentrated colored solution [2,5].

Activated carbons (AC), both granular and powdered, have demonstrated higher adsorbing effects and it is one of the most important general purpose adsorbents in the adsorption technique because of its high adsorption capacity, large surface area and high surface reactivity [7]. Therefore, large numbers of studies have been focused on the production of low cost AC from various plant-based waste materials such as sugar beet molasses, rice husk, hazelnut husk and apricot stone [8–10] and the prepared ACs have been used for the removal of various metal ions or coloring agents from aqueous solutions.

Hazelnut shell (HS) represent a low cost agricultural waste that is generated during hazelnut production, not used for any purpose and generally disposed of by burning in open air in threshing area. Since HS is obtained in large amounts (around 4000 tons per annum in Serbia) and has no economic value, it is thought to be an appropriate source for AC production.

In this study HS agro-based waste material, was used as adsorbent for the removal of methylene blue (MB) from an aqueous solution. Methylene blue was selected as a model compound in order to evaluate the capacity of HS for the removal of dyes from aqueous solutions. During adsorption studies of MB performed by the batch method, effects of three variables; pH values and agitation time, were investigated.

MATERIALS AND METHODS

Chemicals and instruments

Methylene blue was chosen for this study because of its known strong adsorption onto solids. Methylene blue (CI = 52015; chemical formula: C16H18ClN3S; molecular weight = 319.86 g/mol; maximum wavelength = 662 nm) supplied by Merck was used as adsorbate and was not purified prior to use.

An accurately weighted amount of MB was dissolved in deionised water to prepare 1000 mg/L as stock solution, while the working solution was prepared by diluting this solution to the required initial concentrations. The MB concentration evaluation was carried out using UV–visible spectrophotometer (model DR 5000 HACH Lange) at a wavelength of 431 nm. The removal percentage of MB was calculated using the following relationship (1):

$$\%MB\ removal = \left(\frac{Co - Ct}{Co}\right) * 100 \qquad (1)$$

where C_o (mg/L) and C_t (mg/L) are the dye concentration at initial and after time t respectively. The entire experiment was conducted in Accredited Laboratory for the monitoring of living and working environment at Department of Environmental Engineering and Occupational Health and Safety, Faculty of Technical Sciences, University of Novi Sad, Serbia.

Materials

Hazelnut (Corylus avellana L.; the variety is Tonda Istriana) shells (Figure 1) were supplied from the north part of Serbia, Autonomous Province of Vojvodina. Fresh hazelnut shells were washed several times with distilled water to remove surface impurities, dried at 100 0C overnight, crushed by a hammer mill and simultaneously carbonized and activated in microwave oven for 25 minutes.

Afterwards, the granular activated carbon was washed two times with distilled water, dried at 100 0C for 12 h. Dried shells were grinded and sieved to get a powdered hazelnut shell activated carbon (HSAC) and stored in a desiccator.

***Figure 1** Hazelnut shells before and after carbonized and activated in microwave oven*

Methods

For adsorption experiments, 50 mL of dye solution of known initial concentration, in erlenmeyer flasks was agitated on stirrer (model Heidolph Unimax 1010) with a certain amount of adsorbent at desired pH values at room temperature, with speed of 140 RPM for 20 minutes.

pH value of MB solution was 6.0 and during experiments it was adjusted with 0.1 N HCl or 0.1 N NH3OH and measured by using Multi 340i pH-meter with a combined pH electrode. The pH-meter was standardized with NBS buffers before every set of measurement.

RESULTS AND DISCUSSION

Effect of adsorbent dosage

In order to determine the effects of the adsorbent dosage on MB adsorption efficiency on low cost alternative activated carbon, different amounts (50, 100, 100, 200, 400, 600, 1000 and 1500) mg of HSAC was mixed with 50 mL of MB solution, initial concentration of 10 mg/l for 30 minutes.

By increasing the amount of adsorbent, adsorption capacity significantly increased. The removal percentage increased rapidly and further addition has not significantly affected the

MB removal percentage. Therefore, 400 mg of adsorbent was selected for subsequent work (Figure 2).

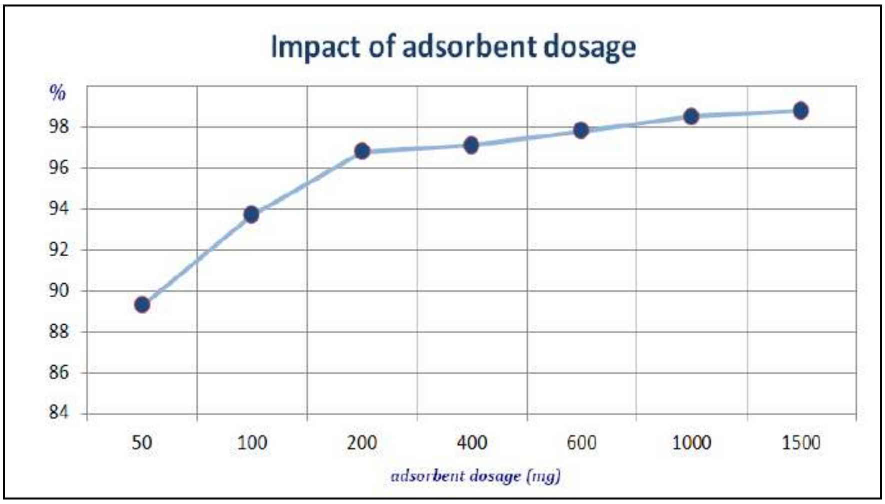

Figure 2 *Mass adsorbent effect on the adsorption of MB onto HSAC (T = 25°C, Co = 10 mg/L, V = 50 mL, contact time = 30 min, pH value ≈5.3)*

Figure 2 shows that on the mass of adsorbents, 400 mg, the efficiency of MB removal is about 97%, with a mass of 1000 mg, efficiency is higher than 98%. With higher dosage of adsorbent, efficiency in the removal of 10 mg/l of MB is 99%.

Effect of solution pH value

After determination of the effects of the adsorbent dosage on MB adsorption efficiency on low cost alternative activated carbon HSAC, using different amounts of adsorbent, it was found that 400 mg is ideal mass for this study and with it was approached to determine a favorable pH value. As it is known, the solution pH has a dominant impact on ions sorption. Figure 3 shows the effect of the solution pH on the adsorption of MB on the HSAC.

The initial MB solution with a concentration of 10 mg/l has the pH value 6.0 and after adding 50 mg of adsorbent in volume sample of 50 ml, pH value was 5.5. The influence of pH values was analyzed at different f points (2, 3, 4, 5, 7, 8, 9) using 0.1 N HCl or 0.1 N NH_3OH. On lower pH values and acidic environment, efficiency of MB removal is lower than in alkaline environment.

Figure 3 shows medium deviations in efficiency of removal MB by HSAC, on lower pH values. The small reduction of the MB adsorption in the acidic solutions could be attributed to the neutralization of free OH groups on the surface of HSAC by bonding with H+ from HCl used for pH adjustment.

Accordingly, since it was found that the highest biosorption efficiency was obtained at pH 5.3, further experiments should be prepared under the same pH condition, respectively, in the future experiments there is not necessary to adjust the pH value of the MB solution, using HSAC.

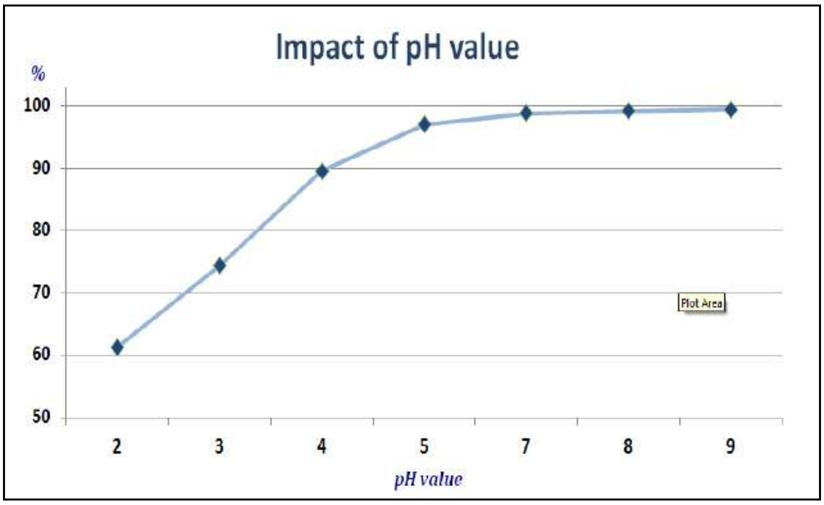

Figure 3 *pH value effect on the adsorption of MB onto HSAC C (T = 25^{o}C, Co = 10 mg/L, V = 50 mL, contact time = 30 min)*

CONCLUSION

The conducted study and presented results demonstrate that it is possible to use HSAC, an agro-based waste biomaterial as a highly efficient adsorbent for the removal of methylene blue from water solutions. The obtained results show that the efficiency of HSAC, for the removal of methylene blue, a non-degradable cationic dye, from aqueous solutions, depends more on the adsorbent amount and not so much of pH value of the dye solution.

HSAC shows excellent abilities in the adsorption process at almost all pH values and the most important data is that during experiments, it is not required to change the pH value of solution, for the cause, efficiency of MB removal on pH value 5.3 is higher than 97%. This study demonstrated that the HSAC could be used as an effective adsorbent for the treatment of wastewater containing MB.

ACKNOWLEDGEMENT

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CONTRIBUTION OF WASTE MANAGEMENT SECTOR IN NOVI SAD TO CLIMATE CHANGE

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Abstract

Waste management system represents the third most important anthropogenic source of emissions of methane, which is considered as primary driver of climate change. This sector produces emissions of methane, carbon dioxide and black carbon, as the main source of particulate matter in the air. Novi Sad, as the second largest city of Serbia, generates significant amounts of municipal solid waste, consisting of more than 50% of biodegradable fraction, which is disposed on landfill without any pre-treatment, and represents the main cause of total greenhouse gas (GHG) emissions (expressed in metric tons CO_2 *equivalent). This paper represents the modelling data for GHG emissions from waste management sector in the city of Novi Sad. The modelling results cover the emissions from all parts of waste management system including: collection and transportation, waste handling at the landfill, waste biodegradation processes and open burning.*

Keywords: Waste management, GHG emissions, methane, climate change

INTRODUCTION

Waste management system represents the third most important anthropogenic source of emissions of methane, which is considered as primary driver of climate change. This sector produces emissions of methane, carbon dioxide and black carbon, as the main source of particulate matter in the air. Novi Sad is the second largest city in Serbia, with a population of approximately 340,000 as of 2014 [1]. Novi Sad and the municipalities of Backa Palanka, Backi Petrovac, Beocin, Zabalj, Srbobran, Temerin, Vrbas, and Becej form the South Backa Waste Management Region (SBWMR) [2]. The SBWMR has a combined population of approximately 600,000 and encompasses approximately 3,000 square kilometers (km^2). General information about SBWMR is presented in Table 1.

The nine municipalities in the SBWMR produce approximately 214,000 tons per annum (tpa) of solid waste. Nearly half of the solid waste generated in the region is organic. Overall, the region produces approximately 65,500 tpa of food waste and 34,500 tpa of garden waste.

The Novi Sad commercial sector (hotels, restaurants, and cafeterias) produces 805 tpa of organic waste from approximately 730 facilities. In addition, the city's schools produce 283 tpa in food waste. Overall, these large-scale generators produce about 1,100 tpa of organic waste, primarily food waste, representing about 3 percent of the total organic waste produced in Novi Sad [3].

Landfilling is primary waste management practice in all municipalities. In addition, recycling is present, but only in certain municipalities and in small percentages. In the city of Novi Sad there is source separation in the downtown, where system with "two underground containers" points (one for recyclables and one for residues) is introduced [4]. From other member municipalities, Bački Petrovac demonstrated some progress in source separation, using plastic bags approach. Relatively greater amounts of recyclable materials are separated within the waste separation line in Novi Sad. Since the input material for the separation line is mostly "low-quality" separated dry recyclables waste stream, the percentage of sorted materials is not high, and does not exceed 10%. Also, the capacity of the current plant is insufficient, and only about 10-15% of the total MSW generated in Novi Sad can be processed [5,6].

Therefore, all biodegradable waste is deposited on landfills without any pretreatment and without controlled emissions of GHG, which poses significant environmental risk. The aim of this paper is to estimate total emissions of methane and black carbon from waste management sector of SBWMR, in order to facilitate decision making regarding mitigation of climate change effects.

Table 1 *General information about SBWMR [1,7]*

	Total population	kg/ capita/ day	MSW (tpa)	Garden waste (tpa)	Food waste (tpa)	Total organic waste (tpa)	Rural population (%)
Serbia	7,164,132						
Autonomous province (AP) of Vojvodina	1,912,095						
Novi Sad	346,163	1.07	135,194	18,075	40,788	58,863	15
Becej	36,663	0.94	12,579	2,533	4,139	6,672	37
Beocin	15,551	0.94	5,336	713	1,610	2,323	52
Backa Palanka	54,631	0.94	18,744	4,658	6,127	10,785	50
Backi Petrovac	13,222	0.86	4,150	838	1,144	1,982	52
Temerin	28,244	0.94	9,691	1,952	3,188	5,140	10
Zabalj	25,873	0.86	8,122	1,641	2,239	3,880	64
Srbobran	16,073	0.94	5,515	1,114	1,520	2,634	26
Vrbas	41,378	0.94	14,197	2,859	4,671	7,530	42
SBWMR	577,798	1.01	213,526	34,384	65,426	99,810	26

EXPERIMENTAL

As part of the research conducted for the purposes of this project, the calculation of baseline GHG emissions is based on implementation of the SWEET tool developed by Abt Associates and SCS Engineers for the US EPA and Climate and Clean Air Coalition (CCAC).

SWEET assists stakeholders in estimating emissions and comparing the emissions reduction benefits of different waste management scenarios. The tool can be used to inform

MSW management decision-making and priority setting and allows cities to benchmark and project their emissions over time [8].

The tool assists users in determining first-order city-level estimates of annual emissions of methane, black carbon, and other pollutants (e.g., carbon dioxide) from various sources including:

- Waste collection and transportation;
- Waste burning (including open burning and fires at landfills and dumpsites);
- Landfills and dumpsites;
- Waste handling equipment (e.g., forklifts, bulldozers);
- Organic waste management facilities (e.g., composting facilities);
- Waste combustion equipment (e.g., waste-to-energy facilities).

Emissions are expressed in metric tons CO_2 equivalent [8].

Except for landfills and dumpsites, the tool generates annual emissions using annual activity data and process-specific emissions factors. For landfills and dumpsites, the tool uses disposal site data to calculate annual methane emissions into the future (i.e., to 2050) using a methodology developed by the US EPA for the Colombia Landfill Gas model [8].

SWEET is designed to provide estimates of waste sector SLCP emissions for cities throughout the world, and to evaluate the effects of alternative waste management strategies on those emissions. Although SWEET uses state-of-the-industry assumptions and calculation methods, the emissions estimates should be considered as approximate and not a substitute for detailed technical analyses and feasibility assessments [8]. Sources of potential model inaccuracies and uncertainties include the following:

- Uncertain emissions factors, particularly for waste burning and landfill methane;
- Uncertain estimates of waste decay rates and methane generation, collection, and
- oxidation rates at disposal sites;
- Limits to the complexity of user inputs, which were made to allow the model to be user-friendly and to limit model sensitivity to lack of data or data error;
- Limits to detailed accounting of site-specific factors influencing emissions.

RESULTS AND DISCUSSION

In order to assess the current state of greenhouse gas emissions using the model described in the previous chapter, it is necessary to define the input parameters that include the following information:

- Population covered by the waste collection system;
- Climate conditions;
- Waste generation data;
- Composition of waste;
- Waste quantities treated by alternative methods (composting, AD, incineration, recycling);
- Number and type of waste collection vehicle;
- Data on uncontrolled incineration of waste (landfill fires and open-air burning);

- Number and type of waste handling machinery at the landfill;
- Landfill information.

The emission results are shown in the Tables 2, and show the emissions of individual greenhouse gas (CH_4, CO_2), as well as particulate matter ($PM_{2.5}$, PM_{10}) resulting from the black carbon emission.

