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GEOME 2
Manuscript received: January 7, 2019
Accepted: May 21, 2019

Geologica Macedonica, Vol. **33**, No. 1, pp. 61–70 (2019)
IISSN 0352 – 1206
e-ISSN 1857 – 8586
UDC: 631.416.84/.88:504.5(497.115)

Original scientific paper

ENRICHMENT OF SOME POTENTIALLY TOXIC ELEMENTS IN SOILS AFFECTED BY Pb-Zn MINING AND METALLURGICAL PROCESSING IN THE MITROVICA REGION, KOSOVO

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A b s t r a c t: The results of a study on the presence and enrichment of potentially toxic elements in surface soil in the Mitrovica region, Kosovo, are reported. The investigated region (301.5 km^2) was covered by a sampling grid of 1.4×1.4 km and a total of 156 soil samples were collected. Inductively coupled plasma - mass spectrometry (ICP-MS) was applied for the determination of anthropogenic association of 12 elements: Ag, As, Au, Bi, Cd, Cu, Hg, Pb, Mo, Sb, Tl and Zn. For data evaluation, parametric and non-parametric statistics methods were used. Soil contamination is assessed on the basis of enrichment factor (EF). The average content of Pb was 19.6-fold; Cd 11-fold; Hg 5-fold; Zn 4.5-fold; As 4.3-fold; Sb 3.8-fold; Cu 3.2-fold and Ag 1.6-fold higher that European average values. Increased levels of the content of these metals showed that mining and smelter processing activities strongly affected in soils of the towns of Zveçan and Mitrovica and their environs. In the close vicinity of the cities of Zveçan and Mitrovica, the contents of the As, Cd, Cu, Pb and Zn were even higher than the corresponding intervention values according to the New Dutch list and were exceed in 122 km^2 of the investigated area.

Key words: soil pollution; potentially toxic elements; Mitrovica; Republic of Kosovo

INTRODUCTION

Soil contamination with heavy metals is considered as serious problem related to mining and smelting activities. The environmental anomalous occurrence, regarding the possible ecological effect of the increasing accumulation of metals, is with growing concern. For this reason, the investigation of heavy metals in soils is necessary since even slight changes in their concentration above the critical level (whether due to the natural or anthropogenic factors) can results in serious environmental harms and subsequent health problems (Kabata-Pendias and Pendias, 2001).

In mining and smelting areas, soils are affected during the mining operations and for years after mine closure (Mileusnic et al., 2014; Morais et al., 2014), by disposal of mine tailings which are often left without proper management (Muhammad et al., 2011), acid mine drainage, and aerial deposition of contaminants from smelters (Navas and Machin, 2002; Ferreira da Silva et al., 2004; Ungaro et al., 2008; Chaoyang et al., 2009; Dayani and Mohammadi. 2010). Thus, tailings and wastes are dispersed by wind and erosion on soils, plants and water in the vicinity of the mining site (Meza-Figueroa et al., 2009; Amune et al., 2012). This dispersion is strongly correlated with local meteorological conditions, mainly on the prevailing wind direction (Kribek et al., 2010). Topsoils in the vicinity of smelters contain elevated levels of trace elements, for this reason, metal contamination can extend several kilometers away from the mine sites (Escarre et al., 2011). Airborne sources of metals include stack or duct emissions of air, gas, or vapor streams, and fugitive emissions such as dust from storage areas or waste piles. Metals from airborne sources are generally released as particulates contained in the gas stream. Some elements such as As, Cd and Pb can also volatilize during high-temperature processing converting to oxides and condense as fine particulates unless a reducing atmosphere is maintained (Smith et al., 1995). Stack emissions can be distributed in long-distance areas by natural air currents until dry and/or wet precipitation mechanisms remove them from the gas stream. The distribution of metals occurred in various forms, depends on the existing chemical environment.

Environment pollution particularly from hazardous heavy metals is an important global problem. Small quantities of some elements, like Fe, Zn, Cu, Co, Cr, Mn, and Ni, are essential for human, but may be toxic at higher levels (Duruиbe et al., 2007). Others like Pb, Hg, Cd and As have no beneficial role and are known for toxic effects on biological organisms and adverse effect on local environments. Many of these elements are bio-accumulative, and their toxicity strongly depends on its chemical form and oxidation state. The non-degradable nature of metallic species and their tendency to bind strongly with soil material can lead to long term contamination.

