A SURVEY OF LEAD POLLUTION IN SURFACE SOILS IN MITROVICA REGION, KOSOVO

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Abstract: The results of study on the spatial distribution of lead in topsoil (0-5 cm) over the Mitrovica region, Kosovo, are reported. The investigated region (301.5 km^2) is covered by a sampling grid of 1.4×1.4 km. In total 159 natural surface soil samples (0-5 cm) from 149 locations were collected. All samples were analysed using inductively coupled plasma – mass spectrometry (ICP-MS). Data analysis and construction of the map were performed using the Statistica (ver. 9), AutoDesk Map (ver. 2008) and Surfer (ver. 9) software. The obtained results show that the average content of lead in the surface soil for the entire study area is 450 mg/kg (with a range of 34–35000 mg/kg) which exceeds the estimated European Pb average of surface soil by a factor of 20. Enormously high contents are found in several sampling sites in towns of Zvečan and its surroundings (from 3400 mg kg^{-1} to 34500 mg kg^{-1}) and Mitrovica (from 5000 mg kg^{-1} to 4900 mg kg^{-1}). The most of the investigated soil samples collected mostly around the industrial zone in Southern Mitrovica, the Trepča mines in Stari Trg and valley of the River Ibar, downstream from the Zvecan, have the content of Pb in range between 1000 mg kg^{-1} to 3000 mg kg^{-1}. The lowest contents were found in the urban zone of the town of Vučitrn. The critically polluted area according to the New Dutch standards (over 530 mg kg^{-1}) covers 113 km^2 with the average content of lead of 530 mg kg^{-1}.

Keywords: Lead, soil, Trepča mines, smelter, spatial distribution, pollution, Mitrovica, Republic of Kosovo

Introduction

The main ores of Pb are galena (PbS) and cerusite ($PbCO_3$), but also in ores anglesite ($PbSO_4$) and crocoite ($PbCrO_4$) (Filipović and Lipanović, 1995). Anthropogenic emission of Pb is much higher than natural whereas biggest part is from internal combustion engine, burning of ore that contain Pb, uses of different Pb material removing of waste materials, making of colours, uses of some insecticide and burning of fossil fuels (Greenwood, 1984). Use of Pb as a fuel additive, its concentration in last 80 to 100 years has increased in environment (Hill, 1992). Lead is a very toxic heavy metal. The toxicity of lead is probably related to its affinity for cell membranes and mitochondria. Symptomatic lead poisoning in childhood is characterized by abdominal pain, anorexia, anemia, etc. In adults, symptomatic lead poisoning is characterized by abdominal pain, headache, irritability, anemia, peripheral motor neuropathy, and deficits in short-term memory. Chronic lead exposure is associated with interstitial nephritis, tubular damage, hyperuremia and chronic renal failure. An additional issue for both children and adults is whether lead that has accumulated in bone can pose a threat later in life, particularly in increased bone resorption (Klassen, 1996).

The effect on the environment pollution of mines and mining industries in Mitrovica is difficult to ascertain as little data exist. The problems are wide from hazardous material to air, soil and water pollution. In particular sites associated to the Trepča Mining Complex are

of major concern as they have a long history on environmental pollution. The amount of metal produced was 2,066,000 t Pb, 1,371,000 t Zn as well as Ag, Bi and Cd (Palariet, 2003; Frese et al., 2004). Only several reports have indicated that current levels of lead exposure are extremely high in the soil and in the air as well (di Lella et al., 2003; Jia et al., 2004; Borgna et al., 2009). The main objectives of the present investigation were to determine the content of lead, to establish its spatial distribution in soils from the broad are of Mitrovica (Fig. 1) and to assess the size of the area affected by the smelter plant situated nearby.

Material and methods

Study Area

The Mitrovica is a city located in the north of Kosovo (Fig. 1) approximately 40 km north of Prishtina (the capital of the Republic of Kosovo). The study area (301.5 km^2) is large (24 NNW-SSE km x 18 WWS-EEN km), which is limited by the coordinates (WGS 84) longitude 20.74528°-20.99235° (E) and latitude 42.78522°-42.99330° (N). About 40% of study area lies at an altitude between 480-600 m (S and SE), but only 5 % has an altitude over 1000 m, mainly in the NE of the investigated area. On the aforementioned plain are located all the major urban zones (Zvečan, Mitrovica and Vučitrn), but also the main industrial zones, particularly around Zvečan and Mitrovica (Aliu et al., 2010, 2010a; Stafilov et al., 2010).