Table 2 *Total annual emissions of selected GHG and particulate matters (tons per year)*

Year	CH_4	CO_2	$PM_{2.5}$	PM_{10}
2019	134.804	8.021	29	14
2020	136.318	8.101	29	14
2021	137.838	8.182	30	15
2022	139.363	8.264	30	15
2023	140.895	8.347	30	15
2024	142.434	8.430	31	15
2025	143.981	8.514	31	15
2026	145.537	8.599	31	15
2027	147.103	8.685	31	15
2028	148.678	8.772	32	16
2029	150.263	8.860	32	16
2030	151.859	8.949	32	16
2031	153.467	9.038	33	16
2032	155.086	9.128	33	16
2033	156.717	9.220	33	16
2034	158.361	9.312	34	17
2035	160.017	9.405	34	17
2036	161.687	9.499	34	17
2037	163.370	9.594	35	17
2038	165.067	9.690	35	17
2039	166.778	9.787	35	17
2040	168.504	9.885	36	18
2041	170.244	9.984	36	18
2042	171.999	10.084	37	18
2043	173.770	10.184	37	18
2044	175.556	10.286	37	18
2045	177.358	10.389	38	19
2046	179.177	10.493	38	19
2047	181.011	10.598	38	19
2048	182.862	10.704	39	19
2049	184.730	10.811	39	19
2050	186.615	10.919	40	19

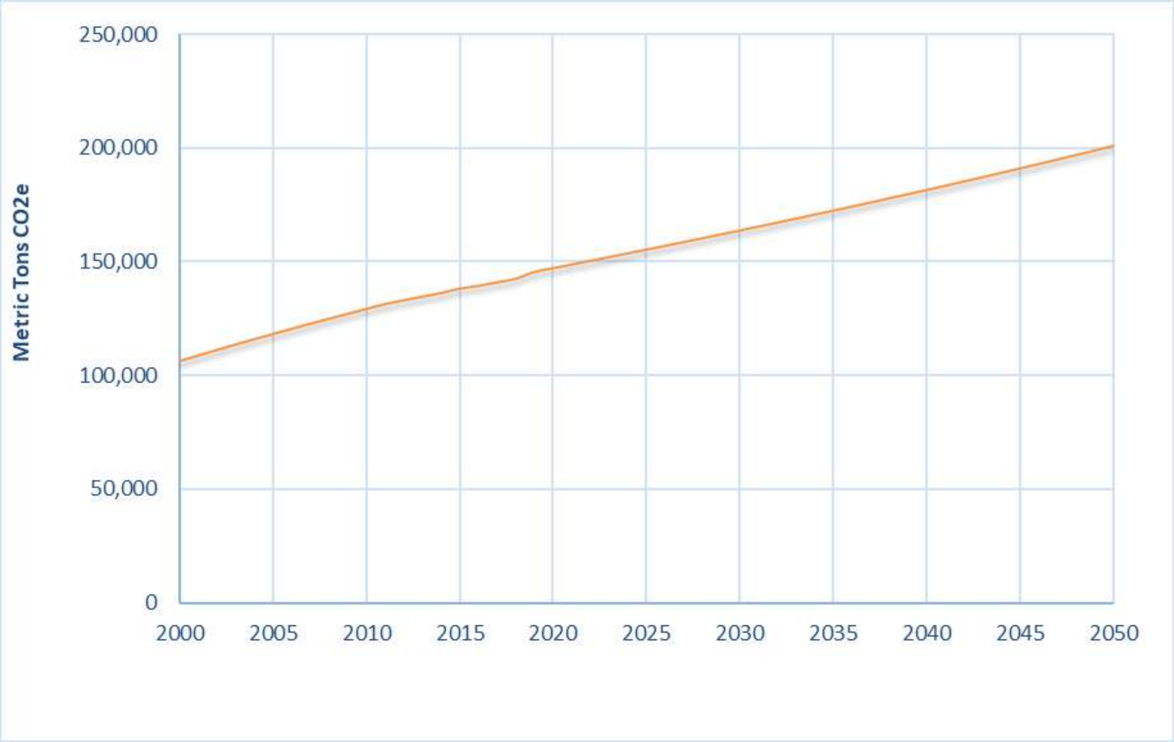

Figure 1 *Total CO_2, NO_x, CH_4, organic carbon, black carbon trends*

Since the baseline waste management scenario in Novi Sad does not imply the treatment of organic waste, total emissions from this sector have a constant growth (Figure 1). In the situation that no improvements of the organic waste management system will occur in the given period, total emissions from this sector are projected to increase by 40% in 2050, compared to the current year.

CONCLUSION

The research was conducted to consider the impact of waste management system in SBWMR on greenhouse gas emissions. Without any changes to waste management practice, emissions will constantly increase and will reach over 200 000 tons of CO_2 equivalent in 2050.

Considering the requirements of the Landfill Directive regarding the reduction of biodegradable waste landfill disposal that should successively reach 65% reductions from the reference year, it turned out that the current system could not result in meeting this objective.

Therefore, in order to reach the biodegradable waste diversion goals, the decision makers within SWMBR will need to start implementing solutions for treatment of biodegradable waste, which include source separation and various treatment options for separately collected organic waste (food waste and green waste).

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OPINIONS AND ATTITUDES OF THE CITIZENS OF NIS ON COMMUNITY NOISE

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Abstract

Community noise is considered a very important environmental factor, due to its harmful effect and increasing exposure. The aim of the study was to assess opinions and attitudes of the citizens of Nis on community noise. A cross-sectional questionnaire survey was performed on 911 adult residents, of whom 388 were men (42.6%) and 523 women (57.4%). Based on noise measurements, parts of the city are divided into a noisy zone (for the daily Leq level ≥ 55 dB A and the night Leq ≥ 45 dB A) and the quiet zone (the daily Leq level ≤ 55 dB A and the night Leq ≤ 45 dB A). The survey used an original questionnaire, adapted to local conditions and requirements, created on the basis of a questionnaire already used in similar surveys. The results showed that the citizens from noisy area ranked noise as the most important risk factor in the 21.20% response, while the same number in quiet streets was 2.5% (χ^2=192.32; p<0.001). The most significant sources of noise for the respondents of both groups were traffic and street works, and the least significant sources of industry and building installations. Respondents to the noisy zone kept windows open for shorter periods of time, more often stating that they would change their apartment due to noise and have worse inter-neighbour relationships.

Keywords: community noise, exposure, population, opinions, attitudes

INTRODUCTION

Due to its detrimental effect and increasing exposure, community noise is considered a very important environmental factor [1]. Long-term noise exposure has a major impact on health and quality of life. In addition to affecting different systems and organs, noise can cause numerous behavioral and social effects that are often complex and indirect. These effects include changing everyday patterns of behavior, changes in social behavior (aggression, hostility, non-hatred), mood swings [2]. Although it is assumed that humans can adapt to noise in their environment, epidemiological studies in residents around noisy roads show that community noise also affects behavior. People living in noisy environments attach special importance to noise, ready to take various measures to protect them from noise, from closing windows facing noisy streets and avoiding going out to streets to filing lawsuits with authorities and changing their place of residence [3]. The aim of this paper was to determine the opinions and attitudes of the citizens of Nis on community noise.

MATERIALS AND METHODS

Traffic noise was measured at six sites in the centre of Nis, of which three were in the city's busiest streets and three in quiet side streets. Measurements were done with a „Brüel & Kjær“ noise level analyzer type 4426. The total number of samples was 9000, with a period of sampling 0.1 s in a fast dynamic range during three day-time (09.00 h to 12.00 h, 13.00 h to 16.00 h and 17.00 h to 20.00 h) and two night-time intervals (22.00 h to 01.00 h and 02.00 h to 05.00 h). Streets with day Leq ≥ 55 dB (A) and night Leq ≥45 dB (A) were regarded as noisy and those with day Leq ≤ 55 dB (A) and night Leq ≤ 45 dB (A) were regarded as quiet, in accordiance with WHO recommendations and Serbian regulation on noise in residential areas. This study was designed as a cross-sectional questionnaire survey. A total of 3000 questionnaires were distributed to residents of three busy streets and three quiet side streets, who served as control. The number of distributed questionnaires corresponded to the number of adult dwellers in each flat. The residents were asked to fill out the questionnaires by the next day, when these were collected. The criteria for inclusion of persons in the research were age between 18 and 80 years and the period of residence in the given apartment is not shorter than a year. The exclusion criteria were exposure to noise at work and hearing loss. Of 3000 distributed questionnaires, 1063 were completed (35.4 %), but applying exclusion criteria, the study included 911 participants, of whom 388 (42.6 %) were men and 523 (57.4 %) women. 463 participants lived in noisy streets and 448 participants in quiet streets. All statistical analyzes were performed using a standard data processing program such as Excel and the SPSS version 16 software package.

RESULTS AND DISCUSSION

Noise measurements showed that the average night Leq was significantly higher in noisy streets than in quiet streets, as well as average day Leq (Table 1).

***Table 1** Characteristics of noise of the investigated areas in Nis*

Measurement parameters	Noisy area	Quiet area	p-value
Leq (dB(A)) day	64.33±2.18	49.62±2.31	< 0.05
Leq (dB(A)) night	61.33±2.31	43±3.46	< 0.05

A comparison of demographic data between the groups showed that noisy area residents were four years older on average, enjoyed fewer square metres of flat area per tenant, and fewer of them had only elementary school education than quiet area residents. The average daily holding time of open windows facing the street during the summer period of the year was statistically significantly shorter for the respondents in the noisy zone. When asked if they would change the apartment because of the noise, over a third of the respondents from the noisy zone and four times fewer respondents from the control zone answered in the affirmative. In the noisy zone respondents, dissatisfaction with their family life, material status and comfort of their apartment was significantly more frequent. Of the total number of respondents, seven reported complaints to the authorities about traffic noise. No statistically significant difference was found between the studied groups (Table 2).

Table 2 *Basic demographic data of examinees*

Variables	Noisy area (N=463)	Quiet area (N=448)	p-value
Age (years) X ±SD	45.0±16.3	41.7±13.6	<0.01*
Males (%)	44.1	41.1	$>0.05^{\#}$
Apartment size (m^2 per tenant)	63.3±18.3	77.7±30.2	$<0.01^{\$}$
Period of residence (years), X ±SD	17.9±13.0	17.9±11.6	$>0.05^{\$}$
Daily time spent in aprtment (h)	14.4±3.4	14.4±3.4	>0.05*
Education (%)			
Elementary	1.9	4.9	$<0.05^{\#}$
Secondary	59.8	58.3	
Higher	10.8	13.4	
University	27.4	23.4	
Keeping windows open during the day (h)	8.2±6.4	12.8±7.9	$<0.001^{\$}$
Very dissatisfied with family life (%)	5.0	2.5	$<0.05^{\#}$
Very dissatisfied with material status (%)	8.7	4.0	$<0.05^{\#}$
Very dissatisfied with the comfort of the apartment (%)	19.0	8.0	$<0.001^{\#}$
The desire to change an apartment (%)	35.4	8.5	$<0.001^{\#}$
Noise complaint (%)	1.1	0.4	$>0.05^{\#}$

*Student's t-test, $^{\#}$Pearson's χ^2 test, $^{\$}$Mann-Whitney U-test

The study showed that the respondents from noisy streets ranked noise as the most important risk factor in the 21.20% response, while the number in quiet streets was 2.5%. The residents from noisy area ranked noise as least important in the 13.0% response, while the number in quiet area was 41.1 % (Table 3).

Table 3 *Rank by importance of different environmental factors*

Rank of importance	Environmonmental factors									
	Air pollution		Waste matter		Noise		Water pollution		Radioactive radiation	
	Noisy	Quiet	Noisy	Quiet	Noisy	Quiet	Noisy	Quiet	Noisy	Quiet
1.	147 (31.7%)	144 (32.1%)	52 (11.2%)	75 (16.7%)	98 (21.2%)	11 (2.5%)	74 (16.0%)	83 (18.5%)	92 (19.9%)	135 (30.1%)
2.	141 (30.5%)	106 (23.7%)	71 (15.3%)	108 (24.1%)	128 (27.6%)	44 (9.8%)	100 (21.6%)	149 (33.3%)	26 (5.6%)	42 (9.4%)
3.	96 (20.7%)	120 (26.8%)	158 (34.1%)	139 (31.0%)	107 (23.1%)	83 (18.5%)	74 (16.0%)	69 (15.4%)	27 (5.8%)	38 (8.5%)
4.	48 (10.4%)	59 (13.2%)	127 (27.4%)	89 (19.9%)	70 (15.1%)	126 (28.1%)	169 (36.5%)	111 (24.8%)	48 (10.4%)	62 (13.8%)
5.	31 (6.7%)	19 (4.2%)	55 (11.9%)	37 (8.3%)	60 (13.0%)	184 (41.1%)	46 (9.9%)	36 (8.0%)	270 (58.3%)	171 (38.2%)
	χ^2=11.42 and p=0.02		χ^2=22.99 and p<0.001		χ^2=192.32 and p<0.001		χ^2=23.33 and p<0.001		χ^2=37.54 and p<0.001	

The most significant sources of noise were traffic and street works, and the least significant sources of noise were industry and building installations (Figure 1).

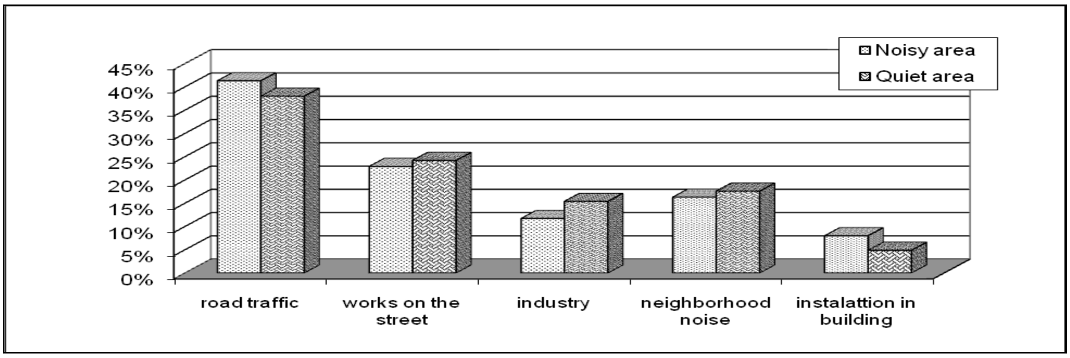

Figure 1 *Rank by importance of the different sources of noise*

In the noisy zone, almost a third of respondents rated their relations with their neighbors as bad or very bad, while this percentage was significantly lower in the quiet zone respondents. The distribution of respondents according to the nature of their relations with their neighbors differed significantly between the groups studied (χ^2 =16.86 and p=0.001).

DISCUSSION

Our study found respondents who lived in the noisy zone were ten times more likely to cite noise as the most significant adverse environmental factor than those who lived in the quiet zone. Noise was rated as the least harmful factor in the noisy zone in 13.0% of responses, and in the quiet zone three times more.

Results similar to ours were obtained by researchers in Hong Kong, where 17% of respondents between the ages of 15 and 69 rated noise as the most important adverse environmental factor [3], as well as a survey in Belgrade (22.9%) [4]. The most significant sources of noise were traffic and street works, and the least significant sources of noise were industry and installations in the building, which coincides with the research of Belgrade authors, where traffic noise was the most significant source for almost 60% of respondents, and street work in one fifth of respondents [4]. Traffic and neighborhood noise were most important for the Copenhagen respondents [5], as well as for the respondents from the eight major European cities included in the large LARES study [6]. On the other hand, a group of Macedonian authors obtained different results. The most significant source of noise in their study among respondents from Skopje was site noise (34%), followed by traffic (24%) [7]. The authors from Slovakia found that the respondents were most disturbed by the noise of fun events [8]. The different results of these studies only confirm the fact that the sources of community noise are numerous, and it is often the case that studies do not all capture and fully capture them. In a Canadian study, respondents were offered eighteen different sources of noise in the questionnaire, and 25% of respondents indicated some new sources of noise to which they attach particular importance. For this reason, future research should well identify all potential sources of noise that could have a negative impact on the exposed population [9].

In any case, no matter what the source of the noise from the outside, one of the measures to protect it from its stressful action is certainly to close the window in the warmer months. People living in noisy areas are more likely to close their windows facing the street, which our research confirmed.

The average daily holding time of open windows facing the street during the warmer period of the year was twice shorter in the noisy zone compared to the quiet and the Belgrade survey [2]. The population opts for this compulsory measure of protection only with extremely high noise interference, as natural ventilation contributes to the improvement of the microclimatic conditions in the dwelling. When the windows are closed, the temperature and humidity of the air in the room increases, which is conducive to the propagation of bacteria and mold. In addition, such conditions on the premises lead to occupant fatigue, decreased concentration and increased susceptibility to infections.

Our research showed that over a third of the total number of subjects in the noisy zone would change their apartment due to noise, while a significantly smaller number of subjects in the control zone would be for this ultimate measure of noise protection. Similar results were found in a survey in Belgrade in which 50% of respondents from the noisy zone were ready to change their place of residence, which is, in fact, the ultimate measure of protection against noise disturbance [2]. Of the total number of respondents, less than 1% complained to the authorities about traffic noise. No statistically significant difference was found between the studied groups. Given the high levels of noise the respondents were exposed to, the small number of them who tried to solve the problem in this way is quite surprising. However, earlier studies have also shown that the number of noise complaints is not a reliable indicator of the extent of population interference, nor is it significantly positively correlated with communal noise levels [3]. Such passive behavior of the respondents is probably due to the population's assessment that the ability of local authorities to solve the noise problem is very limited. Living in a noisy environment probably influenced that, in this study, in the noisy zone respondents, compared to the quiet zone respondents, they were statistically significantly more likely to be dissatisfied with their family life, material status and the comfort of their apartment. Also, a large number of respondents from the noisy zone rated their relations with their neighbors as bad and very bad.

