Božidar V. Đokić, Milun Jovanović*, Olivera Đokić***

HEAVY METALS IN THE SOIL AROUND THE FLOTATION TAILING DUMP OF THE LEAD-ZINC MINE GROT MINE, SOUTHEAST SERBIA***

Abstract

Tailing dump of the mine Grot mine with more than 5.5 million tons of floated material is the highest altitude dump in Serbia. Vegetation is not developed on it at all. The behavior of heavy metals in the flotation tailing dump has recently been analyzed in the literature. Mineralized dust is observed on the surrounding soil demonstrating its recent pollution. This land is tilled in a primitive way. The analysis of soil shows the presence of heavy metals of anthropogenic origin. The concentrations of these materials vary with the configuration of terrain and weather conditions. Lead is the most toxic of found heavy metals in soil.

Keywords: tailing dump, soil, heavy metals, mineralized dust

INTRODUCTION

Many geologists with different research motivations have visited Serbia. Sometimes the results of these studies led to the mine opening. In Serbia, there are many publications that deal with the issues of mines [5,6]. Some of them, especially the more recent researches, were funded from abroad [11].

As there is no mining without waste, the mine dumps are formed near the mines, and in most cases in Serbia they are unsecured. Data on the material in dumps are absent and they are mostly in the form of fund documentation [1]. The impact of dumps on surrounding land, water and air, through which toxic substances are easily introduced into the food chain and the human organism are seldom analyzed. Environmental impact

of tailing dump of the mine is one of the areas where basic information does not exist.

There are many publications in the world treating very precisely this type of waste material [13].

Land around the tailing dump Grot is developed on the Surdulica granodiorite [12].

The local population consumes agricultural products produced on it.

MATERIALS AND METHODS

General information on flotation tailing dump and surrounding soil

Tailing dump Grot is located in the southeastern Serbia (Figure 1 a).

* Geological Survey of Serbia, Belgrade, 12 Rovinjska, Serbia, E mail: djokic.bozidar@gmail.com

** The Highway Institute, Belgrade, 257 Kumodraska, Serbia

*** This work is derived from research within the framework of the "Cadastre of Technogenic Metallic Mineral Raw Materials Tailing Dumps of the Republic of Serbia with Source and Environmental Capacity Risk Assessment", funded by the Ministry of Environment and Spatial Planning (Project No. 310-02-174/2009-02).

a. Geographical position of tailings and soil in the vicinity, N north, SE southeasterly and S south of tailing dump

b. The Surdulica granodiorite at the base of land in the vicinity of tailing dump

c, d. and e. Land north, south east and south of tailing dump

Figure 1 *Geographical position of tailings and the land around*

Position coordinates of the representative tailing dump point are 7596145, 4713975. Grot tailing dump was formed on a plateau by damming the Seliski stream [2]. Ores,

whose mining and processing resulted into formation of tailing dump, are polymetallic. Technological preparation of these ores consists of crushing, grinding and flotation

preparation - treatment with potassium ethyl xanthate, potassium amyl xanthate, sodium cyanide, zinc sulphate, copper sulphate and lime). In this way the various aggregates of

minerals are formed (Figure 2a, b., from [3]). In granulometric way it is constructed of alevritic sand, alevrites and sandy alevrites [3].

a. Class of sulfide minerals to which is glued onto silica. Representative sample of unpolished grain size 0.1 mm. Large plateau flotation tailings Grot

b. Elemental Fe with stuck oxide mineral classes

Figures 2a and 2b. Mineral aggregates, from [3]

Land around the tailing dump is shallow, resulting from specific geological terrain, climate and topography (Fig. 1b). Pedologically, they are ranker brownised-district cambisol (70:30) formed on granite and granodiorite [10]. Lands are formed between nameless streams, on the gentle slopes that gravitate towards tailing dump. Total area of land north of tailing dump is 51 538 m² and representative coordinates are 7596426, 4714352; the southeast area is 134 591 m² and representative coordinates are 7596602, 4713698; the south area is 128 287 m² and representative coordinates are 7596325, 4713560 (Fig. 1c, d and e). Land east and northeast of the dumpsite are not sampled because of the existing homes and religious buildings.