Of the total 301.5 km^2 of the study area, the water surface (rivers and lakes) covers 1.6 km^2 or (0.6 %), open area mainly cultivable land 160 km^2 (53 %), non-cultivable area, 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 %).

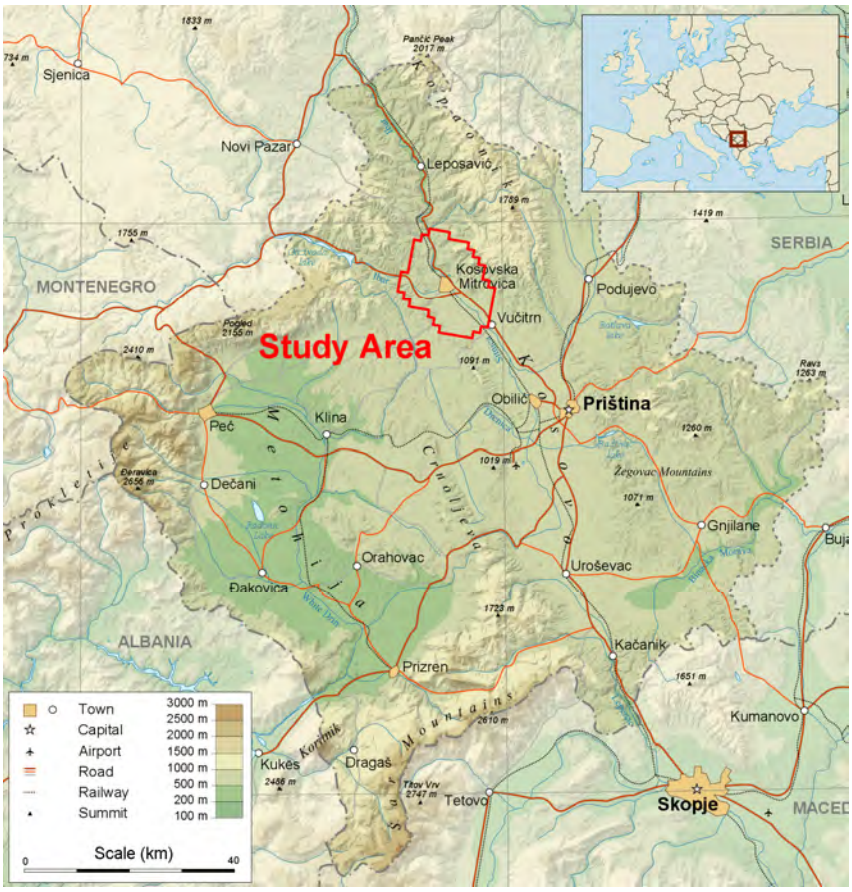

Fig. 1. Location of the study area

Sampling and chemical analysis

The sampling is done from January to May 2009. Surface soil samples (0 cm to 5 cm depth) were collected in the town of Mitrovica and surrounding region (Fig. 1). In total 159 samples were collected from 149 locations, including locations near mining centers of Mitrovica (Aliu, 2009, 2010; Stafilov, 2010). One sample represents the composite material collected at the central sample point itself and at least four points with the radius of 50 m around it towards N, E, S and W. The complete investigated region (301.5 km^2) was covered by a sampling grid of 1.4 x 1.4 km. Soil samples were air dried, crushed, cleaned from extraneous material and sieved through a plastic sieve with 2 mm mesh. The sieved mass was quartered and milled in agate mill. 0.5 g of each sample was used for digestion with HNO_3, HF, $HClO_4$ and HCl according to ISO 14869-1:2001(E) method. Lead was analyzed by using of atomic emission spectrometer with inductively coupled plasma, ICP-AES (Varian 715-ES).

Results and discussion

Clarke of Pb in soil amount to 35 mg/kg (Bowen, 1979). European average of Pb in topsoil is 23 mg kg^{-1} (XRF or mixed acid digestion) and 15 mg/kg after aqua regia digestion (Salminen, et al., 2005). Data from the descriptive statistics of measurements of Pb in topsoil from whole region are given in Table 1. As it can be seen, Pb average in soil for all study area is 450 mg kg^{-1} (median of 370 mg kg^{-1}) in range from 34 mg kg^{-1} to 35000 mg kg^{-1}.