CONCLUSION

Living in a noisy environment caused a significantly higher number of respondents from the noisy zone to consider noise as the most significant adverse environmental factor. The most significant sources of noise for the respondents of both groups were traffic and street works, and the least significant sources of industry and building installations. Respondents to the noisy zone kept windows open for a short period of time, more often stating that they would change their apartment because of the noise and have worse inter-neighbor relationships.

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PHYSICAL-CHEMICAL CHARACTERISTICS OF SM "VELIKI CRLJENI" COAL AND ITS EFFECT ON THE ENVIRONMENT

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Abstract

The aim of this work is to determine the quality of coal in the Kolubara basin, more precisely in the "Veliki Crljeni" mine, which started its operations in 2007. The research comes down to determining the chemical composition, elemental and technical analysis of coal. Significant differences are represented in terms of the geochemical characteristics of coal, the chemical composition, the content of macroelements, the content of heavy metals and other microelements, both in their vertical profile of the main coal layer distribution so as laterally. The results show the differences are particularly pronounced in the contents of some elements, e.g. chromium, manganese, vanadium, arsenic, etc. The environmental impact of coal mining is also briefly overviewed.

Keywords: coal, microelements, macroelements, environment

INTRODUCTION

Coal is a widely available, inexpensive, affordable and reliable source of energy. The geopolitical distribution of the world's reserves is in a much better position than the distribution of oil and gas. Europe's lignite production is still competitive with coal imports, but the economic reserves of major European producers are exhaustive. Efforts to more efficiently and thoroughly exploit coal reserves will reduce the EU's overall energy dependency and as a result, coal in Europe will remain the primary energy source by 2030 [1].

Characteristics of coal

In genetic terms, coal can be humus, derived from the remnants of higher terrestrial plants or sapropellous which originates mainly from lower plants, primarily algae. Coal is almost never pure in the earth's crust; various matter is mixed with a coal substance that reduces its energy (ballast) or pollutes the environment. When decomposed by aerobic conditions, coal loses about 80% of its organic matter, and only 20% remains and participates in synthesis. The elemental composition of the organic mass of coal is characterized by a predominance of carbon (from 65% in brown coals to 98% in anthracite) and a lower amount of oxygen (from 30% to 1%) and hydrogen (from 6% to 1%) [2]**.** Kolubara coal is mostly xylitic and earth-bar, woody structured and with significant content of fusite. Fusite is often mineralized, because its structural openings are filled with clay matter and pyrite. Characteristics of trench coal as a fuel are not the most favorable because, due to the higher content of moisture and minerals, uneven granulation and composition, and therefore low thermal power. Its use is limited to the immediate vicinity of the site. By technological or chemical processing, coal is therefore brought to such a state that it can completely replace the fuels used in high-temperature technological processes, as well as in direct combustion for electricity and heat production [3].

There are two ways to express the composition of coal; by technical analysis, where moisture, volatiles, carbon and ash are determined or by elemental analysis, which determines the chemical composition, content of macronutrients, heavy metals and other microelements. Elemental analysis also allows the thermal value of some coal to be calculated, and the composition of the relays can to be determined [4].

Kolubara basin

The Kolubara basin is one of the largest lignite basins in the Republic of Serbia, located south of Belgrade. It began to be exploited around 1910. The first thermal power plant was built in 1936 within the basin, more precisely in Veliki Crljen. The Kolubara part of the basin covers over 600 km^2 of surface. There are excavation fields A, B, C, D, as well as the mines of Vreoci, Veliki Crljeni, Kolubara, Kosmaj, Baroševac Tamnava etc [5].

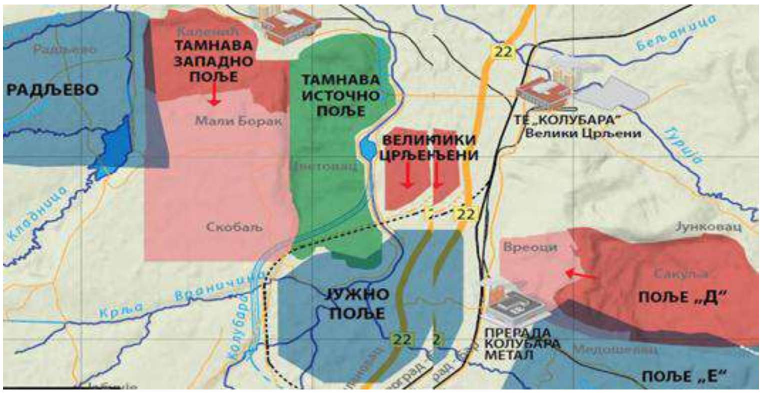

Figure 1 *Surface mines in the area of SM „Kolubara"*

MATERIALS AND METHODS

Coal samples for analysis were taken from the wells of the main coal seam in the „Veliki Crljeni" field, more precisely in the Q_0/ Q_{qr}-120 well located in the western part of the field where the exploitable part extends between the eastern boundary of the SM „Tamnava-Istočno Polje" and the Belgrade- Bar railway line.

A major coal seam is drilled in the well in the depth range from 8.90 m to 26,10 m. The profile was tested with 4 samples, representing vertical intervals from 0.60 m to 5.00 m. During sampling, all cores from the exploratory well had a natural moisture content of the reservoir because they have an impact on the determination of coal quality.

In the first part of the work, the samples were dried at room temperature, ground and pulverized. The content of coarse, hygroscopic moisture, ash content and thermal power were determined. Technical tests were performed in the laboratory of MB Kolubara, using the standard methods [6].

In the second part of the paper, macro and microelements in coal are analyzed. All analyzes were done by X-ray fluorescence spectroscopy, using the device *ARL Optimix (Thermo Electron Corporation, USA)*. This method has also been recognized by the American Geological Society for Coal Analysis (“*Methods for sampling and inorganic analysis of coal”, U.S. Geological Survey Bulletin 1823*). Due to very low concentrations, some microelements were determined by atomic absorption spectrophotometry (AAS): Hg, Cd, Th, U, Se, Be, Co, As.

RESULTS AND DISCUSSION

Coal samples taken from the well represent the entire interval of the punctured layer in the well. The results of the coal analysis of the main coal seam in the "Polje Veliki Crnjani" in the well Qo / Qqr-120 are given in the form of tables.

Table 1 *Technical analysis of the coal of the main coal layer in the "Polju Veliki Crnjani"*

Samples	1	2	3	4	Medium value
Depth (m)	8.90–13.90	13.90–18.50	19.50–24.50	24.50–25.10	
Moisture %	60.80	58.20	59.30	53.80	58.03
Ash %	5.60	6.50	5.10	9.00	6.55
GTE (кJ/кg)	8890	9203	9450	10207	9438
DTE (кJ/кg)	7064	7436	7658	8542	7675
Δ=DTE-GTE (кJ/кg)	1826	1767	1802	1665	1765

The moisture content of coal in the vertical profile of the coal layer shows a trend of declining from the highest to the lowest level, and the ash content shows the opposite trend - it’s increasing in the profile of the layer from top to bottom GTE and DTE in the vertical profile of the coal bed progressively increase from the highest to the lowest part and they are opposite to the trend of changing moisture content (negative correlation). Free moisture, ash and sulfur are not desirable constituents of fuel [7,8].

From this, as well as from a number of other analyzed geological coal wells and the corresponding measured trench coal, discrepancies between geological measurements and measurements during exploitation can be observed. The cause of such phenomena is the secondary presence of tailings and this analysis once again confirmed the dependence of the decline in coal quality and its pollution by the presence of tailings [9].

The forthcoming coal exploitation in this basin has to be viewed through increasingly complex geological conditions, primarily through the increasingly complex geological structure of the coal layers, which are built with an intensive participation of overburden layers with a thickness of more than 1 m. This, in exploitation terms, automatically means an increased participation of "bad lots" coal.

Macro and microelements in coal

The chemical composition of coal, that is, the content of macroelements in coal, in the well profile Qo / Qqr-120 is shown in Table 2.

The most abundant component is SiO_2 (3.26 - 22.65%), and in the lowest part of the coal bed profile it grows fairly progressively and then decreases significantly.

Table 2 *Chemical composition-content of macronutrients in the coal in the „Polju Veliki Crljeni“*

Samples	1	2	3	4	Medium value
Depth (m)	8.90–13.90	13.90–18.50	19.50–24.50	24.50–26.10	
SiO_2	11.6	22.65	10.42	3.26	11.98
TiO_2	0.14	0.11	0.25	0.01	0.13
Al_2O_3	3.93	5.12	2.87	1.24	3.29
Fe_2O_3	1.47	1.31	2.48	1.33	1.65
MgO	0.18	0.20	0.14	0.11	0.16
CaO	2.65	1.43	1.66	3.30	2.26
K_2O	0.40	0.70	0.23	0.07	0.35
P_2O_5	0.01	<0.01	0.01	0.01	0.01
S	1.09	0.945	2.207	1.602	1.460

If the highest interval of the layer is excluded, the aluminum content shows the same trend of down enrichment as for silicon (Figure 2).

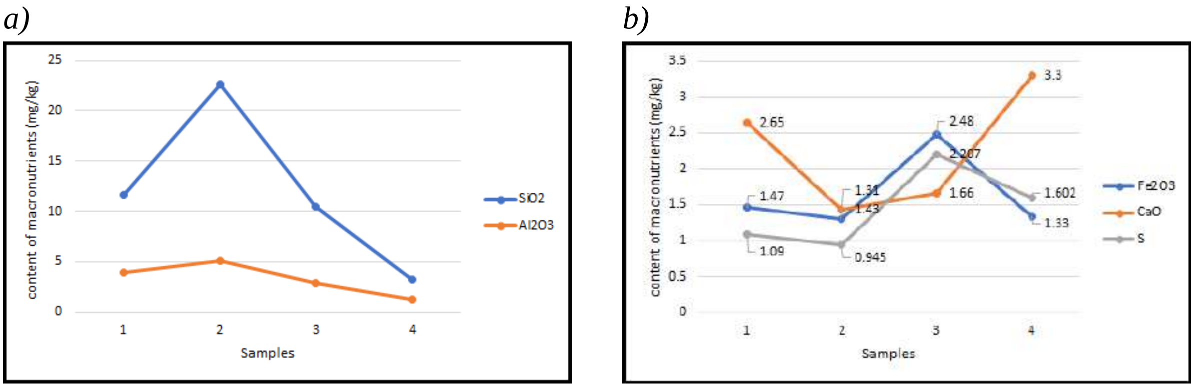

Figure 2 *Change of trace elements concentration with dept*

The contents of S, Fe_2O_3 and CaO correlate very well and they are in smaller quantities in the higher part compared to the lower part. The concentrations of MgO, K_2O, TiO_2 and P_2O_5 are low in all samples [10].

The contents of heavy metals and other microelements in the profile of the Qo / Qqr-120 well are shown in Table 3. The values of the microelements by depth show a parabolic arrangement for all elements except Ni and Zn which show linear dependence with respect to depth. Most elements (As, V, Zr, Hg, Pb) have maximum values at 19.50-24.50 m, except Mn, Ni and Zn which have the highest values at 24.50-25.10 m [11].

Mercury, chromium and manganese, although occurring in low concentrations, pose a threat to the environment [12]. All elements except the Mn, Ni and Zn have minimum values at the greatest depth. If the results in depth are viewed solely through minerals, uneven granulation and composition, then the changes in microelements in depth should be constant growth curves (except for Pb) [13].

Table 3 *Content of heavy metals and other trace elements in coal in the "Polje Veliki Crljeni"*

Samples	1	2	3	4	Medium value
Depth (m)	8.90–13.90	13.90–18.50	19.50–24.50	24.50–25.10	
As	55	45	65	45	53
Ba	175	160	170	55	140
Cr	1070	4540	850	195	1664
Cu	85	90	75	65	79
Mn	225	95	85	430	209
Ni	25	20	30	35	28
Sr	95	55	50	45	61
V	35	30	85	20	43
W	< 1	< 1	< 1	< 1	< 1
Zn	65	60	75	80	70
Zr	8	6	9	7	8
Hg	0.31	0.32	0.28	0.27	0.30
Cd	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Pb	48	44	39	38	42
Th	< 1	< 1	< 1	< 1	< 1
U	< 10	< 10	< 10	< 10	< 10
Se	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Be	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Co	7	12	5	9	8
Cl	200	200	200	300	225

The mechanism responsible for such distribution is petrographic composition, degree of carbonization and deposition.

Sources of harmful substances in various operations in environmental wells

Many years of massive coal exploitation created large quantities of tailings that were landfilled in inappropriate locations. In addition to the depletion of natural resources and pollution of water, air and soil, this fact has also led to significant destruction and degradation of land. Landfills in Serbia are estimated to have between 1.4 and 1.7 billion tonnes of overburden tailings and about 700 million tonnes of flotation and separation tailings.

About 40,000 acres of land have been degraded by surface mines and tailings dumps in large mining basins. Recultivation covered less than 20% of the degraded land area [14,15]. Considering the technology of coal mining on surface mines, sources of harmful substances or environmental hazards may be considered [16].

CONCLUSION

The results of testing of Kolubara coal in the coal field "Polje Veliki Crljeni", in terms of its ability to produce products of the highest calorific value through preparation and processing, indicated that this coal is characterized by the highest ash and coke content, and the lowest GTE and DTE values. In addition to the high percentage of moisture, a larger amount of inorganic matter is present in some samples.

The chemical composition of coal is dominated by Al, Si, Ca, and Fe, and there are also significant amounts of S. At higher concentrations there are B, Cr and Mn, St and Cl, and slightly less Cu, Zn, Pb, As, Ni, and others. Exactly these elements, with a change in pH, can become mobile and bioavailable. Their concentration can increase which leads to human health hazards and environmental pollution.

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IMPLEMENTATION OF QUALITY CONTROL ON SAMPLED SOIL WITH TRIP AND FIELD BLANK

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Abstract

The quality control of the sampled soil is monitored by Trip and Field Blanks according to the ISO 18400-106:2017 standard. Except these blanks, before terrain sampling, it is necessary to form so called Zero Blank, which is analyzed element by element, and on which soil samples are to be analyzed. Returning from the terrain, Trip and Field Blanks are to be analyzed as well. Soil sampling was conducted on the following places: Kostolac, Prahovo and Coka Korugu. After every sampling on this place the quality control was implemented by Field and Trip Blank, as well as by duplicated control samples. Soil sampling on this terrain was carried out every three months. Samples were tested on Cu (ppm) and presented on R-control maps, that also implicate on the absence of the cross contamination in the process of sampling, transport, preparation of the chemical analysis. All this is confirmed by the analysis results which are below the detection limit and alert limit.

Keywords: soil sampling, quality control, Field and Trip blanks, R- control maps

INTRODUCTION

Soil is a complex heterogeneous matrix composed of mineral and organic solid matter, liquid and gaseous components and living organisms. It presents the important part of the urban ecosystem which directly or indirectly has impact on life quality and people's health. Industrial and urban development of human society among many advantages and benefits, results in environmental pollution and soil pollution as well. So, it is of the great importance to do the soil control and analysis more frequently.

Sampling is the beginning and the basis, on which depends the accuracy of the output results of chemical analysis of sampled soil. Mining and Metallurgy Institute has established procedures and standards for quality control.

For the blank forming can be taken any kind of soil, only thing to be known is the zero chemical soil composition so called zero blank. After soil sampling, the chemical composition of trip and field blanks are compared with the chemical composition of the zero blank.

If there are no significant deviations between the blanks and the zero blank, it can be concluded that no cross contamination occurred during the sampling and transport, which guarantees the accuracy of soil sampled chemical analysis [1].

SAMPLING QUALITY CONTROL

Sampling quality control has 3 main goals: Monitoring and detecting errors which may occur in the process of sampling, sampling error control and to present the sampling variability [2].

Precondition for accuracy and reproducibility of analytical results is sampling quality control that includes the following:

- Representativeness of the sampled material;
- Prevention of contamination during the terrain sampling, transport to the laboratory, storage and preservation of samples and preparation for chemical analysis.

Inadequate sampling can lead to the unexpected effects, for example, to the change of chemical composition of samples, which can bring into question the accuracy of chemical analysis inputs. In order to prevent the unwanted effects, in the Mining and Metallurgy Institute laboratory, the quality control is done by:

- Using field and trip blanks;
- Taking double control samples by each sampling in order to check sampling precision.