There are not many data on the environmental impact of mining and metallurgical activities in the Mitrovica region, which started in 1927. Several studies conducted on the heavy metal content in this area were published (Di Lella et al., 2003; Jia et al., 2004; Arditsoglou and Samara, 2005; Borgna et al., 2009). There also have been studies on the spatial distribution of heavy metals and the effects of mining and smelting activities on the soil enrichment with heavy metals (Aliu et al., 2009, 2010, 2014, 2016, 2017; Stafilov et al., 2011). Therefore, this study is aimed on the soil contamination in the Mitrovica region, Republic of Kosovo, with special attention to the enrichment of the heavy metals content in order to define the extent of soil pollution in this area.

MATERIAL AND METHODS

Study area

The Mitrovica region is the largest Pb-Zn mining area in Kosovo. The geologic deposits consist mainly of metal sulfides such as galena (PbS), sphalerite (ZnS), pyrite (FeS_2), arsenopyrite (FeAsS) and plymozite ($Pb_2Sb_2S_5$). To recover metals from ore deposits, extensive mining operations were used in Stan Tërg areas from the 1930s until 2000. The lead concentrates were brought to the lead smelter of Zveçan (capacity 80,000 t/y) and the zinc ores were brought to the zinc smelter of Mitrovica (capacity 50,000 t/y). The metal production was about two million tons of Pb, 1.37 million tons of Zn, as well as about 10000 t of Ag, Au, Cd, and Bi. Metal emissions from the smelters ran at 7.31 t/day Pb, 1.63 t/day Zn, 323.7 kg/day As, 103.8 kg/day Sb, 30.31 kg/day Cd and 37.35 kg/day Ag of crude metal smelted (Dushi, 2002).

Extensive Pb and Zn ore mining and smelting have resulted in contamination of soil that poses risk to human and ecological health. However, an environmental audit ordered by UNMIK and conducted in March and April 2000, warned that it should be closed as an "unacceptable" source for air pollution (Palariet, 2003; Frese et al., 2004; OSCE, 2009). Since then lead and zinc smelters are inactive. Since September 2005, the mine has only produced zinc, lead and copper concentrates at an average rate of 5,000 t/month, and these concentrates have been sold to traders. The silver, gold, bismuth, cadmium, indium, germanium and gallium of the various ore concentrates are extracted by foreign smelters which buy and process the concentrates (together with batches from other deposits).

The size of the investigation region occupies an area of 24 NNW-SSE km × 18 WWS-EEN km and it is limited with the coordinates (WGS 84) longitude 20.74528°–20.99235° (E) and latitude 42.78522°–42.99330° (N). This area occupies the part of the Iber river basin and Sitnica river basin, including area of the Mitrovica town in the middle. Furthermore, the investigation area occupies all the major urban zones (Zveçan, Mitrovica and Vushtrri), but also the main industrial zones, particularly around Zveçan and Mitrovica. Of the total 301.5 km^2 of the study area (Figure 1), the water surface (rivers and lakes) covers 1.6 km^2 (or 0.6 %), while the open area mainly includes cultivable land 160 km^2 (53%), non-cultivable areas, mainly forests 117.5 km^2 (39%), settlements 18.4 km^2 (6.1%) and industrial area (industry zones, mines, quarries and tailings) 4 km^2 (1.3%).

The study area presents a part of the Vardar zone (Bogdanović, 1978; Bogdanović et al., 1978). The geotectonic unit is covered by metamorphic, sedimentary and magmatic rocks of the younger Paleozoic and Triassic ages, Cretaceous flysch, Miocene volcanic rocks with pyroclastites as well as younger Pliocene and Quaternary sediments (Bogdanović, 1978; Bogdanović et al., 1978).