Lands around tailing dump are used for pastures and gardens. They are tilled in a primitive way, so the impact of pesticides on their properties is minimal. A channel protects the lands from the spills of floated dumpsite material. Sedimentation of mineralized dust that is scattered from tailing dump has an enormous influence on

the soil properties. These aggregates fall into the surrounding soil. Metal-mineral aggregates which are visible on the soil surface, indicate the presence of material from flotation tailings.

Dust emission from dry tailing dump area is carried out under the dynamic force that lifts the clusters and breaks them, depending on the dominant wind direction. Configuration of dumpsite environment is also essentially influencing the transport of mineralized dust.

There is no meteorological station in its surroundings that would provide the relevant information on local climate.

QUANTITATIVE AND QUALITATIVE ANALYSES

Sampling for grain-size analysis was carried out in November 2010. The sample is represented with nine probes that were collected from a depth of 15 cm - three soil probes from the north, south east and south of tailing dump.

Samples for chemical analyses of soil are represented with 5 probes collected from a depth of 15 cm. The analyses were carried out on 18 samples from the north of tailing dump, 20 and 22 from the south southeast.

All samples were geopositioned with device GPSMAP 60CSx.

After sample preparation, the grain-size analysis was done with sieves openings 2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm, 0.05 mm and pipetting. Concentrations of elements were carried out with X-ray emission spectrometry with secondary excitation (XRF).

RESULTS AND DISCUSSION

The grain-size analysis of soil sample shows a presence of 35.7% sandy fractions, 61.89% alevritic and 2.5% clay. The most frequent is the 0.02 mm fraction of sandy dust [4].

Concentration of heavy metals was analyzed in the surrounding shallow soils of tailing dump. Mineralized dust was sporadically observed on the surface it which indicates recent contamination.

Lead, iron, zinc, copper, arsenic, tin, cobalt, chromium, vanadium and mercury were found on flotation tailing [3]. Presence of these elements was found in the surrounding soil also.

All analyzed heavy metals have lower content in the soil than in tailing dump.

Lead is the most toxic heavy metal found in the soil. The continuous concentration occurs in the north and northeast, and the extreme contents in the south of tailing dump. The extreme concentrations are local - the most common content (moda) is identical in all soils. This is the reason why the average from the north, especially southeast from the dumpsite is close to maximum concentrations. Due to the large range of concentrations, the median describes a distribution of lead better than average, especially on the soil south of tailing dump. This is confirmed with measures of dispersion - above all, standard deviation is much smaller in north and southeast of the dumpsite, than south (Table 1).

Table 1 Statistical parameters and phytotoxic concentrations of lead, zinc, copper, iron and manganese in the soil around flotation tailing dump Grot

	Land north of tailing dump						Land southeast of tailing dump						The land south of tailing dump						Phytotoxic concentration [8]
	Medium value	Median	Mode	Maximum	Minimum	Standard deviation	Medium value	Median	Mode	Maximum	Minimum	Standard deviation	Medium value	Median	Mode	Maximum	Minimum	Standard deviation	
Pb (ppm)	151	104	100	516	90	106	126	103	100	200	72	44	6835	191	100	73930	42	19921	100-400
Zn (ppm)	97	100	100	300	0	58	80	88	100	100	0	27	433	100	100	4795	0	1102	70-400
Cu (ppm)	3	0	0	35	0	10	5	0	0	32	0	11	293	0	0	3770	0	905	60-125
Mn (ppm)	844	746	500	1700	500	354	1050	1014	1400	1800	587	346	1622	1200	472	7078	472	1446	-
Fe (%)	1.3	1.4	0.9	1.5	0.9	0.2	1.4	1.4	1.0	1.7	1.1	0.2	3.7	1.4	0.9	33.7	0.9	7.1	-

The lead content in the soil is above normal by far, and there are places where the lead content is several times above permitted value in multi-contaminated soils (1-30 ppm, [7]). In most individual analyses, concentrations of lead are in the phytotoxic range, but locally, south of tailing dump, are below (Table 1).

Maximum concentration of lead content is reached in the northern part of the

great plateau of tailing dump [2, 3]. Maximum concentration of lead in the soil in the south of tailing dump is in relation to the exogenic geochemical cycle where it concentrates in the clay minerals that have the ability to absorb lead from tailing dump [7]. This material is scattered from there and, depending on the wind, spreads out into the environment.

Lead was determined in precipitators for measurement (intensity) of air pollution. The highest concentration determined in the intervals July-September in the south-southeast of the dumpsite [3].