They provide information which ideally rejects all mistakes of possible sources of contamination, sampling inconsistency and check of applied analytical technics.

ZERO FIELDS AND TRIP BLANKS

For blank forming can be used soil of different chemical and physical characteristics. It is recommended to use unpolluted areas. Parameters on which zero, trip and field blanks are analyzed must be known before the coming on the terrain, they must be the same as the parameters where the sampled soil is to be analyzed [2–4].

Trip blanks are used to detect prospective mutual contamination of blanks during the transport and are also used to confirm or eliminate possible cross contaminations of samples. The sample must go through the entire process, from transport to the laboratory, preparation on the ring mill and chemical analysis.

Trip blank is analyzed on chemical elements, on which the soil samples will be analyzed, before going to the terrain. The sample must go through the entire process, from the field sampling, transport to the laboratory, preparation on the ring mill and chemical analysis. This way confirms or eliminates possible inconsistency in entire process, considering transport than preparation and chemical analysis at the end.

Comparative analysis of field and trip blanks with zero blanks, determines possible contamination of sampled soil, proper sampling method with previously established sampling plan or excludes the possibility for negative outputs.

CHEMICAL ANALYSIS AND SAMPLE PREPARATION

All samples including, control samples, field and trip blanks are transported to the laboratory for preparation and are stored according to the ISO18400 Soil quality-sampling-part105: Packaging, transport, storage and preservation of samples standard [4,5].

Preparation includes the following steps: sample drying at 40ºC, or on the air, exemption of representative samples for particle size analysis by aerometric, exemption of representative samples for chemical analysis and grinding the sample in the ring mill on the particle of 85-90% -75 µ. The prepared soil samples, in ring mill, are dissolved in the automatized system for digestion "Vulcan-Questron Technologies", with the addition of 3 different acids (HCl, HNO_3 and $HClO_4$) and the process of digestion is done in Teflon container on the temperature of 200ºC.

Measured soil amount is 0.25 g and after the dissolving, the samples are moved to the normal container and the final volume of the dissolved sample was 25 mL. The prepared samples are further tested for copper content by ICP MS method.

An Agilent SPS 4 autosampler was used to deliver the samples. Standard Ni-cones were used. The operating conditions are shown below.

Multi-element standard solution for ICP MS, concentration 10 µg/ml, Calibration Standard#2, Ultra Scientific (Al, As, Ba, Be, Bi, Cd, Ca, Ce, Cr, Co, Cu, Ga, In, Fe, Pb, Li, Mg, Mn, Ni, K, Rb, Se, Na, Sr, Tl, U, V, Zn) was used to prepare the external calibration curve (from 1 to 200 µg/L). All solutions were prepared using Milli-Q® water (18 $M\Omega \cdot cm^{-1}$). To prevent contamination, all glassware and plasticware were acid-washed before use.

All the blanks undergo the same way of preparation, and are analyzed with all samples on the same element after coming from terrain. Exceptions are zero blanks whose composition must be known before going on the terrain. For each location are formed zero, trip and field blanks.

RESULT AND DISCUSION

Soil sampling is conducted according to the criteria which is applied in the Republic of Serbia, and are in accordance with standard norms [5–8].

In Tables 1, 2 and 3 are presented rezults of analyzed blanks for the given sampling periods. Results of analyzed control samples are presented in Table 4 and Table 5 presents limits of R-chart, on the basic calculated values of relative range.

According to the values of relative range, the control limits of R-chart are calculated for control samples, central lines, warning limits, detection limits, and presented on R-charts. From R-charts can be clearly seen that there is no outliery-the values that bounced off from the calculated limits [1,8].

Looking at the results of chemical analysis on copper for indicated period we can come to possitive constatation , according to the cross contamination during the transport, preparation and chemical analysis at the end, which leads to the conclusion that the sample contamination during the entire process is excluded and any inconsistency in the entire process from sampling to the the preparation and chemical analysis did not occur.

By comparative analyse of the sample, trip and fild blanks, zero blank we come to the minimal deviations, which can be regarded as negligible.

Table 1 *Comparative chemical analysis zero blank with field and transport blank, Cu content (ppm) - mean of two measurements, sampling site of Čoka Korugu*

Month of sampling Sample name	January	March	Jun	September	December
Zero blank	34.0	33.9	33.6	33.6	34.0
Trip blank	34.4	34.3	34.5	34.7	34.4
Field blank	34.1	34.2	34.1	34.3	34.1

Table 2 *Comparative chemical analysis zero blank with field and transport blank, Cu content (ppm) - mean of two measurements, sampling site of Kostolac*

Month of sampling Sample name	January	March	Jun	September	December
Zero blank	44.7	44.6	44.7	45.0	44.9
Trip blank	45.0	45.1	44.2	44.7	44.0
Field blank	44.4	45.0	44.0	45.4	45.5

Table 3 *Comparative chemical analysis zero blank with field and transport blank, Cu content (ppm) - mean of two measurements, sampling site of Prahovo*

Month of sampling Sample of name	January	March	Jun	September	December
Zero blank	51.5	51.8	51.8	51.0	51.6
Trip blank	49.9	51.2	49.6	50.0	50.5
Field blank	50.0	52.2	49.9	50.5	51.5

Table 4 *Chemical analysis of control samples on Cu content (ppm), sampling sites of Čoka Korugu Kostolac, Prahovo*

Month of sampling Sample of name	January	March	Jun	September	December
KK1ČK	52.9	53.2	54.0	53.4	53.5
KK2ČK	51.7	52.2	51.8	53.0	51.3
KK1K	64.3	65.2	63.6	65.1	64.5
KK2K	64.7	65.3	64.1	66.5	65.7
KK1P	70.0	71,1	68,9	71.3	73.5
KK2P	71.6	73.3	70.0	69.2	73.8

Table 5 *Results of R-chart , CL- center line, CL, WL alert limit, and AL detection limits, ppm*

Month of sampling	January			March			Jun			September			December		
Sample of name	CL	WL	AL	CL	WL	AL	CL	WL	AL	CL	WL	AL	CL	WL	AL
KK1ČK	0.22	0.552535	0.718901	0.22	0.552535	0.718901	0.22	0.552535	0.718901	0.22	0.552535	0.718901	0.22	0.552535	0.718901
KK2ČK	0.18	0.452074	0.588191	0.18	0.452074	0.588191	0.18	0.452074	0.588191	0.18	0.452074	0.588191	0.18	0.452074	0.588191
KK1K	0.24	0.602766	0.784255	0.24	0.602766	0.784255	0.24	0.602766	0.784255	0.24	0.602766	0.784255	0.24	0.602766	0.784255
KK2K	0.22	0.552535	0.718901	0.22	0.552535	0.718901	0.22	0.552535	0.718901	0.22	0.552535	0.718901	0.22	0.552535	0.718901
KK1P	0.21	0.505625	0.662143	0.21	0.505625	0.662143	0.21	0.505625	0.662143	0.21	0.505625	0.662143	0.21	0.505625	0.662143
KK2P	0.3	0.753457	0.980319	0.3	0.753457	0.980319	0.3	0.753457	0.980319	0.3	0.753457	0.980319	0.3	0.753457	0.980319

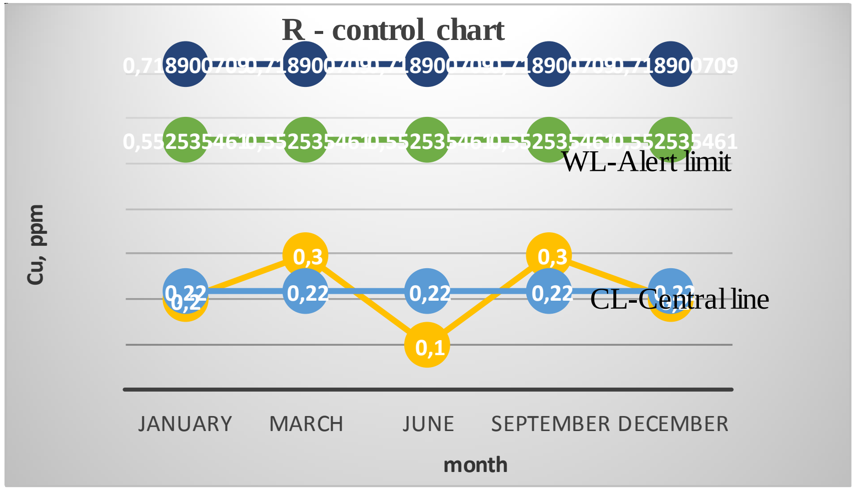

Figure 1 *R chart of control sample KK1ČK*

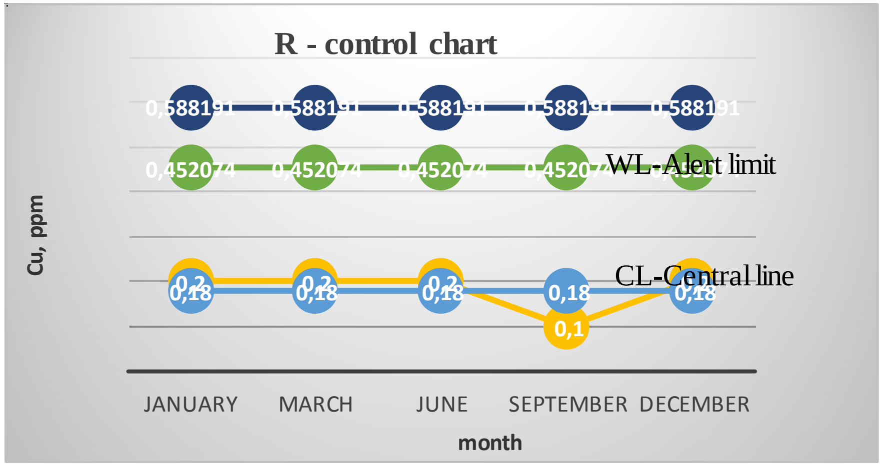

Figure 2 *R chart of control sample KK2ČK*

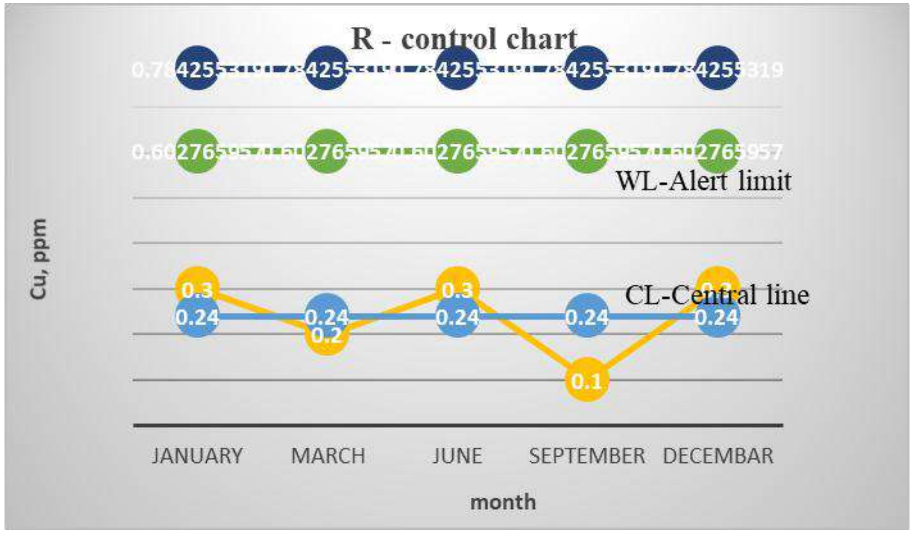

Figure 3 R chart of control sample KK1K

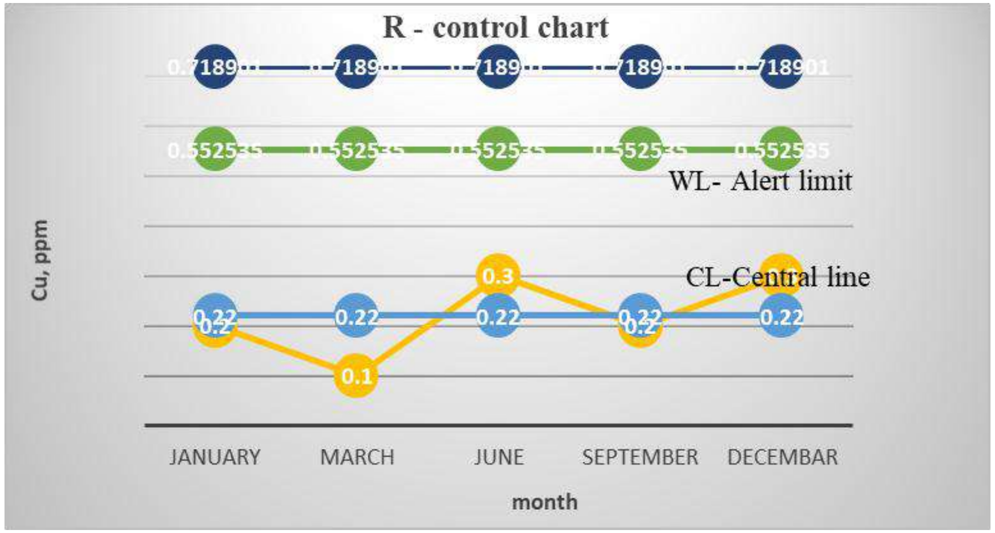

Figure 4 R chart of control sample KK2K

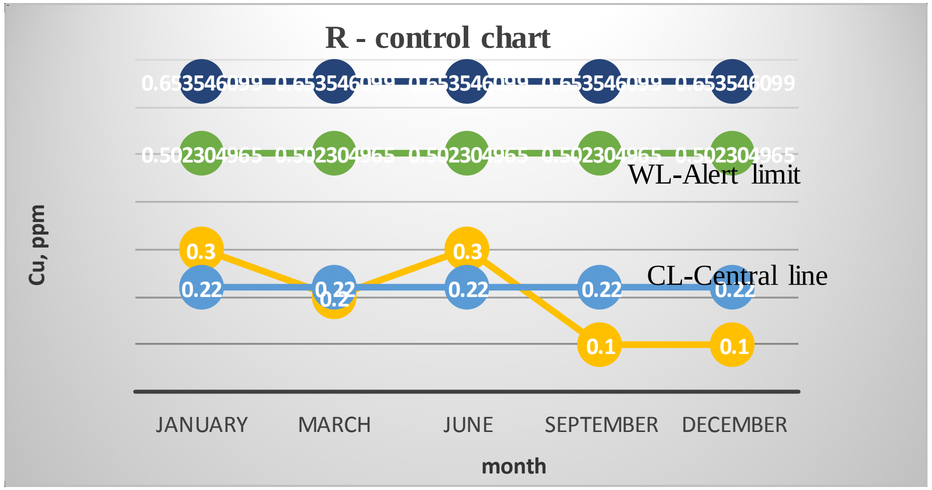

Figure 5 R chart of control sample KK1P

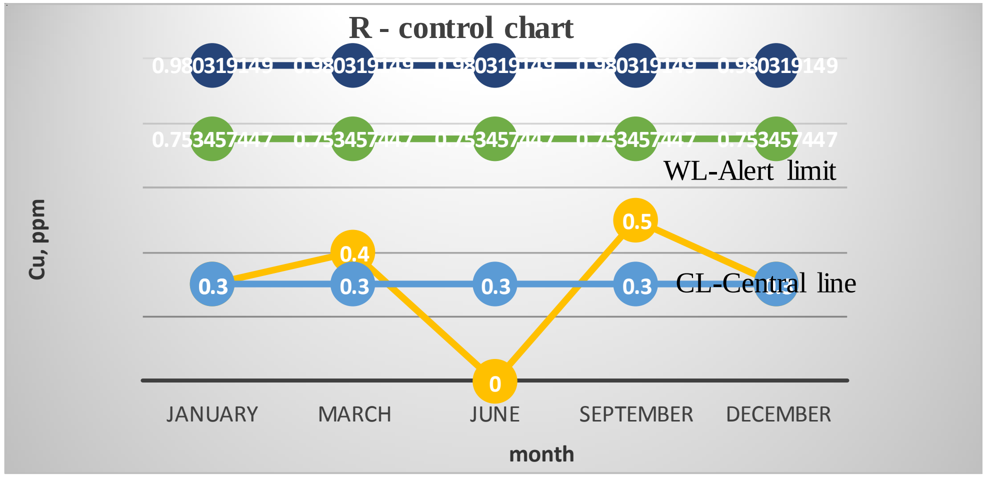

Figure 6 R chart of control sample KK2P

CONCLUSION

On the locations Coka Korugu, Kostolac i Prahovo, the soil sampling was done every 3 months according to the standards norm. Results of the analyzed parameter, copper, on the sampled soil are not part of this work, for justified reasons, except the copper content in blanks and control samples. The sampling and sampler control was done in laboratory in two ways:

- with field and transport blanks;
- and with taking control samples in duplicate.