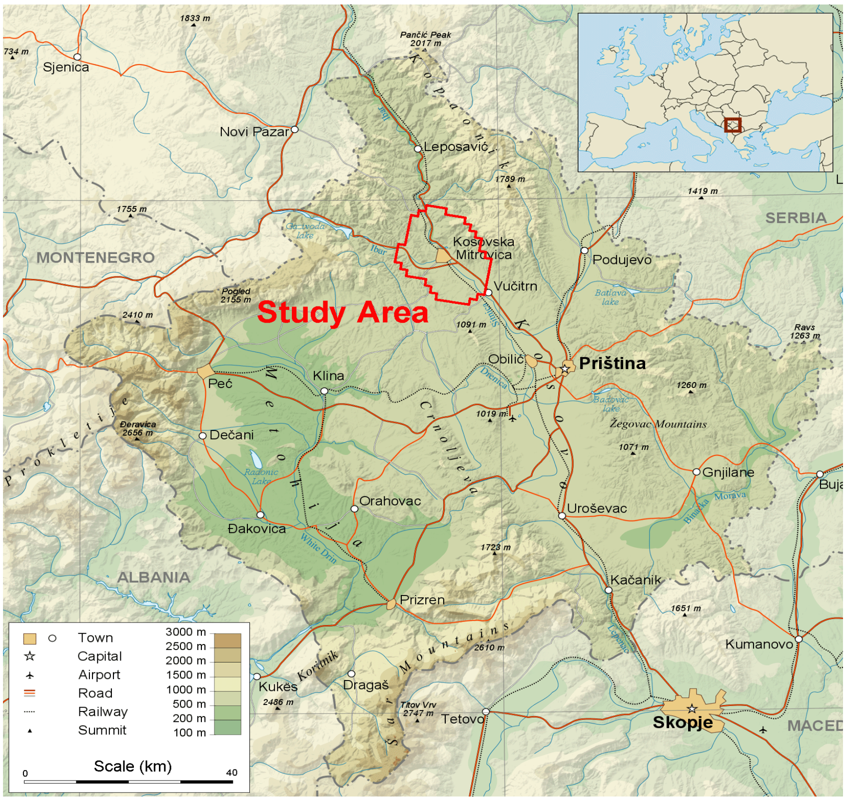

Fig. 1. Location of the study area

This area is characterized by a temperate continental climate with warm summers and cold winters. The average annual temperature is 10.3°C (15.8–4.9°C), the average temperature in January is –1°C (–5 to 3°C) and in August is 21°C (28–14°C). Mean annual precipitation is about 900 mm. Thermal inversion is frequent, especially in the winter months. About 40% of study area lies at an altitude between 480 and 600 m (S and SE of the study area), but only 5 % has an altitude over 1000 m, mainly in the NE of the investigated area.

Sampling and chemical analysis

The complete investigated region was covered by a basic sampling grid of 1.4×1.4 km^2, but in the diagonal cross-section of each entire grid cell, one more sample was added (Figure 2). From the whole investigated area 156 surface soil samples were collected at a depth of 0 to 5 cm in an area of 301.5 km^2 where the soil had not been recently disturbed and away from the waste locations. One sample represented the composite material collected at the central sample point itself and at least 4 points within a radius of 50 m around it towards N, E, S and W (Darnley et al., 1995).

Soil samples were air dried indoors at room temperature for about two weeks. Then, they were crushed, cleaned of extraneous material and sifted through a plastic sieve a mesh size of 2 mm (Salminen et al., 2005). The shifted mass was quartered and milled in an agate mill to an analytical grain size less than 0.125 mm.

Due to expected extreme contamination with heavy metals, the following zones were determined: zone I – areas extremely affected by heavy metals (57 km^2); zone II – areas strongly affected by heavy metals (117 km^2); zone III – areas relatively little affected by heavy metals (128 km^2). The first zone included 30 sampling sites, zone II included 65 sampling sites and zone III included 61 sampling sites (Figure 3). Additionally, groups of samples that covered the main urban area were defined (cca. 90% of the entire population). The wider urban area of the city of Zveçan was covered by 5 sampling sites, Mitrovica by 11 sampling sites, and Vushtrri by 8 sampling sites.

The elements content of twelve elements (Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl and Mo) was determined by ICP-MS at ACME Laboratory Ltd., Vancouver, Canada (ACME, 2010; http://acmelab.com) following an aqua regia digestion (mixture of HCl, HNO_3 and water at 95°C-1DX method).