In the North and northeast part of the dumpsite, zinc occurs in continuous values very close to the median average concentrations. South of the dumpsite occurs locally in extreme content, therefore in this part the median is the representative parameter. The most frequent concentrations were the same in all soils. The standard deviation is much lower in samples from north and southeast than south which confirms the representativeness of average concentrations.

Zinc has the property to cling to clay minerals and oxides and hydroxides of iron and manganese [7]. There are parts of tailing where maximum concentrations of zinc coincide with maximum concentrations of iron [3]. Clay minerals and iron oxides and hydroxides that are scattered from the dumpsite fall around and thus raise the concentration. The concentration of zinc is in the phytotoxic range, locally and above (Table 1).

Zinc is an essential element that is included in a number of physiological responses, but its toxic effects are well known too which depend on the interaction with iron, copper and calcium. Zinc was determined in precipitators for measurement (intensity) of air pollution in the cumulative deposition interval from October to December and July-September in the south-southeast of the dumpsite [3].

Copper occurs in most analyzes below the detection method, and locally, in higher concentration, in the south part of the dumpsite (Table 1). This element is the most essential for living organisms, but its toxic effects are also well known. They are manifested through kidneys and skin. Human poisoning with copper is rare because its salts are excreted from the body [7].

Iron is continuously present in high concentrations in the soil. Although it is one of the essential elements, its toxic effects are identified in the liver, respiratory, endocrine,

nervous and cardiovascular systems [3]. Excessive concentrations of iron lead to disease hemochromatosis [9].

Manganese occurs in uniform concentrations with slightly increased values in the southeast and southern parts of tailing dump. North and southeast of tailing dump are the values where average and median are close. In soil, in one locality southeast of dumpsite, tin and antimony were observed. Antimony occurs in phytotoxic concentration range.

Around the dumpsite nor molybdenum, mercury, chromium, cadmium, nor tungsten were found although these heavy metals were found in the flotation tailing. Cadmium in the time interval July-September was found in the south-southeast of tailing dump in the precipitators for determining the air pollution in excess value, which is untypical for unoccupied and reactive areas [3].

CONCLUSION

In the Seliska stream valley about 5.5 Mt of tailing material treated with chemicals, during the preparation for flotation, that cause cancer and mutagenic changes in the environment, was deposited.

Mineralized dust was found in the soil surface surrounding the tailing dump, which indicates recent pollution.

Lead, zinc, copper, iron, manganese and tin, and antimony as heavy metals were found in the soil around the dump. Their contents in the soil were always less than in the dump. Their presence in soils are of anthropogenic origin and depend on the Grot mine processing activities, but their concentration depends of the terrain morphology and weather conditions. Despite the absence of meteorological data which could indicate the dominant wind directions (the nearest are in Vranje and Bosilegrad - so far away from the tailings and high altitude differences are not relevant), the observed macroscopic soil mineralization indicates that the predominant wind direction are from north to the south.

Lead is the most toxic heavy metal that is continuously determined in the soil

environment. Lead, concentrated in the surface layer of shallow soil horizons, penetrates in deeper horizons. Grot mine, from whose activity largely depends the quality of the living environment, is practically the only company where local population of Vranje, one of the least developed municipalities in Serbia, can find the job.

Further research will be focused in determining the presence of these elements in the soil vegetation in the area and determining their bioavailability. The applied sequence analysis will give potential evaluation of heavy metal toxicity.