Results of chemical analysis of control samples are presented on R-maps. R-control map is made of the range of two measurements and of the difference in results of two measurements. The value of the arithmetical range is used as a central line (CL). Standard deviation is used for calculation of control limits where the Al is limit of action and WL is warning limit.

Results from the R-control map present that all the results of analyzed parameters on blanks and control samples, go into range of measuring and are acceptable, and can be used for further statistic data, as well as the quality of sampling and measurements in specific period of time.

The double samples are used for monitoring the sampling quality and precision of analytical laboratory processes. Field and trip blanks illustrate the effects of managing the samples, they reveal the contaminations such as dust and atmospheric precipitation.

Examining and analyzing result from the Tables 1, 2 and 3 we can conclude that the deviation values of field and trip blanks are minor in comparison to the zero blank. The entire process of sampling, transport, to the preparation and analyze of the samples is conducted in adequate and accurate way relying on previously mentioned standards, relevant legislation and examining methods.

The conclusion is that the adequately conducted quality control on soil sampling on the terrain results in high accuracy of chemical analysis outputs. R-control charts of field, transport and zero blanks, because of the limited number of pages, were not presented in this work [8,9].

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support TR 33023 and 34005.

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ENERGY, RENEWABLE ENERGY SOURCES, POTENTIALS AND APPLICATIONS

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Abstract

The need for the use of renewable energy sources has surfaced over the past several decades since alarming data has been released on the effects of greenhouse gases emitted by combustion of fossil fuels. Renewable energy sources include the energy of watercourses, wind, solar energy, biomass and geothermal energy. The use of renewable energy sources is imposed as a very acceptable option in providing energy for the future and for stopping further environmental degradation.

Keywords: renewable energy sources, energy, environmental

INTRODUCTION

While energy is at the heart of economic and social development, its production, transportation and use are the cause of a wide range of major environmental problems at the local, national and global levels. The demand for energy, mostly met with fossil fuels (particularly oil and coal), has increased steadily during recent years, with an average growth in demand of roughly 2% per year in the 1990s. Demand is expected to continue growing, especially in developing countries, as access to energy plays a critical role in alleviating poverty through rural job creation, education, improved health and living conditions.

The energy systems developed so far to meet this demand are clearly unsustainable, as they lead directly or indirectly to health-damaging levels of air pollution, acidification of ecosystems, land and water contamination, loss of biodiversity, and global warming.

ENERGY

Energy is closely linked to economic development and to environmental quality. It is central to the world economy, providing the power needed for industrial production, transportation and (increasingly) agriculture.

Energy is a major contributor to health, wellbeing and productivity, making possible the existence of services that include heating, lighting and refrigeration. The energy chain delivering these services starts with the collection or extraction of a primary energy source – for example, coal – which may be transformed into another form of energy such as electricity, transported or transmitted to the point of use, and finally used to power a piece of equipment such as a heater, lamp or motor. Figure 1 shows an energy chain, using coal as an example.

Primary energy sources include fossil fuels (coal, oil, natural gas) and renewable sources such as biomass (wood, other plant sources, dung), hydropower, solar power, wind power, tidal power and geothermal energy. A small but significant proportion of the world’s electrical energy is also provided by nuclear power. The ways in which these primary sources are extracted, transformed, delivered and used have enormous environmental impacts at local and global levels. They also have both positive and negative effects on human health.

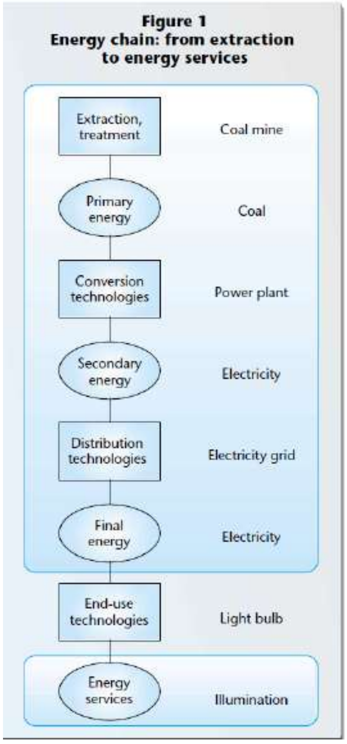

Figure 1 *Energy chain: from extraction to energy services*

RENEWABLE ENERGY SOURCES, POTENTIALS AND APPLICATIONS IN SERBIA

The need to use renewable energy sources has emerged over the past few decades as alarming data on the effects of greenhouse gas emissions from fossil fuel combustion have been published. This has led to climate change in the world, which is primarily reflected in the increase in average temperature, ie global warming. Climate disturbances have not bypassed Serbia either - temperatures have been rising since the early 1980s, and due to climate disturbances, dry and warm summers can be expected, extreme weather changes, temperature fluctuations, periods of unstable climate, occurrences such as floods and the city. The EU has committed itself to reducing greenhouse gas emissions, including carbon dioxide, by 20% from 1990, by 2020 to combat climate change, to increase the share of renewable energy to 20% and to take measures energy efficiency achieves savings of 20%.

Serbia's energy profile is expressed through a brief description of the country's basic macroeconomic indicators as well as an analysis of the energy sector. Serbia is a middle-income country with great potential for rapid economic development, as the country is endowed with natural and mineral resources and fertile and arable agricultural land. Serbia's GDP declined dramatically during the 1990s. However, since 2000, GDP has grown steadily and in 2006 it was almost 30% higher than in 2000. Strong economic progress has been made since 2001, especially in expanding private sector participation in the economy. Macroeconomic stability, which was quickly achieved in the early years of transition, has largely been maintained. Serbia has a total dependency of 40%, and compared to the energy dependency of other EU27 + countries, the country's energy dependence is considered average [1].

The energy sector is a major polluter in Serbia, mainly due to the use of domestic lignite, which burns with old equipment without adequate emission reduction technology. Indeed, energy efficiency in Serbia is inefficient. In fact, it uses five times the amount of energy to produce one unit of GDP compared to the EU average [2]. The carbon intensity in Serbia by GDP is 6.8 times higher than the world average and 10.8 times the OECD average [3]. Transmission and distribution losses in 2008 were 2.79% and 14%, respectively [4]. In 2007, the country's total primary energy consumption was 15.8 Mtoe (Table 1). The most significant role in this amount is played by coal, which has a share of 49.8%, followed by oil and its products (27%), natural gas (12.4%) and RES (10.8%), a share which is slightly reduced compared to 2005 (41%) [5]. The current capacity of hydropower plants is 10,200 GVh / year, while the potential capacity is estimated at 14,200 GVh / year. Energy production sectors have had various problems in the past, including inadequate pricing of services, lack of adequate maintenance and investment costs, lack of competition, over-employment and the resulting large fiscal wastage of government resources [6]. As can be observed, with respect to transmission and distribution systems (Table 1), Serbia suffers from transmission and distribution losses, either due to catastrophes caused by war or due to system obsolescence. Therefore, the main goal for Serbia is the need to reconstruct the transmission and distribution system.

Table 1 *Total energy data and economic profile*

Indicator	Serbia	EU 27+
GDP/capital (2018)	5,992.28 (USD)	40,088.65 (USD)
GDP (2018)	41.42 (mil.USD)	12,589.50 (mil.USD)
Inflation (2018)	2 %	1.1 %
Exchange rate (2020)	1.14 € for USD	1.3948
Population	7306,677	340.72 (mil.)
Production	9,751	31,736
Import (2019)	2,327.40 (mil.USD)	165,403 (mil.€)
Export (2019)	1,753.50 (mil.USD)	183,341(mil.€)
Reserves change	20.40	N/A
Transmission and distribution - system status	Increased losses in transmission and distribution of electricity	N/A

ENERGY RESOURCES AND POTENTIALS OF THE REPUBLIC OF SERBIA

Table 2 represents energy resources and potentials of the Republic of Serbia consist of fossil, conventional (coal, oil and natural gas) and unconventional fuels (oil shale), as well as renewable energy sources [7].

Table 2 *Geological reserves of fossil fuels (million tonnes of oil equivalent (toe))*

Energy resource	Balance and off-balance geological reserves	Total geological reserves
Stone coal	2,77	4,02
Dark coal	37,7	45,17
Carbon black coal	134,25	193
Lignite	1583 (780*)	3,698
Oil	10,14	50
Natural gas	3,37	50
Oil shale	-	398**
Stone coal	2,77	4,02
Dark coal	37,7	45,17
Carbon black coal	134,25	193

*witout Kosovo; **Kerogen-organic part of oil shale.

The total technically available potential of renewable energy in the Republic of Serbia (Table 3) is estimated at 5.65 million toe per year. Of this potential, 1,054 million toe biomass (mostly as firewood) and 909 thousand toe hydropower is already used [8].

Table 3 *Total technically available potential of renewable energy sources*

Type of RES	Available technical potential used (million toe/year)	Unused available technical potential (million toe/year)	Total available technical potential (million toe/year)
BIOMASS	1,054	2,394	3,448
Agricultural biomass	0,033	1,637	1,67
Agricultural crop residues	0,033	0,99	1,023
Residues in fruit growing, viticulture and fruit processing		0,605	0,605
Liquid manure		0,042	0,042
Wood (forest) biomass	1,021	0,509	1,53
Energy plantings			NA
Biodegradable waste	0	0,248	0,248
Biodegradable municipal waste	0	0,205	0,205
Biodegradable waste (excluding municipal waste)	0	0,043	0,043
HYDRO ENERGY	0,909	0,77	1,679
For installed capacity up to 10 MW	0,004	0,151	0,155
For installed capacity up to 10 MW up to 30 MW	0,02	0,102	0,122
For installed capacity exceeding 30 MW	0,885	0,517	1,402
WIND ENERGY	≈0	0,103	0,103
THE ENERGY OF THE SUN	≈0	0,24	0,24
For the production of el. Energy	≈0	0,046	0,046
For the production of thermal energy	≈0	0,194	0,194
GEOTERMALNA	≈0	0,1	0,18
For the production of el. Energy	≈0	≈0	≈0
For the production of thermal energy	0,005	0,175	0,18
Total from all RES	**1,968**	**3,682**	**5,65**

THE RATE OF RENEWABLE ENERGY SOURCES IN SERBIA

In Serbia, most energy comes from coal, which is used most in addition to oil and natural gas. Coal is the dominant raw material in electricity production. In Serbia, only hydro potential and biomass are used to a greater extent than renewable sources. The production and consumption of energy from renewable sources are also calculated according to EU regulations for large hydropower plants, but those in the field of environmental protection are not considered as ecological plants due to the adverse effects of the construction of dams on the environment. In this context, without large hydro plants, the share of electricity from renewable sources is very small.

Considering the current situation in Serbia, the lack of quantitative indicators in the planned fields of application of renewable energy sources, as well as the need for much more pronounced efforts to promote their use, must be emphasized [9]. The share of energy from renewable sources in Serbia is around 6% (including large hydro power plants) and is projected to remain stable in the coming period. The Energy Development Strategy by 2015 foresees that the share of new renewable sources (excluding large hydro power plants) in total primary energy consumption should increase from 1.07 to 1.21% in 2015 (Table 4) [9].

Table 4 *The share of energy from renewable sources in the total primary energy consumption, according to the Energy Development Strategy, scenario of dynamic economic development [9]*

	2006	2009	2012	2015
Total primary consumption energy (in PJ)	615	647	715	753
Share of renewable energy sources (no large hydro)	0.8	1.1	1.05	1.1

The share of energy generated in Serbia from renewable sources is small, and Table 4 shows the fact that its increased share is not foreseen until the end of 2015. Currently in Serbia, only about 1% of energy is generated from alternative sources, which is negligible if one considers the natural potentials and requirements of the Kyoto Protocol.

When it comes to establishing and raising the share of renewable energy in the country's energy supply, Serbia's example is not positive. In order for a country to think at all about promoting renewable energy, it needs to have these resources at its disposal. With a renewable energy potential of 3.83 miltoe (tons of oil equivalent), Serbia is very much in line with this requirement. What is missing is an adequate strategic plan for a much more ambitious implementation of RES into the country's energy potential [8–10].

CONCLUSION

Serbia has considerable energy potential in renewable energy sources, but it has not been sufficiently utilized. The use of energy from renewable sources is still in its infancy and in the world, except in some developed countries, and the greatest challenge is the transition to cleaner technologies while achieving economic viability.

In addition to the environmentally friendly, the use of renewable energy sources is also of economic importance– it can contribute to the reduction of fossil fuel imports, the development of local industries and job creation, but also to savings for households.

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APPLICATION AND PROPERTIES OF NATURAL FIBER-BASED BIOCOMPOSITE MATERIALS – A REVIEW

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Abstract

Natural fiber-based biocomposite materials are increasingly present on the market primarily due to their environmental, economic, and recyclable properties. Compared to man-made polymers, which represent non-biodegradable materials derived from petroleum products, nowadays natural fiber-based biocomposites are gaining more attention because of their performance. Biocomposites are a group of materials consisting of matrix and reinforcement (fillers). Natural fibers, which usually have a reinforcing role in biocomposite materials, are derived from biomass (e.g. kenaf, flax, hemp). Also, the matrix can come from renewable sources. Biocomposite materials exhibit better properties than conventional or biopolymer materials. Their use reduces the negative impact on the environment and thus achieves greater sustainability. The increasing presence of these materials is mainly due to good mechanical and thermal properties. For example, they play a very important role in the production of many interior and exterior parts for cars, ships, aircraft. They are widely used in the household, medicine, and pharmaceutical industry, etc.

Keywords: biomass, natural fiber, environment, material

INTRODUCTION

Composite materials are increasingly being developed and redesigned to produce materials with improved properties [1]. Natural fiber-based materials have been used in recent years due to their significant environmental and economic performance. The use of composites based on natural fibers leads to the development of rural areas, increasing employment and thus reducing the poverty rate, on the basis of which it can be conclude that they play a very important role in socio-economic development, and overall sustainability.

Biocomposite materials represent composites in which at least one of the constituents is of natural origin. Their properties depend on the matrix, the natural filler (reinforcement), the fiber size, and the interconnection of the fiber and the matrix. These fibers could have a natural or synthetic origin. The natural fibers represent an alternative to synthetic fibers (e.g. carbon, glass), which represent reinforcements in polymeric materials. In the composite industry, they are often referred to as plants fibers. Plants fibers are based on cellulose, hemicellulose, and lignin, which can be obtained from the bark of wood, leaves, seeds, fruits, and reeds. Biocomposite materials have the great advantage that they can be used in many industries, such as the aerospace, automotive, and pharmaceutical, etc. [2].

PROPERTIES AND DIVISION OF NATURAL FIBERS

The properties of natural fibers are influenced by many factors, such as cultivation location, the nature and age of the plant, and the method of extraction used. Advantages of natural fibers, compared to synthetic fibers, are greater availability, renewability, short plant growth period, cost-effectiveness, biodegradability, and recyclability, as well as lower energy consumption, i.e. energy efficiency, and reduction of carbon dioxide emissions during production. Several natural fibers derived from palm wood, banana, jute, wheat, sugarcane, cotton, silk, coconut, bamboo represent effective stiffening of matrices [3]. Natural fiber based composites can be used in various structures due to their high specific strength [4]. They are of great use in the design of spacecraft [5]. The use of natural fiber-based composite materials has led to market growth. There are multiple divisions of natural fibers. Some of the divisions are given in Figure 1 and Table 1.

Figure 1 shows the division according to the biological origin of the constituent parts, where the composites can be classified into partly ecological and green. Green composites are composites where all components are from renewable sources, thereby reducing carbon dioxide emissions. While partially ecological, only one of the constituents comes from renewable sources and the other comes from non-renewable sources (petroleum products) [1]. Natural fiber properties are affected by the size, number, shape, arrangement [6].

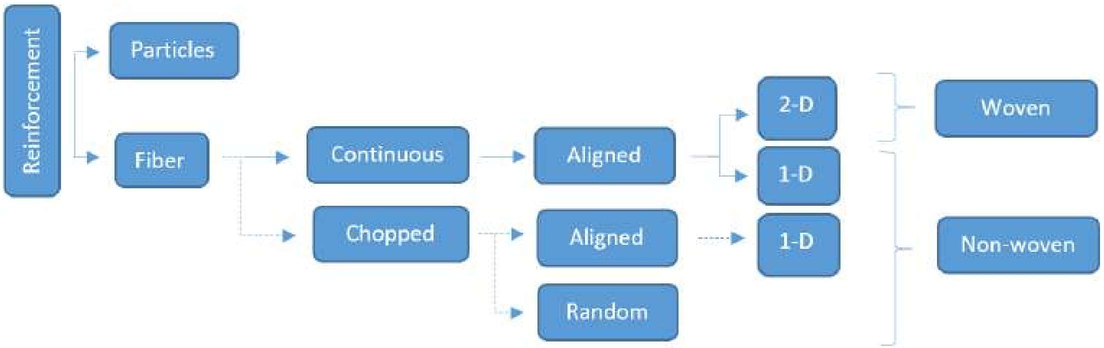

Figure 1 *Type of natural fibre reinforcements [7]*

The classification of natural fibers according to their origin and the world annual production is shown in Table 1.