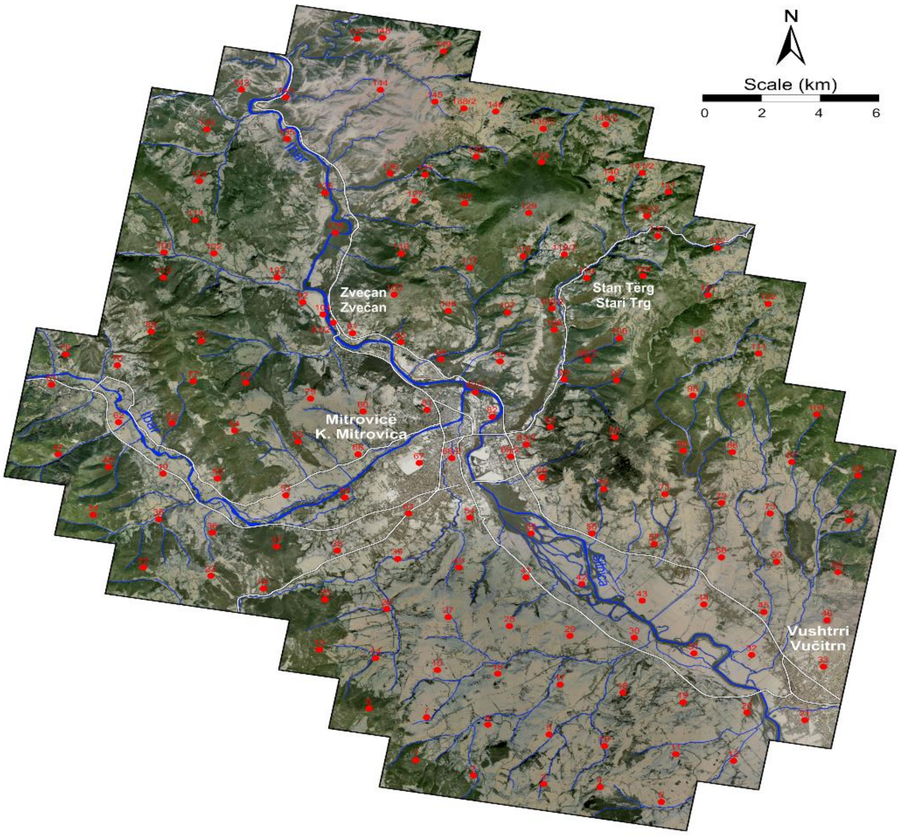

Fig. 2. Soil sample locations in the study area

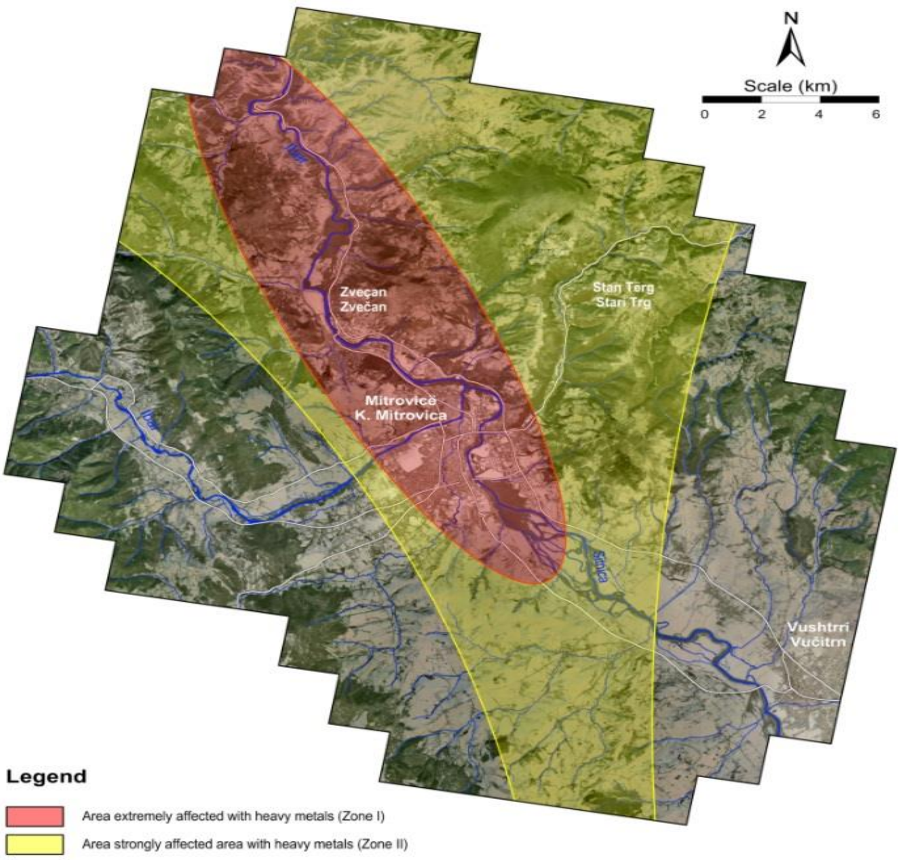

Fig. 3. Determined polluted zones in the study area

Data processing

For data evaluation, parametric and non-parametric statistics methods were used (Snedecor and Cochran, 1967; Le Maitre, 1982). The degree of association of chemical elements in the soil was assessed by the linear coefficient of correlation between their contents in the samples. Universal kriging with a linear variogram interpolation method was applied to construct maps of the spatial distribution of particular elements and factor values in topsoil.

RESULTS AND DISCUSSION

According to our previous investigation (Šajn et al., 2013), the application of factor analysis (FA) reveal five geochemical associations of elements (F1 to F5) which were connected with regard to geochemical similarities. However, the association marked as F1 shows strong association of Ag, As, Au, Bi, Cd, Cu, Hg, Pb, Mo, Sb, Tl and Zn, representing metals that are most probably with anthropogenic origin. For that issue descriptive statistics of these elements are reported in Table 1.

T a b l e 1

Descriptive statistics of measurements for anthropogenic elements included in Factor 1 (n=156)
(values are in mg/kg)

Element	Dis	X_g	s_g	Md	P_{10}	P_{90}	Min	Max	A	E
Ag	Log	0.44	4.2	0.40	0.050	3.2	0.050	58	0.80	0.95
As	Log	30	3.1	25	9.2	150	2.1	3900	1.27	2.74
Bi	Log	1.5	3.3	1.1	0.50	7.2	0.10	110	1.18	2.06
Cd	Log	1.6	3.0	1.4	0.40	10	0.10	47	0.43	-0.05
Cu	Log	42	2.3	35	17	120	9.0	1600	1.25	2.93
Hg	Log	0.20	3.0	0.18	0.060	0.74	0.020	11	0.99	1.74
Pb	Log	450	3.4	370	110	2300	34	35000	0.84	1.07
Mo	Log	0.68	2.0	0.70	0.30	1.5	0.050	5.7	-0.31	1.91
Sb	Log	2.3	4.2	1.7	0.60	16	0.10	1400	1.24	2.71
Tl	Log	0.33	2.6	0.30	0.10	1.2	0.050	7.7	0.58	0.98
Zn	Log	240	3.0	170	76	1200	32	12000	0.89	0.49