REFERENCES

- [1] Đokić B. V., Jovanović M. (2006-2010): Cadastre of Technogenic Metallic Mineral Raw Materials Tailing Dumps of the Republic of Serbia with Source and Environmental Capacity Risk Assessment, Annual Report, Geological Institute of Serbia, Belgrade (in Serbian);
- [2] Djokic B. V., Jovic V. M., Jovanović M., Ciric A., Jovanović D. (2012): Geochemical Behaviour of some Heavy Metals of the Grot Flotation, Southeast Serbia, Environmental Earth Sciences, Vol. 66, No. 3, pp. 933-939 (in Serbian);
- [3] Đokić B. V. (2012): Geochemical Characteristics of the Grot Mine Flotation Tailing Dump (Southeast Serbia), Doctoral Dissertation (in Serbian);
- [4] M. Jovanovic, B. Djokic V. (2012): Geochemical Map of Serbia, Geological Institute of Serbia, Belgrade (in Serbian);
- [5] Jankovic S. (1990): Ore deposits of Serbia, Regional Metallogenic Location, Environment Creation and Types of Deposits, Republican Social Fund for Geological Research, Department of Economic Geology, Mining and Geology, Belgrade (in Serbian);
- [6] Janković S., Jelenković R., Vujić S. (2003): Mineral Resources and Potential Prognosis of Metallic and Non-metallic Mineral Raw Materials in Serbia and Montenegro at the end of the XXth century, Engineering Academy of Serbia and Montenegro, Department for Computers Application in Mining and Department for Economic Geology, Faculty of Mining and Geology, University of Belgrade (in Serbian);
- [7] Jović V. and Jovanović L. (2004) Geochemical Basis of Ecological Management, Society for Dissemination and Application of Science and Practice of Environmental Protection of Serbia and Montenegro, Ekologika, Belgrade (in Serbian);
- [8] Kabata-Pendias A., Pendias H (1984): Trace Elements in Soils and Plants. CRS. Press. Boca Raton;
- [9] Mandić Lj (2012): Heavy Metals from Food to Toxic Effects. Can heavy metals be Good and Bad for Human Health? www.docstoc.com/docs/107557502, available 15.03 2013;
- [10] Nikoloski M., Antonović G., Čakmak D., Saljnikov E., Maksimović S., Koković N., Perović V. (2011): Soil Map, Section Vlasotince 3, 1:50 000, Detail, Institute of Soil, Ministry of Agriculture, Forestry and Water Management of Serbia, Belgrade (in Serbian);
- [11] Nishikawa Y. (2008): The Study on Master Plan for Promotion of Mining Industry in Republic of Serbia, Final Report, Japan International Cooperation Agency Economic Development Department, Belgrade;
- [12] Simić M. (2001): Metallogeny of Mačkatice-Blagodot-Karamanica Zone, Special Editions of Geo Institute, Book 28, Belgrade (in Serbian);
- [13] Commission of the European communities, 2003: Proposal for a Directive of the European Parliament and the Council on Management of Waste from Extractive Industries, Presented by the Commission, 319, Final, Brussels.

Božidar V. Đokić*, Milun Jovanović*, Olivera Đokić**

TEŠKI METALI U ZEMLJIŠTU OKO FLOTACIJSKOG JALOVIŠTA OLOVNO - CINKANOG RUDNIKA GROT, JUGOISTOČNA SRBIJA***

Izvod

Jalovište rudnika Grot sa više od 5.5 miliona tona flotiranog materijala je deponija na najvećoj nadmorskoj visini u Srbiji. Vegetacija nije razvijena ni na jednom njegovom delu. U literaturi je u novije vreme analizirano ponašanje teških metala na jalovištu. Na zemljištu koje ga okružuje uočena je mineralizovana prašina koja ukazuje na njegovo recentno zagađivanje. Ovo zemljište se primitivno obrađuje. Analizama zemljišta konstatovani su teški metali antropogenog porekla sa deponije. Koncentracije ovog materijala zavisi od konfiguracije terena i od meteoroloških uslova. Najtoksičniji teški metal konstatovan u zemljištu je olovo.

Cljučne reči: jalovište, zemljište, teški metali, mineralizovana prašina

UVOD

Brojni geolozi su sa različitim istraživačkim pobudama pohodili Srbiju. Rezultati tih istraživanja nekada dovode do otvaranja rudnika. U Srbiji su brojne publikacije koje tretiraju problematiku rudnika [5,6]. Neka, posebno novija istraživanja, finansirana su i iz inostranstva [11].

Kako rudarenja nema bez otpada - u blizini rudnika formiraju se deponije koje su u Srbiji uglavnom neobezbeđene. Podaci o materijalu u deponijama izostaju - uglavnom su u formi fondovske dokumentacije [1]. Uticaji deponija na okolno zemljište, vodu i vazduh, preko koga se toksične materije najlakše uvode u lanac ishrane i čovekov organizam retko su analizirani. Uticaji na okolinu jalovišta rudnika Grot je jedno od

područja odakle izostaju i osnovne informacije.

U svetu su brojne publikacije koje veoma precizno definišu odnose prema ovoj vrsti otpadnog materijala [13].