Table 1 *Classification of natural fibers, origin, world annual production and cost [8]*

Fiber type (plant)	Botanical name	Origin	Production (10^3 ton)
Abaca	*Musa textilis*	Leaf	91
Bagasse	*Saccharum officinarum L.*	Stem	102,000
Banana	*Musa uluguruensis Warb.*	Leaf	200

Table 1 *continued*

Bamboo	*Gigantochloa scortechinii* *Dendrocalamus apus*	Stem	10,000
Coir	*Cocos nucifera L.*	Fruit	650
Cotton	*Gossypium spp.*	Seed	19,010
Flax	*Linum usitatissimum*	Stem	830
Hemp	*Cannabis sativa L.*	Stem	214
Jute	*Corchorus capsularis,* *Corchorus olitorius*	Stem	2850
Kapok	*Ceiba pentandra*	Seed	123
Phormium	*Phormium tenax*	Leaf	-
Pineapple	*Ananas comosus Merr.*	Leaf	-
Ramie	*Boehmeria nivea Gaud*	Stem	100
Sisal	*Agave sisalana*	Leaf	318.8

BIOPOLYMER MATRIX

The mechanical properties of biocomposite materials are influenced by a polymer matrix, which can be thermoplastic or thermosetting. Polymers used in matrix production may be of plant or animal origin, or synthetic (carbon-based) origin. Mechanical properties, chemical resistance, stability, manufacturing process, in order to achieve biodegradability or recyclability play a crucial role in the selection of polymeric material. The recycling efficiency of a biopolymer matrix, at the end of its working life, depends primarily on the nature of its elements. Thermocouple dies, on the one hand, are more used because they have good thermal properties, high chemical resistance and excellent mechanical properties, while on the other hand, they are very difficult to recycle, making it difficult to reuse (although some studies indicate that they can be easily reused) [9]. Thermoplastic dies can be comfortably melted, and they are also recyclable as opposed to thermosetting. The aim is to adapt mechanical, chemical, and thermal properties to achieve a recyclability process [10,11].

APPLICATION OF NATURAL FIBER REINFORCED COMPOSITE MATERIALS

Industries, such as automotive, construction, aviation, aim to produce, whose products are environmentally friendly and come from renewable sources [12–14]. The use of composite materials based on natural fibers contributes to the employment of people in rural and less developed areas, thereby achieving sustainable development. The aim is to reduce the poverty rate, to develop new innovative ideas, to create sustainable cities and communities, to make the process of production and consumption rational. Based on these facts, we can conclude that they play a very large role in the socio-economic development of society. In the production processes, the most common are the fibers based on the figure, which include (jute, flax, hemp, and kenaf), leaf (abaca, sisal, and pineapple), seeds based on seeds (coconut, and cotton), grass fibers, reeds (wheat, maize, and rice), wood-based fibers, roots [14].

Some countries cultivate different types of fiber, while others import. In the European automotive industry, flax and hemp, which are mainly grown, are the most used, while jute and kenaf are imported from Bangladesh and India. Bananas are imported from the Philippines, sisal from South Africa, the United States, and Brazil.

Biocomposite Materials in the Automotive Industry

The use of biocomposite materials in the automotive industry dates back to the 1940s when the scientist Henry Ford produced the first cannabis-based parts [15]. Then in the 1950s, the production of bodywork based on biocomposite materials for the German Trabant [15]. In the automotive industry, by using natural fibers, mass reduction is achieved, leading to a reduction in fuel consumption and carbon dioxide emissions into the atmosphere. Studies show that the use of natural fibers in the automotive industry achieves cost reductions of about 20% and weights of about 30% [15]. Natural fibers are made mainly of the interior of the car, such as dashboards, doors, seat covers, while the use of exterior components is limited. The interior parts of German cars, such as Mercedes, Volkswagen, Audi, and Ford, are made of natural fibers. Figure 2 shows the process of manufacturing hemp doors.

***Figure 2** Production of the door from hemp fibre [16]*

In the German automotive industry, which is one of the largest manufacturers of natural fiber-based parts, the matrix used in combination with these fibers is polypropylene (PP). It is noted that on average, each car contains about 3.6 kg of natural fibers (e.g. wood, cotton, flax, hemp, and kenaf). Flax fibers are used in the manufacture of brakes [17]. Their advantage is that they reduce the coefficient of friction.

Application in other branches of industry

The use of biocomposite materials is also prevalent in sectors such as medicine, pharmacy, packaging, household, and construction. The reason for their use in the mentioned areas is in the lower economic costs, less weight.

For medical purposes, combinations of fibers, such as sisal/glass fibers or sisal/silk fibers, are used to reduce the use of titanium, cobalt, chromium. By their use for orthopedic purposes, internal and external fixations are achieved when a bone is fractured [18]. They are also used in the construction of water tanks and chemicals [19,20].

Household items, such as garden furniture, chairs, floor coverings, are made of jute and coconut fibers [21]. Kenaf fibers are used in construction because of their low cost and low mass [22].

CONCLUSION

The aim of this paper was to present the properties and application of natural fiber-based biocomposite materials, which achieve significant savings during the production process in many industries. The use of these materials achieves economic, environmental, and energy efficiency. Unlike synthetic fibers, natural fibers are more widespread, more recyclable, plant growth periods are shorter, carbon dioxide emissions are lower. The nature of the matrix affects the mechanical properties. It can be thermoplastic and thermosetting. Unlike thermoplastics, thermosetting matrices have good thermal, mechanical properties and high chemical resistance, but their disadvantage is that they are difficult to recycle, making it difficult to reuse them. These materials are widely used in many industries, such as automotive, construction, aviation, and many others. The largest use has been reported in the automotive industry, primarily because of the reduction in car weight, costs, and environmental impact. In the automotive industry, they are mainly used in the manufacture of interior car parts. Also, they are very widely used in the manufacture of various items, such as helmets, cases, mailboxes, garden furniture, floor coverings, panels, and various packaging products, etc. Likewise, the use of composites based on natural fibers leads to the development of rural areas, increasing employment and thus reducing the poverty rate, on the basis of which it can be conclude that they play a very important role in socio-economic development, and overall sustainability.

ACKNOWLEDGEMENT

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PLANET PRESERVATION THROUGH CLIMATE ACTIONS AND CREATING QUALITY JOBS ONLY

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Abstract

Climate changes are affecting all countries on all continents. It has a negative impact on national economies and on people's lives, already creating additional costs for people, communities and countries that will be even greater in the future. The whole world needs a change in leadership and political direction that would move away from the neoliberal and conservative models of the past, focusing on quality jobs for their populations, a healthy environment, social security, and an economic cost-cutting inequality-solving model. The status quo is not an option. A radical change is needed in order to build a project for the future that everyone in the world can trust in. Creating quality jobs will remain a major challenge for almost every economy even after 2019.

Keywords: climate change, planet, jobs

INTRODUCTION

Climate change is one of the most serious challenges our world faces with today. Our planet is undergoing significant and accelerating climate change that has begun more than a century ago. Most scientists agree that the planet is heating up faster than ever because of the huge amount of greenhouse gases that are being pumped into the atmosphere as a result of human actions. These include activities such as burning fossil fuels (coal, oil and gas), driving cars, and cutting down forests.

Many of us have seen, and even experienced, the effects of climate change. It is not just about the extreme weather conditions such as floods, droughts and hurricanes. Slower and less noticeable changes in our climate could completely change the way we live. The good news is that in December 2015 in Paris, 195 countries (literally the whole world) entered into a first legally binding global agreement on combating climate change.

In the EU and around the world, governments, companies and individuals are already trying to reduce the causes of climate change and adapt to the changes it brings. We all have a role to play because climate change is a global problem that can affect us all. We share one planet, and the changes we make in one place can affect other distant places as well. It could be said that our behaviour leaves a lasting impression, like a footprint. Therefore, by our actions and choices, each of us can undertake measures to leave smaller footprints and help combat climate change.

Many changes are needed to preserve the planet. In order to continue to live, it is necessary to ensure that we have and continue to have the basic resources needed for survival, such as water, food and energy.

Being sustainable means taking care of the planet and living within the limits of what it can provide to us. Waste prevention is becoming increasingly important as the global population grows and we are slowly consuming our limited reserves of natural resources. Also, one of the burning issues is to provide quality jobs only, all with a goal to preserve the planet [1]**.**

PRESERVATION OF THE PLANET THROUGH CLIMATE ACTIONS

Climate actions in the fight against climate change

Without the further emission reductions policy, it is estimated that the average world temperature could rise by 1.1ºC and 6.4ºC during this century. Human activities such as the combustion of fossil fuels, deforestation and agriculture result in the production of carbon dioxide (CO_2), methane (CH_4), nitrogen oxide (N_2O) and fluorocarbon emissions. These greenhouse gases retain the heat released from the Earth's surface and prevent its expansion into space and thus causing the global warming [2].

As we have already stated, climate change affects all countries on all continents. It has a negative impact on the national economies and people's lives, creating, even today, additional costs that will be even greater in the future for people, communities and countries.

People are already experiencing the significant consequences of climate change, which include the changes in weather patterns, rising sea levels and more extreme weather conditions. The emissions of greenhouse gases, as a result of human activities, lead to climate change that continues to increase. Today, they are at higher levels than ever in history. Without any actions, the average temperature on the planet is predicted to rise during the 21st century, which is likely to exceed 3 degrees Celsius.

The poorest and most vulnerable people are, unfortunately, the most affected. Today, many affordable solutions are available to enable countries to move to cleaner and more resilient economies. More and more people are turning to renewable energy sources and other measures that reduce the emissions and contribute to adaptation efforts. Climate change is a global challenge which does not recognize national boundaries. The emissions at one location affect people in a wider environment.

This is an issue that requires solutions and coordination at the international level, and the international cooperation which will assist developing countries and their advance towards a low carbon economy. In order to address climate change, countries adopted a global agreement in Paris in December 2015. The measures to reduce climate change need to be integrated into national policies, strategies and plans. In addition, there is a need for improved education, raising awareness, as well as human and institutional capacity to mitigate and reduce the impact of climate change, from adaptation to early warning.

Preserve and sustainably use the oceans, seas and marine resources for sustainable development

The world oceans - their temperature, chemical composition, currents and life in them, are very important for the global systems that make the Earth fit for a human life. Rain, drinking water, weather conditions, climate, shores, a good portion of our food, and even the amount of oxygen we breathe in, ultimately is given and controlled by the sea. Throughout history, the oceans and seas were vital for commercial and transportation purposes. Therefore, a careful management of this essential global resource is key to a sustainable future.

By the end of 2025, all types of pollution of marine resources, especially those coming from the land, should be prevented or significantly reduced. By the end of 2020, a sustainable management of marine and coastal ecosystems should be ensured; they should be protected from all negative impacts, and actions should be taken to rebuild them to make the oceans healthy and productive again [3].

The plan is to efficiently regulate the catch of fish and to end the excessive fishing as well as the destructive fishing practices. Furthermore, the plan is to apply the management plans prepared on a scientific basis in order to restore the stock of fish as soon as possible. On the other hand, small professional fishermen should be provided with access to marine resources and trade markets.

Sustainable use of terrestrial ecosystems

Forests cover 30 percent of the Earth's surface, and apart from being a source of food and shelter, forests are the key to help fighting climate change and preserving biological diversity. It is estimated that 13 million hectares of forest are lost annually. Deforestation and desertification - caused by human activities and climate change - represent major challenges for sustainable development and affect the lives and livelihoods of millions of people in the fight against poverty. Efforts have been taken to improve forest management and to combat desertification.

By the end of 2020, plans are being made to stop deforestation, restore destroyed forest and significantly increase afforestation on a global scale. It is necessary to fight against desertification, to restore degraded soil and to neutralize soil degradation.

By the end of 2020, the preservation, restoration and sustainable use of inland freshwater ecosystems and their environment, in particular forests, wetlands, mountains and dried land, should be ensured in accordance to commitments adopted through international agreements.

One of the goals is to undertake urgent and significant actions to reduce the degradation of natural habitats, to stop the loss of biological diversity by the end of 2020, to protect endangered species and to prevent their extinction. By the end of 2020, it is important to integrate ecological values and biological diversity into national and local planning, development processes and poverty reduction strategies. In order to achieve this goal, it is necessary to mobilize and significantly increase financial resources from all sources to conserve and sustainably use biological diversity of the ecosystems, sustainable forest management and afforestation, fight against poaching and trade of protected species through the increase of the capacity of the local communities.

Better jobs

In order to preserve the planet, we need better jobs, which need to be created in the future. One example of better jobs is definitely cleaner industry.

Factories whose products we use and power plants that produce the electricity we need in our households, schools, and offices, emit large amounts of CO_2 and other greenhouse gases. In order to reduce these emissions, the EU has designed the world's first and largest system which limits the amount of greenhouse gases emitted and according to this system the companies need to pay for the emission of the greenhouse gases that they release into the atmosphere. The EU Emissions Trading System (EU ETS) was launched in 2005 and is the key part of the EU's climate policy. It covers more than 11,000 power plants and industrial plants and also includes the emissions from intra-EU flights [4].

The EU Emissions Trading System (EU ETS) sets limitations on the annual amount of greenhouse gases that the companies can emit. The total amount decreases every year, and since companies have to report their emissions we can be certain this system reduces the pollution.

The more the companies emit greenhouse gases, the more they have to pay, so it is in their interest to emit as little as possible, for example, by investing in cleaner technologies that emit less CO_2.

Today, there are similar systems around the world, such as in China, South Korea and California. For sectors that are not covered by the EU Emissions Trading System, such as transport, buildings, agriculture and waste, the responsibility for reducing greenhouse gas emissions is shared by all EU countries by setting targets at national levels.

The support for new EU technologies helps to develop innovative low carbon technologies through a special fund raised through the EU ETS. So far, around € 2.1 billion have been used to support 38 renewable energy projects across Europe. Some of them are focused on renewable energy sources, such as offshore wind farms, geothermal energy and biofuels, and others on new technologies that capture carbon and store it underground.

The EU and its member states will continue to support research and development of low-carbon related innovations through the Innovation Fund and the EU Framework Program for Research. The key goal is to turn ideas associated with low carbon into practical solutions in many areas of life. We can only imagine buildings and cars of the future with no carbon-rich steel or cars that function as mobile batteries and contribute to the energy demands of households!

On the other hand, underground carbon storage is a carbon capturing and storaging technology that captures, stores and transports carbon dioxide emitted by power plants and industrial installations to convenient underground storages.

This has a considerable potential for combating the climate change in Europe and around the world, because underground, literally all carbon dioxide can be stored for hundreds, even thousands of years. However, this technology is currently very expensive and in Europe there are only two functional commercial projects. Therefore, the EU provides basic funding to support carbon capture and storage projects and has created rules that ensure the application of this technique in an environment - friendly manner [5].

Many people in the world are looking for new future interests and want to build a career within the latest and most up-to-date technologies. Today, there are many jobs in the fields such as renewable energy sources that have not existed ten years ago.

Some EU countries have even set up special training centres for the handling and maintenance of offshore wind farms.

CONCLUSION

The Earth's climate has changed over time, gradually becoming warmer or colder over long periods of time. There have been a dozen ice ages in the last millennium, with much warmer periods in between. Those changes happened due to natural causes, such as the changes in the degree of the planets, solar activities and sea currents. But the changes we witness today are different - and we are responsible! By releasing more gases that have the ability to trap heat in the atmosphere, we cause a very rapid rise of the Earth's temperature.

Climate change is caused by the increase in the Earth's temperature (global warming) which is caused by the release of the unnaturally large amount of greenhouse gases into the atmosphere. These additional greenhouse gases are mainly generated by the burning of fossil fuels for the production of energy, as well as for other human activities, such as logging, agriculture, livestock farming and chemical production. Certainly, one of the ways to preserve the planet is to carry out many climate actions, at the global level, and to create high-quality jobs only.

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PREVENTION OF CONTAMINATION OPEN WATERCOURSES FROM EVACUATION MINE WATER FROM SURFACE MINE TURIJA

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Abstract

Evacuation water from surface mines into open watercourses is increasingly complex due to stricter environmental regulations. Mine water pumped from the lowest points of a mine often contains a certain amount of particulate matter that is stirred by the pumping itself and in the production process. Before discharging water into an open watercourse, it is necessary to provide conditions for their deposition, that is, the water meets the criteria prescribed by applicable legal solutions.