Dis. – distribution (Log – lognormal); X_g – geometrical mean; s_g – arithmetical or geometrical standard deviation; Md – median; P_{10} – 10 percentile; P_{90} – 90 percentile; Min – minimum; Max – maximum; A – skewness; E – kurtosis

As it can be seen from the results presented in Table 1, lead has the highest content in soil up to 35,000 mg/kg with an average of 450 mg/kg. The content of lead was extremely high in all samples, differing considerably in dependence on the distance of the sampling point from the potential pollution source. Most of the samples from the locations exhibit high values for the content of Pb exceeding 3000 mg/kg. Zinc has also high concentration in soils varied from 32 to 12,000 mg/kg with an average of 240 mg/kg with a very similar spatial distribution having very high content in soil samples from the zone I. Similar spatial distribution was found for the other elements from this association which confirm the pollution from the mining and smelter activities in this area.

In order to identify the origin (i.e. natural or anthropogenic) and to find the extent of heavy metals in the surface soils, the enrichment factor (EF) of the metals was calculated in this study as a ration between the obtained mean values and the European average value of surface soil (Salminen et al., 2005) and the New Dutch List (http://www.co nta minatedland.co.uk/std-guid/dutch-l.htm) used as the reference values. The obtained data for the content of Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl and Mo in surface soil for entire study area show high enrichment compared with the European values (Figure 4). Figure 4 shows that for entire study area lead, cadmium and mercury had significant EF of 19.9, 11 and 5.5, respectively. Zinc, arsenic, antimony, copper, bismuth and silver showed lower EF of 4.56; 4.24; 3.83; 3.23; 3.0 and 1.63, respectively. Mo had minimal EF of 1.03 in all the soil samples. EF of thallium in surface soil was lower than 1.