Table 1. Descriptive statistics of measurements for lead in soil (values given in mg/kg)

N	*Dis.*	X, X_g	s, s_g	*Md*	P10	P90	Min	Max
156	Log	450	1141	370	110	2300	34	35000

N – number of observation; *Dis.* – distribution (Log – lognormal); *Md* – median; X – arithmetical mean, Xg – geometrical mean; s – arithmetical standard deviation; s_g – geometric standard deviation; *Min* – minimum; *Max* – maximum; P_{10} – 10 percentile; P_{90} – 90 percentile.

Distribution of Pb average in surface soil according to the determined zone provides the highest concentrations are in the Zone I, extremely contaminated part of the study area (Table 2, Figs. 2 and 3). As it is expected the concentrations are decreasing from the Zone I to the Zone III. Enormously high concentrations are found in several following sampling sites in Zvečan and its surroundings (from 3400 mg kg^{-1} to 34500 mg kg^{-1}) and Mitrovica (from 5000 mg kg^{-1} to 4900 mg kg^{-1}). The dozen sampling sites have the concentrations of Pb in range between 1000 mg kg^{-1} to 3000 mg kg^{-1} mostly around the industrial zone (Pb smelter, battery and accumulator factory in Southern Mitrovica), the Trepča mines in Stari Trg and valley of the River Ibar, downstream from the Zvečan. The lowest concentrations were found in the urban zone of Vučitrn. In both, the determined zones and the main urban areas, the concentrations are very high according to the EU average for Pb in soil (Fig. 3).

Table 2. Average of the lead according to zones and urban area (in mg kg^{-1})

	Median EU	Study area	Zone (I)	Zone (II)	Zone (III)	Zvečan	Mitrovica	Vučitrn
N	-	156	30	65	61	5	11	8
Pb	23	450	2600	540	160	16000	1700	250

N – number of samples; Mean (EU) – European topsoil average (Salminen et al., 2005); Zone (I) – Extremely affected area with heavy metals (57 km^2); Zone (II) – Strongly affected area with heavy metals (117 km^2); Zone (III) – Relatively little affected area with heavy metals (128 km^2); Zvečan urban area; Mitrovica urban area; Vučitrn urban area

In the cross section of the profile A-B which showing distance from the point A to B in length of 26 km, it is possible to see change in concentrations (Fig. 4). The lowest concentrations are found in the SSE of the study (point B) around urban zone Vučitrn. The maximum values are again between Mitrovica and Zvečan, which decrease towards the point A. Even in the NNW part of the study are found samples with high concentrations of Pb.

Spatial distribution of Pb in surface soils of all study area is provided in the Fig. 5. The high content of this chemical element can be found in almost all study area, but the highest content is related for the the urban areas Mitrovica and Zvečan, the Trepča mine complex as well as for the alluvial plains of the river Ibar. Contamination expands to the north of the study area, towards the slopes of Mountain Kopaonik and to the NNE, towards the Rogozna Mountain.

The main source of Pb pollution is consequence of smelting activities in area of Zvečan. Pollution of study area with Pb is very strong. Concentrations of Pb exceed optimum (referent) value (The New Dutchlist) in approximately 287 km^2 and action value (The New Dutchlist) in 113 km^2 (Fig. 6). In general terms, these results obtained for Pb content in soils in Mitrovica and surrounding area (35,000 mg kg^{-1}) are in agreement with those obtained by Borgna et al., 2009 (37,123 mg/kg).