Keywords: mine water, evacuation, environment

INTRODUCTION

The Turija surface mine is spatially located on the former source the Turija River, which has lost its main source by opening the mine. Following the disruption of hydrogeological conditions, the occurrence of leachate as well as smaller sources that occasionally form and disappear in the area are frequent [1].

As with most surface mines, one of the important segments its stable operation is the adequate solution evacuation the resulting water in the crater the mine itself. Part of the water is generated by atmospheric precipitation itself, while part the water occurs as groundwater. Evacuation or pumping of water from a mine crater represents a complex process, especially in today's time when legal solutions to environmental protection are increasingly stringent.

Depicting a catchment area gravitating to the surface mine Turija

The catchment area that gravitates toward the Turija surface mine consists the 6 catchment areas presented in the following Table 1.

Table 1 *Display of catchment areas [2]*

Catchments area	Area (m^2)	Water gravity direction
Area 1	615 000	North peripheral canal
Area 2	75 000	North peripheral canal
Area 3	890 000	The main water collector
Area 4	1 920 000	The main water collector
Area 5	2 450 000	Water collector on point 340
Area 6	850 000	Southern peripheral canal
TOTAL	6 800 000	

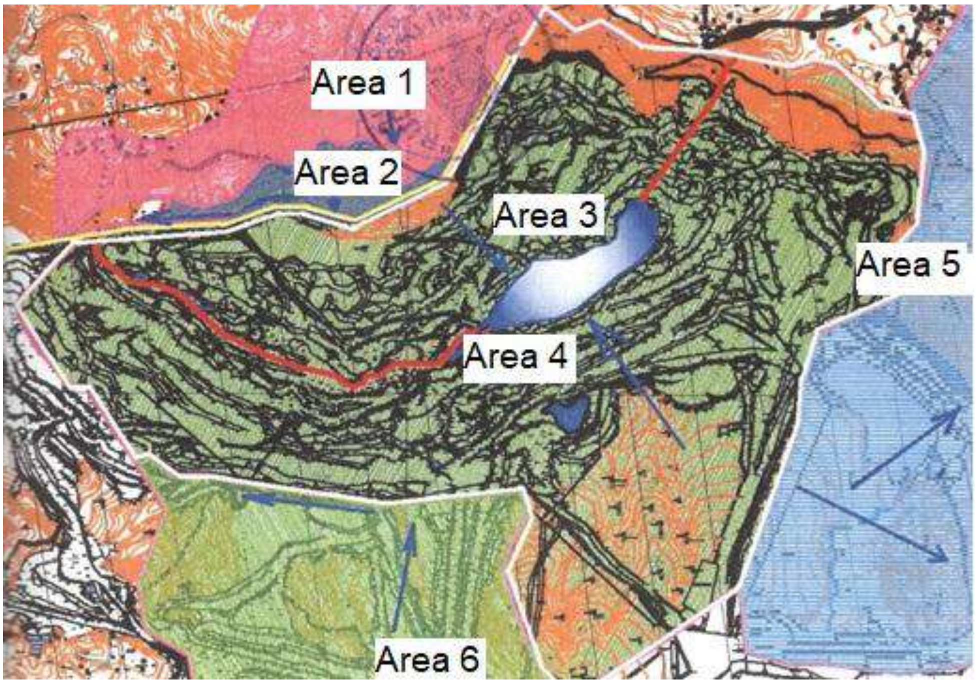

Figure 1 *Catchments areas gravitating towards the mine Turija*

According to the analysis the catchment areas (Figure 1), it is evident that the lowest mine level are gravitated by the catchment areas 3 and 4 with a total area of 2810000 m^2 or 2.81 km^2, which is the highest burden on the inflow water into the mine crater. The waters from the catchment area 1, 2 are poured into the northern circumferential canal, while the catchment 5 is flows into the water collector on point 340 located outside the pit and pumped separately into the control canal 2 [2].

Waters gravitating from the south flow into the concrete canal regulation 1 and drains towards Ramičko lakes and further in the direction of the River Turija.

Location and dimensions of mine water treatment facilities

In order to more efficiently purify mine technological waters from surface mine Turija, three sedimentary pools (Table 2) were constructed before the mine water was discharged into the open recipient. The location, size and description of the pool are described in this chapter.

Table 2 *Dimensions of sedimentation pools*

Sedimentation pool parameters	Poll 1	Poll 2	Poll 3	TOTAL
Length (m)	126	126	82	
Width (m)	21	21	21	
Height (m)	4	4	4	
Over flow discharge height (m)	0.5	0.5	0.5	
Height of water column (m)	3.5	3.5	3.5	
Angle of the side of the poll (^{0})	60	60	60	
The bright surface of the water (m^2)	2 646	2 646	1 743	7 035
The volume of water in the poll (m^3)	7 929	7 929	5 160	21 018

The basic parameters for the physical contamination water or the content of suspended materials are: the volume of the suspended materials, the particle size, the deposition rate (Table 3), and the amount of particles in the volume unit [6].

The size suspended materials will be set in the range of 0.2 mm (fine sand) up to 0.005 mm (clay), for such quantities, the deposition rate was calculated by the formula [3]:

$$v_t = C \cdot d^2 \tag{1}$$

where: C – constant for a given type of material

Table 3 *Tabular view of calculated deposition rates*

Material	Particle deposite rate (m/s)				
	d=0.2 mm	d= 0.1 mm	d=0.05 mm	d=0.01 mm	d=0.005 mm
Coal roof	$8.7x10^{-2}$	$2.18x10^{-2}$	$5.45x10^{-3}$	$2.18x10^{-4}$	$5.45x10^{-5}$
Coal	$5.81x10^{-2}$	$1.45x10^{-2}$	$3.6x10^{-3}$	$1.45x10^{-4}$	$3.6x10^{-5}$
Lower level of coal	$1.02x10^{-1}$	$2.54x10^{-2}$	$6.35x10^{-3}$	$2.54x10^{-4}$	$6.35x10^{-5}$

The characteristic parameter the sedimentation pool is the bright surface and is obtained by the form:

$$F_s = \frac{Q}{v_t \cdot \eta_h} \quad (m^2) \tag{2}$$

where:

Q – digging capacity from the mine (m^3/s)

V_t – particle deposition rate (m/s)

η_h – hydraulic sediment coefficient (0.7-0.9)

The lowest particle deposition rate is for coal, so for the particle velocity of coal particles 0.005 mm which is Vt = $3.6x10^{-5}$ m/s and maximum pumping capacity Q = 0.225 m^3/s.

$$F_s = \frac{0{,}225}{3.6x10^{-5} \cdot 0.9} = 6\,944.4 \quad \approx 7000 \quad (m^2) \tag{3}$$

The total bright water surface is 7035 m^2 and the volume water of 21018 m^3 in displaced sedimentation pool (Figure 2) is higher than the defined minimum dimensions and meets the optimum water purification parameters.

The depth of the sedimentation pool is maximum 5 m, while the retention time the water in the pool is at least 1/4 days and 6 hours, respectively, with a maximum capacity extraction from the mine.

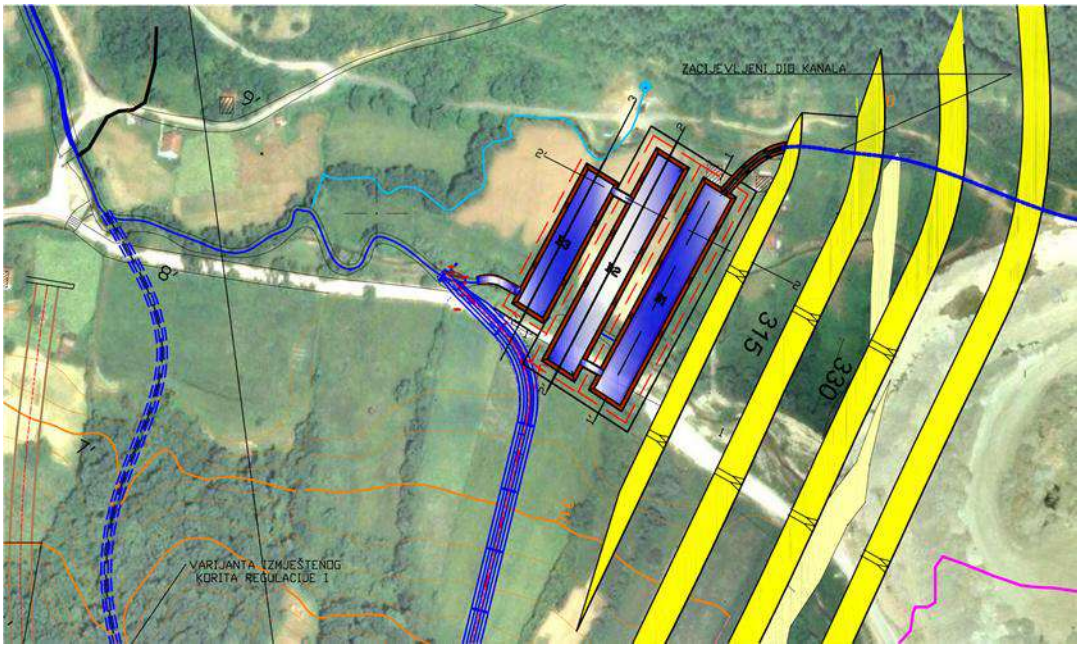

Figure 2 *Construction of sedimentation pools*

Quality control of mining water

In order to be sure the quality or composition mine water ejected from the mine crater, it is obligatory to control them in accordance with the legal solutions in force in our country (Table 4). Measurements process wastewater and sampling are performed at the connection points technological collectors or at discharge points in order to monitor average and maximum values.

In this connection, it should be stressed that solutions have been imposed that require constant monitoring the quality mine water discharged into open watercourses, where authorized companies and institutions perform quality controls on a monthly basis and elaborate on realized or measured values.

Accordingly, since the mine is a large producer, it also discharges several thousand m^3 into the watercourses and is obliged to monitor certain parameters every month.

Table 4 *Number of binding measurements in relation to the amount of wastewater [4]*

Waste water flow m^3/day	Number of tests per year
<5	1
5-20	2
20-50	4
50-100	6
100-500	8
>500	12

Measurement results

Considering that Banovići Mine belongs to the category of large consumers whose water flow exceeds several 1000 m^3 water, it is a legal obligation to carry out a detailed analysis of water at a discharge point once a month by an authorized institution [5]. The Table 5 gives a brief overview some the measured parameters obtained by measuring in 2019.

***Table 5** Results of measurement parameters for 2019 year*

Overall results of measurement and testing of basic parameters at measurement site E-1 In 2019						
Name of pollutant			RMU Banovići			
Location			PK TURIJA			
Municipality and Canton			Banovići, Tuzlanski kanton			
Wastewater Recipient			River Turija			
The catchment area			River Bosna			
Name of the river areas			The Sava River catchments			
Sampling performed			TQM d.o.o. Lukavac			
Parameter tested	Flow m^3/day	Temperature °C	PH value		Total suspended matter mg/l	
			Measured values	Limit values	Measured values	Limit values
JANUARY	3510	14.7	7.85	6.5-9	19	35
FEBRUARY	3904	11	7.2		32	
MARCH	9774	12	6.95		28	
APRIL	3160	12	7.5		30	
MAY	3120.8	13	7.7		29	
JUNE	2764.9	16	8.1		24	
JULY	2240.3	20	8.3		29	
AUGUST	1890.6	23.1	7.93		24	
SEPTEMBER	1859.3	20.1	7.81		21	
OKTOBER	1795.2	18	7.59		20	
NOVEMBER	2140	11.7	7.66		27	
DECEMBER	1994.2	12.4	7.46		31	
AVERAGE	3179.44	15.33	7.85		26.16	

CONCLUSION

Adequate treatment mine water has a major impact on the quality the water discharged into open recipients.

The analysis the parameters presented in the preceding table in 2019 at the measuring point E-1 outlet into the Turija River recipient give certain results that show us the extent to which the mining work affected the quality of the water discharged from the mine crater.

The results show that the average flow per day at the measuring point E-1 is 3179.44 m^3/day, and it is directly dependent on the amount of rainfall and the amount water entering the crater. The temperature of the discharge water is conditioned by the outside temperature and ranged from 11-23.1 °C.

By analyzing water by pH, the results obtained did not exceed the permissible limit values of (6.5-9).

Total suspended solids ranged from the E-1 limit values and averaged 23.16 mg/l compared to the 35 mg/l limit. This parameter is particularly important because under experimental conditions (artificially induced) the values of this parameter ranged up to several hundred times greater than measured by this measurement. All this tells us that by an adequate deposition process solid suspended particles, this is reduced to the limit to fit the limit values.

It is of course important to point out that the auxiliary sedimentation pools (main and auxiliary water reservoirs) located in the pits certainly have a significant influence on the measured sizes because they have a function in front of the precipitator.

The analysis of the measured quantities leads to the conclusion that the water quality meets the measured parameters. There is no exceeding of limit values, that is, the made sedimentation pools fulfil their role, they are designed in accordance with the needs of the surface mine Turija.

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CROP’ CONTRIBUTION TO SEASONAL CARBON EXCHANGE IN TEMPERATE CLIMATE OF CENTRAL LITHUANIA

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Abstract

This study comprised carbon exchange rate, specifically, emitted and absorbed CO_2 *fluxes closed chamber method. For the evaluation of* CO_2 *emissions in different agro-ecosystems the biomass and leaf area index (LAI) at different plant growth stages have applied. The leaf area index significantly affected (*$p = 0.04$*) the differences in absorbed atmospheric* CO_2 *amounts during vegetation period. The significant strong correlation (*$r = 0.6–0.7$*) has confirmed between soil respirational emissions and LAI. Soil and crops respiration composed in average 21% and 16% of agroecosystem carbon exchange, respectively. Generally, the total respirational emissions evidently have recovered by crop’ gross primary production (GPP) in all agroecosystems. As a result, the crops promoted reduction of atmospheric* CO_2 *content. The maximum mean GPP and NEP values were determined for ley and maize due to the biggest LAI and yield removed from fields. These agro-ecosystems sank the maximum atmospheric C rates, and consequently they potentially be considered the most sustainable items between crops. Considering the data, crop rotations might be improved by right selection of cultivated crops as well as their area in terms to mitigate their effect on environment and climate.*

Keywords: CO_2 fluxes, bio-parameters, environment, crops

INTRODUCTION

Agricultural areas cover considerable ranges of terrestrial land, near 12% in total and 30% of Europe continent, and thus emitted significant rates of greenhouse gas (GHG) [1,2]. Agricultural contributes to the emissions ca. 12% of anthropogenic issues in total, and ca. 10% in EU countries. Soil management produces 4.94% of biospheric fluxes [4,5]. Nonetheless, soil sequestered over 53% of total carbon [6–8].

Amongst measured biospheric fluxes, gross primary production (GPP) exhibited the atmospheric CO_2 volumes photosynthetically assimilated by autotrophs in ecosystems [9]. Respiration of all organisms including plants represents the opposite process to photosynthesis that emits carbon to atmosphere. Accumulated net carbon identified as net ecosystem production (NEP) [10]. These parameters related to seasonal environmental conditions and plant growth [11–13]. In addition, leaf area (LAI) also performed photosynthesis and carbon assimilation [14,15]. Carbon fluxes between atmosphere, plant and soil depend on certain crops, their rotational system, applied agro technology, longevity and environment conditions of growth period [16,17]. Former studies revealed strong reliance (r=0.7) between carbon emissions and temperature and precipitation [18]. Recent conventional agro technologies mostly focused on commercial incomes but not on environment protection including soil fertility, biodiversity, etc. Commercial purposes and severe application of agro chemicals in conventional farming often approval over-exploitation of environmental resources and thus leading to soil over-cropping and irreversibly changing environment in ecosystems. Therefore, sustainable agro technologies of ecological farming, crops and field technologies must be chosen [19].

In this research, the main aim was to analyse and compare the seasonal variation of soil and plant respirational emissions, gross ecosystem production and net ecosystem production during growth period in conventional agroecosystems of ley, winter wheat, maize, barley and spring rapeseed. Crop parameters, i.e. density, leaf area index and yield were applied for explicate the carbon fluxes.

MATERIALS AND METHODS

Measurement object and location

Investigations of seasonal C exchange of conventional farming (CF) ley (L), winter wheat (W), maize (M), spring rapeseed (R) and barley + ley undercrop (B) were carried out during growth period in 2014–2016 at the Training Farm of Vytautas Magnus University (54°52' N, 23°49' E) (Table 1). The cropland soil types were *Hapli-Epihypogleyic Luvisol*, *LVg-p-w-ha*, [20].