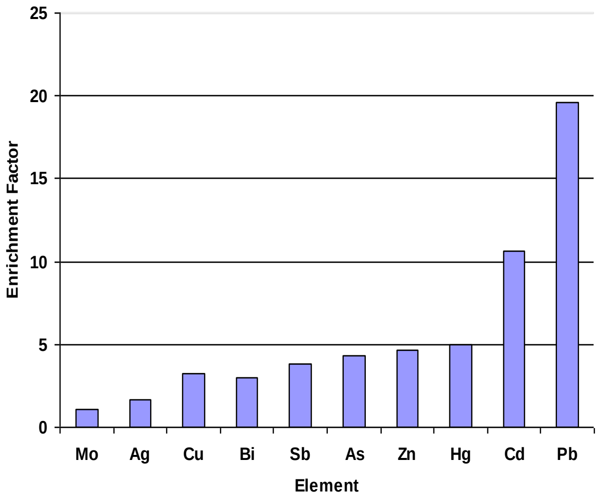

Fig. 4. Enrichment factor of the study area (average content in topsoil versus average content in European topsoil)

On the basis of the spatial distribution and the EF values of the analyzed elements in the study area, three contamination zones were determined (Figure 3). The obtained data for the content of the anthropogenic elements in topsoil according to the determined zones show that the highest contents were found in zone I, the extremely contaminated parts of the study area. Zone I (the extremely polluted area), occupies an area of 57 km^2. Zone II (significantly polluted area) occupies 117 km^2 while zone III (uncontaminated area) occupies 128 km^2. As expected, the contents of the anthropogenic elements decreased from zone I to the zone III. For Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl and Mo, calculations are made also for the enrichment ratios between their contents in the surface soil area of zone I versus those for zone III. High contents as well as the enrichment ratios in surface soil are noticeable (Figure 5). Typical for this element assemblage is the enrichment from 2.1-fold for Mo and 3.7-fold for Cu and Tl, to 11-fold for Zn, 12-fold for Cd and Bi, 16-fold for Pb, 19-fold for Sb and 27-fold for Ag.

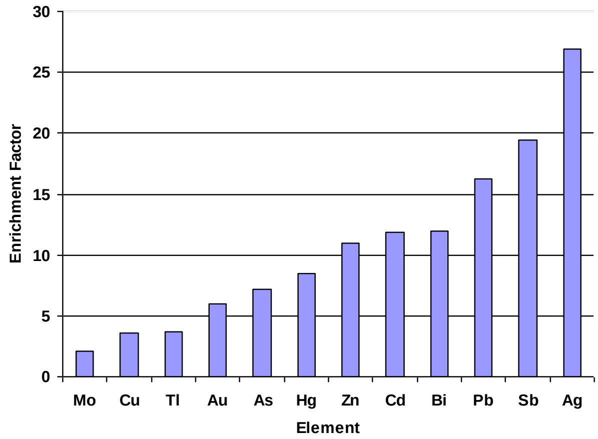

Fig. 5. Enrichment ratio of the study area surface soil comparing the results for zone I/zone III areas

This study has also been undertaken to assess the impact of mining and smelting upon the local environments, *i.e.* the cities of Zveçan, Mitrovica and Vushtrri. The highest contents of Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Tl and Mo are found in the vicinity of the industrial complex (Lead smelter, Refinery, Concentrator, Battery recycling plant and the Energy plant) of the town of Zveçan, and in soil around the industrial complex (Zinc Metallurgy, Fertilizer Factory and Battery Factory) of the city of Mitrovica. Because of high metal emissions from the ore processing and metallurgical process (7.31 t/day Pb, 1.63 t/day Zn, 323.7 kg/day As, 103.8 kg/day Sb, 30.31 kg/day Cd and 37.35 kg/day Ag) and their high degree (21–25 % Zn, 2.7 % Pb, 0.15 % Cd, 0.06 % Sb and 0.25 % Cu) in industrial waste disposed around the smelters (Palariet, 2003) it was expected these metals to have significantly higher content in urban soil samples from the town of Zveçan and in the city of Mitrovica.

Values of EF for Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Tl and Mo for the soil samples from the cities of Zveçan, Mitrovica and Vushtrri together with medians for European soils (Salminen et al., 2005) are given in Table 2.

Table 2 shows that in soils taken from the city of Zveçan lead had the highest EF (mean for the city's soils versus European mean) of 708, followed by cadmium with a value of 138. Silver, mercury and bismuth showed similar EF with a value of 107, 105 and 102, respectively. The EF value for As was 81, while for Zn it was 66.5. For Cu, Sb, Mo and Tl EF values are 39, 31.7, 2.9 and 2.42, respectively. High values of EF of Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Tl and Mo in soils of the city of Zveçan indicate the strong impact of anthropogenic activities developed in this area.