Zemljišta u okolini jalovišta Grot su razvijena na surduličkom granodioritu [12].

Lokalno stanovništvo konzumira na njemu proizvedene poljoprivredne proizvode.

MATERIJALI I METODE

Generalne informacije o jalovištu i okolnom zemljištu

Deponija Grot se nalazi u jugoistočnoj Srbiji (sl. 1 a).

* Geološki zavod Srbije, Rovinjska 12, Beograd, Srbija, E mail: djokic.bozidar@gmail.com

** Institut za puteve, Kumodraška 257, Beograd, Srbija

*** Ovaj rad je proistekao iz istraživanja, u okviru Projekta "Katastar jalovišta tehnogenih mineralnih sirovina Republike Srbije sa procenom rizika izvora i kapaciteta životne sredine" koji se finansira sredstvima Ministarstva životne sredine i prostornog planiranja (Projekat br. 310-02-174/2009-02).

a. Geografski položaj jalovišta i zemljišta u okolini, N severno, SE jugoistočno i S južno od jalovišta

b. Surdulički granodioriti u bazi zemljišta u okolini jalovišta

c., d. i e. Zemljište severno, jugoistočno i južno od jalovišta

Sl. 1. Geografski položaj jalovišta i zemljišta u okolini

Koordinata reprezentativne tačke položaja jalovišta je 7596145, 4713975. Jalovište rudnika Grot je formirano na visoravni pregrađivanjem Seliškog potoka

[2]. Rude čijom eksploatacijom i preradom je formirano jesu polimetalične. Tehnološka priprema ovih ruda se sastojala u njihovom drobljenju, mlevenju i flota-

cijskoj pripremi - tretiranju sa kalijum-etil ksantatom, kalijum-amil-ksantatom, natrijum-cijanidom, cink-sulfatom, bakar-sulfatom i krečom. Na ovaj način formirani

su materijalno različiti agregati minerala (sl. 2a, b., iz [3]). Jalovište je granulometrijski izgrađeno od alevritskog peska, alevrita i peskovitog alevrita [3].

a. Sulfidne klasa minerala na koju je nalepljena silikatna. Reprezentativni nepolirani uzorak veličine zrna 0,1 mm, veliki plato flotacijskog jalovišta Grot

b. Elementarno Fe sa nalepljenim oksidnim klasama minerala

Sl. 2a i 2 b. Mineralni agregati, iz [3]

Zemljišta u okolini jalovišta su plitka, što je posledica specifične geološke podloge, klime i reljefa (sl. 1b). U pedološkom smislu predstavljaju ranker posmeđen-distrični kambisol (70:30) formiran na granitu i granodioritu [10]. Zemljišta su formirana između bezimenih potoka, na blagim padinama koje gravitiraju ka deponiji. Površina zemljišta severno od jalovišta je 51.538m², a reprezentativna koordinata 7596426, 4714352; površina jugoistočno je 134.591m² reprezentativna koordinata 7596602, 4713698 i površina južno je 128.287m² a reprezentativna koordinata 7596325, 4713560 (sl. 1c, d i e). Zemljišta istočno i severoistočno od jalovišta nisu oprobavana iz razloga što su na tim prostorima izgrađene kuće i sakralni objekti.

Zemljišta u okolini jalovišta se koriste za pašnjake i bašte koje se primitivno obrađuju, pa je uticaj pesticida na njihova svojstva minimalan. Kanalom su zaštićena od izlivanja flotiranog materijala sa jalovišta. Na svojstva zemljišta u velikoj meri utiče sedimentacija mineralizovane prašine koja

se razvija sa jalovišta. Ovi agregati razvijani sa jalovišta dospevalaju na okolno zemljište. Na površini zemljištu su vidljivi metalni mineralni agregati koji ukazuju na prisustvo jalovinskog materijala.

Emisija prašine sa suvih površina jalovišta se vrši pod dinamičkom silom koja podiže klase i obara ih, u zavisnosti od dominantnog pravca vetra. Konfiguracija okoline jalovišta je takođe jedan od diskriminacionih elemenata za transport mineralizovane prašine.

U bližoj okolini ne postoji meteorološka stanica koja bi pružila relevantne podatke o lokalnoj klimi.