***Table 1** Agroecosystem parameters*

Agroecosystem	Area, ha	Mineral fertilisation
Ley (L)	22.86	Ammonium nitrate, 150 kg ha^{-1} (N 51 kg ha^{-1}); in 2nd yr. autumn - manure 50 t ha^{-1}
Wheat (W)	13.7	NPK 8-20-30, 200 kg ha^{-1} Ammonium nitrate, 140 kg ha^{-1} (N 48 kg ha^{-1})
Rapeseed (R)	47.59	Ammonium sulphate, 300 kg ha^{-1} (N 63 kg ha^{-1}) Ammonium nitrate 100 kg ha^{-1} (N 34 kg ha^{-1})
Maize (M)	46.68	NPK 8-20-30. 280 kg ha^{-1} Ammonium sulphate, 300 kg ha^{-1} (N 63 kg ha^{-1}) Ammonium nitrate, 170 kg ha^{-1} (N 58 kg ha^{-1})
Barley (B)	14.51	NPK 8-20-30, 200 kg ha^{-1} Ammonium nitrate, 160 kg ha^{-1} (N 54 kg ha^{-1}) Ammonium nitrate, 120 kg ha^{-1} (N 41 kg ha^{-1})
Crop rotation	Ley 1-yr. + Ley 2-yr. + winter wheat + maize + spring rapeseed + barley with ley undercrop	

A 2-cut system was applied in ley (04 06 and 11 08 2014; 02 06 and 06 08 2015; 08 06 and 04 08 2016). Thecrop density (un. m^{-2}), leaf surface area (cm^{2} m^{-2}) were determined and leaf area index (LAI, m^{2} m^{-2}) was calculated in the plots of 0.25 m^{-2} (0.5 m x 0.5 m) in six replications. Fresh plant biomass (FM, g m^{-2}) and dry matter content (DM, g m^{-2}) were determined by the weighing method. Dry matter content was determined by drying plant samples (80^{o}C thermostat Tritec HANNOVER).

C exchange investigation

Agroecosystems' seasonal C exchange was investigated by measuring the rate of gross primary production (GPP, µmol m^{-2} s^{-1}) and respiration emissions of soil and autotrophs (R_{s+a}, µmol m^{-2} s^{-1}) applying closed chamber method [22] using LCpro system (ADC Bioscientific LTD) every 7–10 days with regard to plant growth stages (BBCH-scale) [21]. C exchange of each agroecosystem was evaluated by net ecosystem production (NEP, µmol $m^{-2}s^{-1}$) [23] which was calculated by the formula: NEP=GPP- R_{a+s} [24].

Meteorological conditions

Crops germination, growth, development, maturity and yield depended on meteorological conditions. Crops growth has slowed down due to drought periods in the summer of 2014–2016 (Table 2).

Table 2 *Hydrothermal coefficients (HTK) of 2013–2016*

Year / Month	03.	04.	05.	06.	07.	08.	09.	10.	11.	Mean
2013							2.81	1.62	4.15	2.86
2014	1.83	0.78	2.03	1.13	0.82	2.02	1.98	1.61	4.15	1.81
2015	3.21	2.15	1.30	0.35	1.34	0.11	1.32	1.96	3.46	1.68
2016	2.94	1.85	0.77	1.62	2.93	2.18	0.6	2.69		1.94

Statistical analysis

Standard deviation for LAI, FM, DM, R_{a+s}, GPP, NPP was determined with standard error (mean ± SE). The correlation coefficient r between respiration emission, GPP, NEP and environmental conditions, biometric parameters was determined.

RESULTS AND DISCUSSION

Plant growth and C exchange parameters closely depended on meteorological (Figure 1) and soil physical conditions. During vegetation period plant respiration (R_a) varied from 0.202 in March to 2.384 µmol m^{-2} s^{-1} in August. Soil respiration (R_s) ranged between 0.225 and 2.526 µmol m^{-2} s^{-1} and composed insignificant part in total C exchange. Strong negative correlation determined between precipitation and R_a ($r = -0.6$) and R_s ($r = -0.7$). Though the decrease of soil humidity due to climate change is recently referred [25], occurrence of moisture surplus supressed aerobical respiration R_s in soil during spring or autumn seasons in investigated agroecosystems.

Agreeing to Haboudane *et al.* [26], crop LAI also depends on environmental conditions that determine seasonal intensity of physiological processes at different growth stages (Figure 2). The maximum LAI of maize exceeded LAI of L, W, R and B in average by 41%, 28%, 21% and 57%, respectively [27]. Maize belongs to C_4 photosynthesis type plant [28], whereas L, W, R and B are C_3 type, therefore anatomic structure of leaves, size of chloroplasts determined different photosynthesis intensity of these crops [29].

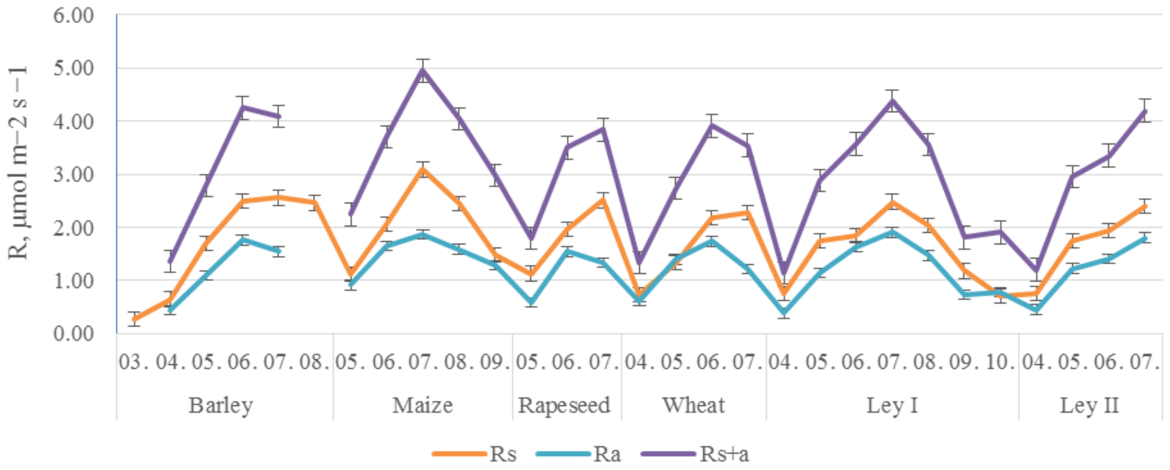

Figure 1 *Soil (R_s), plant (R_a) and total ($R_{s+}R_a$) respirational emissions in conventional agroecosystems during the vegetation period. Mean ± SE, $p < 0.05$*

Assimilated atmospheric carbon in biomass was estimated by GPP parameter that strongly depended on T_a (r = 0.7) and FM, DM and LAI (r = 0.8). Some researchers concluded that environmental conditions and bio-parameters determined GPP and NEP variation [8,30]. In our investigation, the NEP enlarged from 6.22 µmol m^{-2} s^{-1} to 10.09 µmol m^{-2} s^{-1} in spring, and from 11.91 µmol m^{-2} s^{-1} to 18.06 µmol m^{-2} s^{-1} in summer season. Between the agroecosystems, M and L assimilated the maximum rates of atmospheric CO_2, which has accumulated in their biomass (Figure 2), that has harvested and removed from the field. Consequently, M and L can significantly sink atmospheric $CO_{2,}$ and contribute to climate change mitigation.

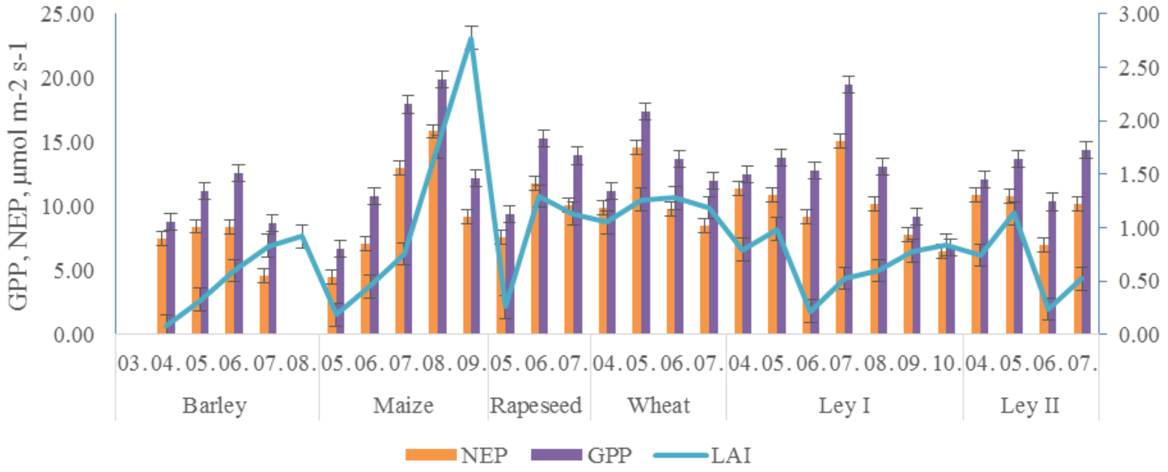

Figure 2 *Assimilated and sequestered carbon and LAI rates in agroecosystems of conventional crops during vegetation period. Mean ± SE, $p < 0.05$*

As exhibited the data of carbon exchange, the correct choice of the cultivated plant species and appropriately changed areas might approve the aims of environmental sustainability in agroenvironment. The data of this and previous studies take a significant value in order to enhance of the alteration and areas of crop in rotational systems so that advance correct mitigation strategies of climate change.

CONCLUSION

Photosynthetic surface and rates of assimilated atmospheric CO_2 depended on bio-parameters, specifically crop density and LAI in agro-ecosystems. Maize and ley developed the highest CO_2 assimilation capacity between crops. Therefore, the data revealed that appropriate choice of plant species and alteration their area in rotational systems can enhance assimilation of atmospheric CO_2, increase agroenvironment sustainability and mitigate to climate change.

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Student Section

HONEY BEES AS BIOINDICATOR OF ENVIRONMENTAL POLLUTION

MEDONOSNA PČELA KAO BIOINDIKATOR ZAGAĐENJA ŽIVOTNE SREDINE

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Abstract

Honey bee and bee products are very good indicators of pollution. The bee is active throughout the area surrounding the hive. The bee can range over long distances, even up to ten kilometers under exceptional circumstances: a hive can keep an area of seven square kilometers under its control. The bee as a biological indicator possesses several important morphological and ecological factors. Keeping the bees can have a good effect on humans. The bee acts as a detector of environmental pollution in two ways. First as a high mortality rate from the presence of toxic molecules and over residues in honey, pollen and larvae of the presence of heavy metals, fungicides and herbicides. Bees are exposed to many contaminants during feeding, pollutants from the air can be easily applied to their hairs during the collection of pollen and nectar from flowers or through water. Bees can carry to the hive many contaminants deposited on plants. Pesticides used in agriculture may not only be a cause of high bee mortality, but may also enter the bee product. One of the methods used in pollen analysis is the GC-MS/MS analytical method. This method was used for the determination of multiple residues of 26 pesticides in pollen has been developed and validated in accordance with the recommendations of the European Union SANCO guide. The presence of xenobiotic in these products can compromise their quality and properties and endanger human health. Bee samples are collected in three periods: March, June and September. Sampling choices should be closely related with seasons and different insect activities. Beekeeping, in addition to environmental studies, is used to produce ecological and health maps for specific areas. A large problem in honey is heavy metals. Heavy metals are coming from the industries. Not just industries area are affected, a lot of pollution are travelling by air or water and that affected to an area with very clean nature. In Table 1 are analyzed levels of different metals in honey.

***Table 1** Data are expressed as mg/g of honey for the first group of metals (Al to Zn) analyzed and as µg/g of honey for the second group (As to Ti)*

Metals	May	August	November
Al	114.69±16.7	79.61±11.11	128.83±32.5
B	174.64±35.21	191.64±24.91	181.72±17.9
Ca	9889.96±976.4	10114.31±910.15	10103.37±959.13
Cu	226.59±18.9	239.96±16.8	225.56±20.15
Fe	1201.67±157.8	1170.39±71.3	1151.76±92.56

Table 1 *continued*

K	17779.13±1134.4	17.192.42±656.15	16.875.86±1500.63
Mg	9288.43±641.25	9126.76±239.97	9052.62±705.56
Mn	1239.51±293.53	1501.84±157.39	1285.41±88.54
Na	4833.71±299.31	4588.18±101.57	4362.16±528.49
Si	556.4±74.25	586.31±102.62	608.79±53.69
Zn	1302.34±57.82	1333.13±125.35	1195.84±31.38
As	357.02±57.42	312.44±37.37	335.47±39.31
Cd	3654.57±441.54	4336.48±126.76	4347.66±291
Co	1117.42±147.38	1273.06±170.98	1112.75±37.37
Cr	6835.71±1506.8	8369.91±1761.01	7849.12±1329.58
Ni	2484.15±234.6	2614.26±274.44	2993.54±295.18
Pb	816.06±330.27	534.39±58.74	585.41±161.7
Sb	41.45±19.2	53.52±59.27	25.83±2.67
Se	968.42±187.7	877.3±229.69	798.42±177.76
Ti	180279.31±10342.0	187846.41±19091.61	174537.76±7871.31

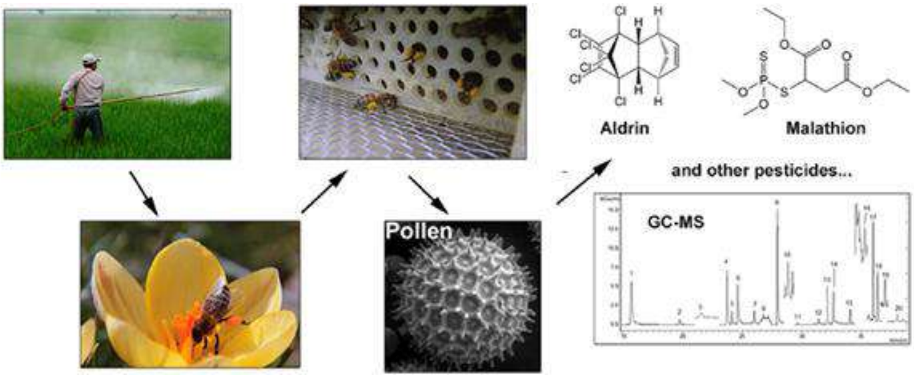

Figure 1 *Pollen analysis*

Keywords: Honey bee, Pollutions, Biomonitoring, Environmental marker

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THERMOSTABLE PLASTIC POLYMERS

TERMOSTABILNI POLIMERI PLASTIKE

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Abstract

Thermostable polymers are a class of polymers obtained by curing or crosslinking thermo-resins. These are polymers that use heat or radiation energy with the addition of some hardener, in the presence or without the presence of a catalyst. Thermostable polymers are obtained by various chemical processes, polymerization, condensation or addition. Once the polymer mass has solidified, it can no longer change shape. The most significant representatives are:

-epoxy resins;

-formaldehyde and phenolic resins;

-polyurethanes;

-polyesters;

-silicone organic polymers (silicones).

Epoxy resin is a thermostable polymer composed of epoxy groups in its molecular structures, and is formed by the condensation reaction between bisphenol A (BPA) and epichlorohydrin (ECH).

Phenol-formaldehyde polymers are the first synthetically produced polymers. Phenol-formaldehyde resins are obtained by condensation in the presence of acidic or basic catalysts during the polymerization of phenol and formaldehyde. When the conditions of preparation are such that there is more formaldehyde than phenol, a resol is obtained, and when the case is opposite, a novolac is obtained. Phenolic resins are prepared in both acidic and base environments. They can be divided into several groups, of which the most significant are:

- phenol-formaldehyde polymers (PF);

- amino-formaldehyde polymers (AF):

- urea-formaldehyde polymers (UF);

- melamine-formaldehyde polymers (MF);

- melamine-urea-formaldehyde polymers (UMF).

Polyurethanes are obtained by exothermic alcohol reactions with two or more reactive hydroxyl groups (-OH) per molecule (diols, triols, polyols) and isocyanates. One of the significant representatives of this group is poly-thiourea, which contains S in its structure.

Depending on the characteristics of the catalyst, there are two different tipes of activation, nucleophilic and electrophilic activation.

Polyesters are obtained by the condensation of multibasic acids and polyhydroxyl alcohols. Condensation produces quality products only when the water is completely removed.

Thermostable silicones are made of linear silicone polymers, most commonly polydimethyl-siloxane. Silicones with organic polymers contain a C-Si bond, and many silicones instead of carbon contain a Si-Si bond, which is more unstable than a C-Si bond. Silicones can be divided into four groups: silicone gels, silicone fluids, silicone elastomers and silicone resins. The poor properties of thermostable polymers, such as low flexibility and low recyclability and biodegradability, are being studied and eliminated, so the use of biodegradable, thermostable plastics polymers is expected in the near future.

Keywords: Plastic, epoxy resins, formaldehyde and phenolic resins, silicones

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