Relatively high EF was also obtained for the soil in the city of Mitrovica for Pb (75.2), Cd (48.3), Zn (17.8), Hg (14.6), Sb (13.2), Bi (9.0), Ag (7.8), Cu (6.15), As (5.0) and Mo (1.48). Enrichment Factor of thallium in surface soil was very low (<1) (Table 2).

In the soils taken in the city of Vushtrri (Table 2) lead had the highest contamination factor of 11.1, followed by cadmium with a value of 9.0. For Hg, Zn, As, Cu, Sb and Bi the EF values were 4.86; 3.42; 3.13; 2.61; 1.83 and 1.62, respectively. EF of Ag, Mo and Tl in surface soil was below 1 (Table 2).

Table 2

Enrichment factors of heavy metals in soils according to urban area (mg/kg)

	Median EU	Zveçani Zvečan	Mitrovica Mitrovica	Vushtrri Vučitrn
N	840	5	11	8
Element	mg/kg	EF	EF	EF
Ag	0.27	107	7.8	0.96
As	7.0	81	5.0	3.13
Bi	0.50	102	9.0	1.62
Cd	0.15	138	48.3	9.0
Cu	13	39	6.15	2.61
Hg	0.04	105	14.6	4.86
Mo	0.62	2.9	1.48	0.90
Pb	23	708	75.2	11.1
Sb	0.60	31.7	13.2	1.83
Tl	0.66	2.42	0.68	0.39
Zn	52	66.5	17.8	3.42

N = number of samples; EU = European average value; EF = Enrichment Factor

The anthropogenic contamination is a consequence of historical Pb-Zn mining, processing and smelting operations that resulted in high concentrations of all anthropogenic elements in topsoil. Based on the results of this study, it was found that Pb, Cd, Zn, Cu, As, Hg, Pb and Cd are among those considered most problematic elements in terms of environmental pollution and toxicity. It was also concluded that the contents of As, Cd, Cu, Hg, Pb and Zn set out in the New Dutch List recommendations. Thus, for the entire study area the content of Cu exceeds the target value recommended by the New Dutch List for 1.17-fold; Cd for 2-fold; Zn for 1.71-fold and Pb 5.29-fold. Moreover, Figure 6 shows that the contents of As, Cd, Cu, Hg, Pb and Zn exceed the target values in the soil samples from zone I for 2.8-fold for Cu and Hg; 3.45-fold for As; 7.86-fold for Zn; 9.5-fold for Cd and 31-fold for Pb. In general, their high contents exceed the target levels of contaminant elements over the whole study area, while the intervention levels of the aforementioned elements are exceeded in an area of about 122 km^2 (Figure 7).

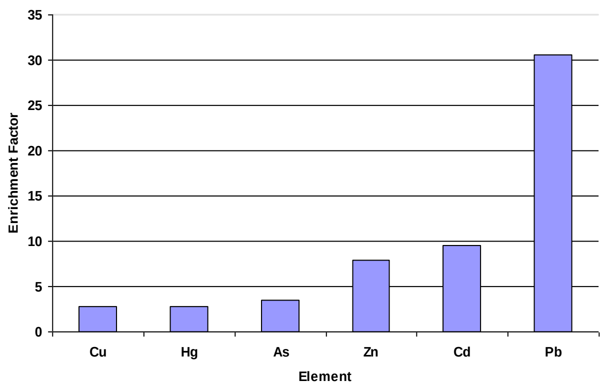

Fig. 6. Enrichment factor of the study area surface soil comparing optimal values according to the New Dutch List