KVANTITATIVNE I KVALITATIVNE ANALIZE

Oprobavanja za granulometrijske analize su vršena u novembru 2010. godine. Uzorak predstavlja reprezent 9 proba koje su prikupljene sa dubine 15 cm - po tri probe zemljišta severno, jugoistočno i južno od jalovišta.

Uzorci za hemijske analize zemljišta predstavljaju reprezent od 5 proba prikupljenih sa dubine od 15 cm. Analizirano je 18 uzoraka severno od jalovišta, 20 jugoistočno i 22 južno.

Svi uzorci su geopozicionirani uređajem GPSMAP 60CSx.

Granulometrijska analiza je rađena nakon pripreme uzorka prosejavanjem na sitima sa otvorima 2 mm, 1 mm, 0,5 mm, 0,25 mm, 0,125 mm, 0,05 mm i pipetiranjem.

Koncentracije elemenata su utvrđivani rendgenskom emisionom spektrometrijom sa sekundarnim pobuđivanjem (XRF).

REZULTATI I DISKUSIJA

Granulometrijska analiza uzorka koji reprezentuje zemljište pokazuje zastupljenost peskovite frakcije od 35,7 %, alevritske 61,89 % i glinovite 2,5 %. Najzastupljenija je frakcija peskovitog praha 0,02 mm [4].

U plitkim zemljištima koja okružuju jalovište analizirana je koncentracija teških metala. Na površini je mestimično

uočena mineralizovana prašina koja ukazuje na recentno zagađivanje.

Na flotacijskom jalovištu konstatovani su gvožđe, olovo, cink, bakar, arsen, kalaj, kobalt, hrom, vanadijum i živa [3]. Prisustvo ovih elemenata je utvrđivano i u okolnom zemljištu.

Svi analizirani teški metali su u nižim sadržajima u zemljištu nego u deponiji.

Najtoksičniji teški metal konstatovan u zemljištu je olovo. U kontinuiranim koncentracijama se javlja severno i severo-istočno, a ekstremne sadržaje ostvaruje južno od deponije. Ekstremne koncentracije su lokalne - najučestaliji sadržaj (moda) identični su u svim zemljištima. Ovo je i razlog što je srednja vrednost severno, a posebno jugoistočno od jalovišta bliska maksimalnim koncentracijama. Zbog velikog raspona koncentracija, medijana bolje karakteriše distribuciju olova od srednje vrednosti, posebno na zemljištu južno od jalovišta. Ovo potvrđuju mere disperzije, pre svih standardna devijacija koja je mnogo manja severno i jugoistočno od jalovišta, nego južno (tabela 1).

Tabela 1. Statistički parametri i fitotoksične koncentracije olova, cinka, bakra, gvožđa i mangana u zemljištu u okolini flotacijskog jalovišta rudnika Grot

	Zemljište severno od jalovišta						Zemljište jugoistočno od jalovišta						Zemljište južno od jalovišta						Fitotoksična koncentracija [8]
	Sr. Vrednost	Medijana	Moda	Maximum	Minimum	Standardna devijacija	Sr. vrednost	Medijana	Moda	Maximum	Minimum	Standardna devijacija	Sr. vrednost	Medijana	Moda	Maximum	Minimum	Standardna devijacija	
Pb (ppm)	151	104	100	516	90	106	126	103	100	200	72	44	6835	191	100	73930	42	19921	100-400
Zn (ppm)	97	100	100	300	0	58	80	88	100	100	0	27	433	100	100	4795	0	1102	70-400
Cu (ppm)	3	0	0	35	0	10	5	0	0	32	0	11	293	0	0	3770	0	905	60-125
Mn (ppm)	844	746	500	1700	500	354	1050	1014	1400	1800	587	346	1622	1200	472	7078	472	1446	-
Fe (%)	1.3	1.4	0.9	1.5	0.9	0.2	1.4	1.4	1.0	1.7	1.1	0.2	3.7	1.4	0.9	33.7	0.9	7.1	-

Sadržaji olova u zemljištu mnogo, a negde i višestruko prevazilaze dozvoljene u zagađenim zemljištima (1-30 ppm, [7]). U većini pojedinačnih analiza koncentracije olova su u fitotoksičnom opsegu, a lokalno, južno od jalovišta, su ispod (tabela 1).

Koncentracije olova maksimalne sadržaje dostižu na severnim delovima velikog platoa jalovišta [2,3]. Maksimalne konc-

tracije olova u zemljištima južno od deponije su u vezi sa egzogenim geohemijskim ciklusom kojim se ono koncentriše u mineralima glina koje imaju moć da ga absorbuju sa jalovišta [7]. Ovaj materijal se odatle razvejava i u zavisnosti od ruže vetrova obara u okolinu.

Olovo je konstatovano i u taložnicima za merenje (intenziteta) aerozagađenja. Naj-

veće izmerene koncentracije su u vremenskim intervalima jul - septembar južno-jugoistočno od jalovišta [3] .

Cink se severno i severoistočno od jalovišta javlja u kontinuiranim sadržajima sa medijanom veoma bliskom prosečnim koncentracijama. Južno od jalovišta lokalno se javlja u ekstremnim sadržajima, pa je u ovim delovima medijana reprezentativniji parametar. Najfrekventnije koncentracije su u svim zemljištima iste. Standardna devijacija je mnogo niža u uzorcima severno i jugoistočno nego južno što potvrđuje reprezentativnost prosečne koncentracije.

Cink ima osobinu da se vezuje za minerale glina i za okside i hidrokside gvožđa i mangana [7]. Na jalovištu se podudaraju delovi sa maksimalnim koncentracijama cinka i gvožđa [3]. Minerali glina i oksidi i hidroksidi gvožđa koji se razvejavaju sa jalovišta svojim obaranjem na zemljište u okolini formiraju zone njegove povećane koncentracije. Koncentracije cinka su u fitotoksičnom opsegu, lokalno i iznad (tabela 1).

Cink je esencijalan element koji učestvuje u brojnim fiziološkim reakcijama, ali su poznata i njegova toksična dejstva koja zavise od interakcije sa gvožđem, bakrom i kalcijumom. Konstatovan je u taložnicima za merenje (intenziteta) aerozagađenja u kumulativnom intervalu taloženja oktobar-decembar i jul-septembar u pravcu jug-jugozak od jalovišta [3].

Bakar se u većini analiza javlja ispod granice detekcije metode, a lokalno, južno od jalovišta, u povišenim koncentracijama (tabela 1). Ovaj element je uglavnom esencijalan za živi svet, ali su poznati i toksični efekti koji se ispoljavaju na bubrezima i koži. Kod ljudi su trovanja bakrom retka jer se njegove soli izlučuju iz organizma [7].

Gvožđe je kontinuirano prisutno u visokim koncentracijama u zemljištu. Iako spada u esencijalne elemente, uočeni su njegovi toksični efekti u jetri, respiratornom, endokrinom, nervnom i kardiovaskularnom sistemu [3]. Prevelike koncentracije gvožđa dovode do bolesti hemohromatoze [9].

Mangan se javlja u ujednačenim koncentracijama nešto povećanim jugoistočno i južno od deponije. Severno i jugoistočno od jalovišta su vrednosti srednje vrednosti i medijane bliske.

U zemljištu, na jednom lokalitetu jugoistočno od jalovišta konstatovani su kalaj i antimon. Antimon se javlja u fitotoksičnom opsegu koncentracija.

U okolini jalovišta nije konstatovan molibden, živa, hrom, volfram i kadmijum mada su ovi teški metali konstatovani u flotacijskom jalovištu. Kadmijum je u vremenskom intervalu jul-septembar konstatovan južno-jugoistočno od jalovišta u taložnicima za utvrđivanje aerozagađenja u sadržajima većim od dozvoljenih za nastanjanje i rekreativna područja [3].

ZAKLJUČAK

U dolini Seliškog potoka deponovano je oko 5.5 Mt jalovinskog materijala koji je pri svojoj flotacijskoj pripremi tretiran sa hemikalijama koje izazivaju kancerogene i mutogene promene na životnoj okolini.

Na površini zemljišta u okolini jalovišta konstatovana je mineralizovana prašina koja ukazuje na recentna zagađivanja.

Od teških metala sa deponije, u zemljištu su konstatovani olovo, cink, bakar, gvožđe, mangan i kalaj i antimon. Njihovi sadržaji u zemljištu su uvek manje nego u deponiji. Prisustvo u zemljištu je antropogenog porekla i zavisi od prerađivačkih aktivnosti rudnika Grot, a koncentracija od morfologije terena i od meteoroloških uslova. Uprkos odsustvu podataka meteoroloških stanica koje bi ukazale na dominantne pravce vetrova (najbliže su u Vranju i Bosilegradi – zbog velike udaljenosti od jalovišta i velike razlike nadmorskih visine nisu relevantne), uočena makroskopska mineralizacije na zemljištu ukazuje da su dominantni pravci vetrova mogu biti od severa prema jugu.