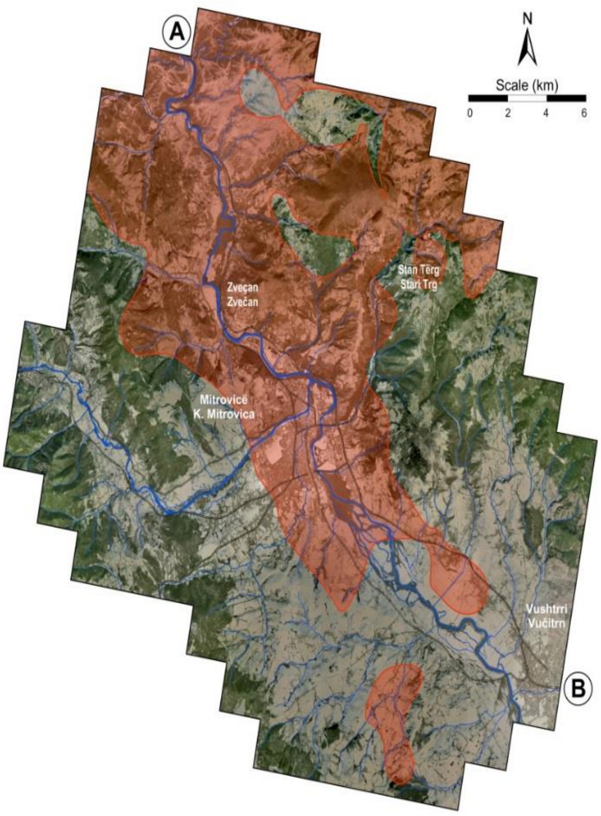

Fig. 7. Critically polluted soil with heavy metals (As, Cd, Cu, Pb and Zn) according to the New Dutch List standards

CONCLUSION

The geochemical study of the distribution of heavy metals in the surface soil over the Mitrovica region, Republic of Kosovo, has shown that metals such us Ag, As, Au, Bi, Cd, Cu, Hg, Pb, Mo, Sb, Tl and Zn may have been derived from the anthropogenic activities developed in the area. These metals also have shown high enrichment comparing with the European values. Thus, the average content of Pb was 19.6-fold higher than European averages; Cd 11-fold; Hg 5-fold; Zn 4.5-fold; As 4.3-fold; Sb 3.8-fold; Cu 3.2-fold and Ag 1.6-fold higher that European average values. Increased levels of heavy metals showed that mining and processing activities around the lead and zinc mines and smelter plants strongly affected in soils of the town of Zveçan and soils of the city of Mitrovica and there environ. In the close vicinity of the cities of Zveçan and Mitrovica, the contents of the As, Cd, Cu, Pb and Zn were higher than the corresponding intervention (critical) values according to the New Dutch List (Dutch standards) and were exceed in 122 km^2 of the investigated area.

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Р е з и м е

ЗБОГАТУВАЊЕ НА ПОЧВИТЕ СО НЕКОИ ПОТЕНЦИЈАЛНО ТОКСИЧНИ ЕЛЕМЕНТИ ПОРАДИ Pb-Zn РУДАРСКИ И МЕТАЛУРШКИ АКТИВНОСТИ ВО РЕГИОНОТ НА МИТРОВИЦА, КОСОВО

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Клучни зборови: загадување на почвите; потенцијално токсични елементи; Митровица; Република Косово

Презентирани се резултатите од испитувањето на застапеноста и збогатувањето со потенцијално токсични елементи во површинските почви (0–5 cm) од регионот на Митровица, Република Косово. Од испитуваното подрачје (301.5 km^2), кое беше покриено со мрежа за земање примероци од 1.4×1.4 km, се земени вкупно 156 примероци почва. Со примена на масената спектрометрија со индуктивно спрегната плазма (ICP-MS) е извршено определување на антропогена асоцијација од 12 елементи: Ag, As, Au, Bi, Cd, Cu, Hg, Pb, Mo, Sb, Tl и Zn. Обработката на добиените податоци е извршена со примена на параметриски и непараметриски статистички метод. Загадувањето на почвите е

утврдено врз основа на факторот на збогатување (EF). Така, средната вредност на содржината на Pb е 19,6 пати поголема од средната вредност на неговата содржина во почвите во Европа, на Cd за 11 пати, на Hg за 5 пати, на Zn 4,5 пати, на As за 4,3 пати; на Sb за 3,8 пати, на Cu за 3,2 пати, на Ag за 1,6 пати и на Mo за 1,01 пати. Зголементите вредности на содржината на овие метали покажуваат дека рударските и металуршките активности извршиле силно влијание врз почвите во градовите Звечан и Митровица и во нивната непосредна околина. Така, почвите од непосредната околина на Звечан и Митровица на површина од 122 km^2 имаат содржина на As, Cd, Cu, Pb и Zn повисока од соодветните интервентни вредности според холандските стандарди.