Olovo je najtoksičniji teški metal koji je kontinuirano utvrđen u zemljište u okolini. Olovo koncentrisano u površinskom

horizontu inače plitkog zemljišta prodire dublje u horizonte.

Rudnik Grot od čijih aktivnosti uveliko zavisi kvalitet životnog okruženja, je praktično jedina kompanija u kojoj posao može da nađe lokalno stanovništvo koje teritorijalno pripada opštini Vranje - jednoj od najnerazvijenijih u Srbiji.

Dalja istraživanja će biti usmerena na utvrđivanje prisutnosti ovih elemenata u vegetaciji zemljišta u okruženju i u utvrđivanju njihove biodostupnosti. Primene sekvencijalne analize bi dale ocenu potencijala toksičnosti teških metala.

LITERATURA

- [1] Đokić B. V., Jovanović M. (2006-2010): Katastar jalovišta tehnogenih mineralnih sirovina Republike Srbije sa procenom rizika izvora i kapaciteta životne sredine. Izveštaji. Geološki institut Srbije. Ministarstvo prirodnih resursa, rudarstva i prostornog planiranja. Begrade.
- [2] Djokic B. V., Jovic V. M., Jovanović M., Ćiric A., Jovanović D. (2012): Geochemical Behaviour of Some Heavy Metals of the Grot flotation, Southeast Serbia. *Environmental Earth Sciences*. Vol. 66 br. 3, str 933-939.
- [3] Đokić B. V. (2012): Geohemijske karakteristike flotacijskog jalovišta rudnika Grot (jugoistočna Srbija). Doktorska disertacija. Univerzitet u Beogradu, Rudarsko-geološki fakultet
- [4] Jovanović M., Djokić B. V. (2012): Geohemijska karta Srbije. Geološki zavod Srbije. Beograd.
- [5] Janković S. (1990): Rudna ležišta Srbije. Regionalni metalogenetski položaj, sredine stvaranja i tipovi ležišta. Republički društveni fond za geološka istraživanja. Katedra ekonomske geologije. Rudarsko - geološki fakultet, Beograd.
- [6] Janković S., Jelenković R., Vujić S. (2003): Mineral Resources and Potential Prognosis of Metallic and Non-metallic Mineral Raw Materials in Serbia and Montenegro at the End of the XXth Century. Engineering Academy of Serbia and Montenegro. Department for Computers Application in Mining and Department for Economic Geology, Faculty of Mining and Geology University of Belgrade.
- [7] Jović V. and Jovanović L. (2004): Geohemijske osnove ekološkog menadžmenta, Društvo za širenje i primenu nauke i prakse u zaštiti životne sredine Srbije i Crne Gore „Ekologika“ Beograd.
- [8] Kabata-Pendias A., Pendias H (1984): Trace Elements in Soils and Plants. CRS. Press. Boca Raton.
- [9] Mandić Lj (2012): Teški metali od hrane do toksičnih efekata. Mogu li teški metali biti i dobri i loši za ljudsko zdravlje? www.docstoc.com/docs/107557502, dostupno 15.03 2013
- [10] Nikoloski M., Antonović G., Čakmak D., Saljnikov E., Maksimović S., Koković N., Perović V. (2011): Pedološka karta, sekcija Vlasotince 3, 1:50000, detalj, Institut za zemljište, ministarstvo poljoprivrede, trgovine, šumarstva i vodoprivrede Republike Srbije, Beograd.
- [11] Nishikawa Y. (2008): The Study on Master Plan for Promotion of Mining Industry in Republic of Serbia. Final Report. Japan International Cooperation Agency Economic Development Department, Beograd.
- [12] Simić M. (2001): Metalogenija zone Mačkatica-Blagodot-Karamanica. Posebna izdanja Geoinstituta, knjiga 28, Beograd.
- [13] Commission of the European communities, 2003: Proposal for a Directive of the European Parliament and of the Concil on the Management of Waste from Extractive Industries. Presented by the Commission, 319, Final, Brussels. Alpha