Fig. 2. Determinate polluted zones in the study area

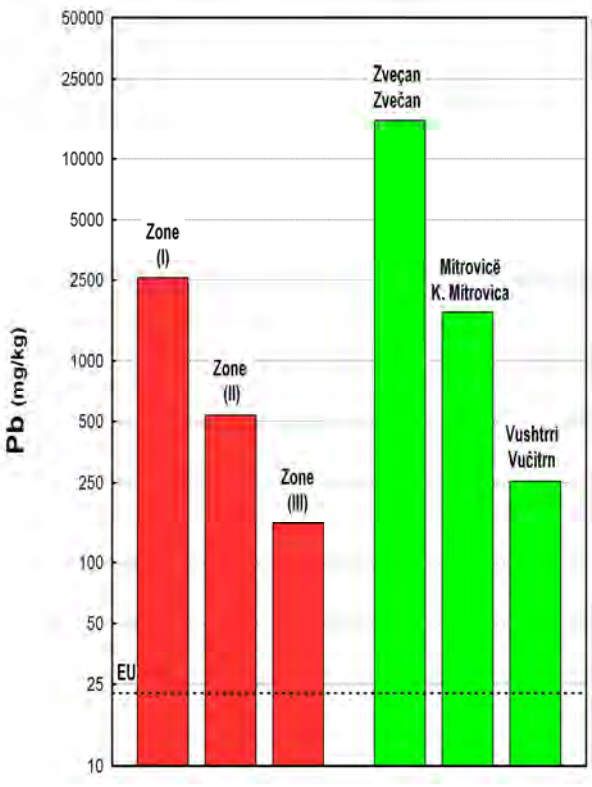

Fig. 3. Distribution of lead in topsoil according to zones and urban areas

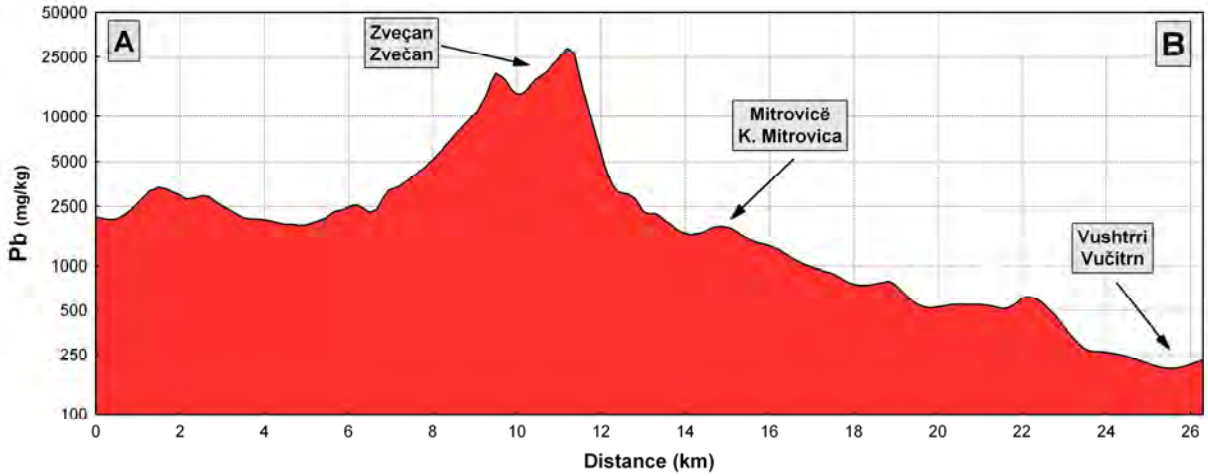

Fig. 4. Distribution of lead in topsoil (cross section - profile A-B)

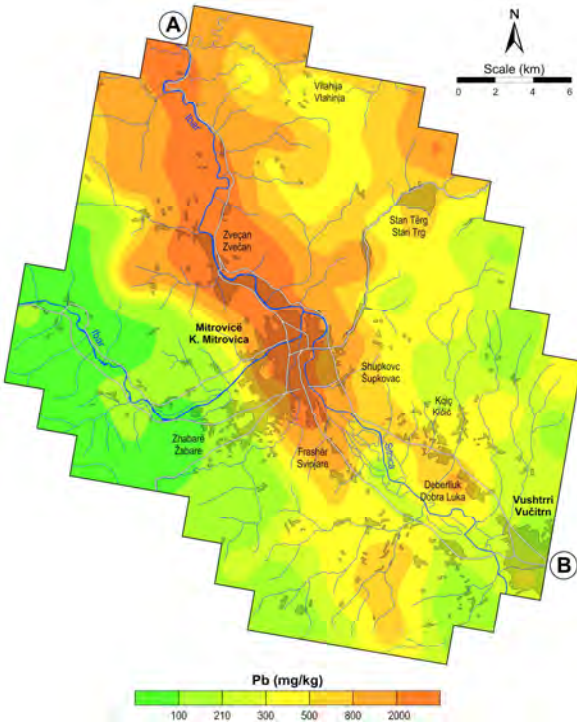

Fig. 5. Spatial distribution of lead in Mitrovica area

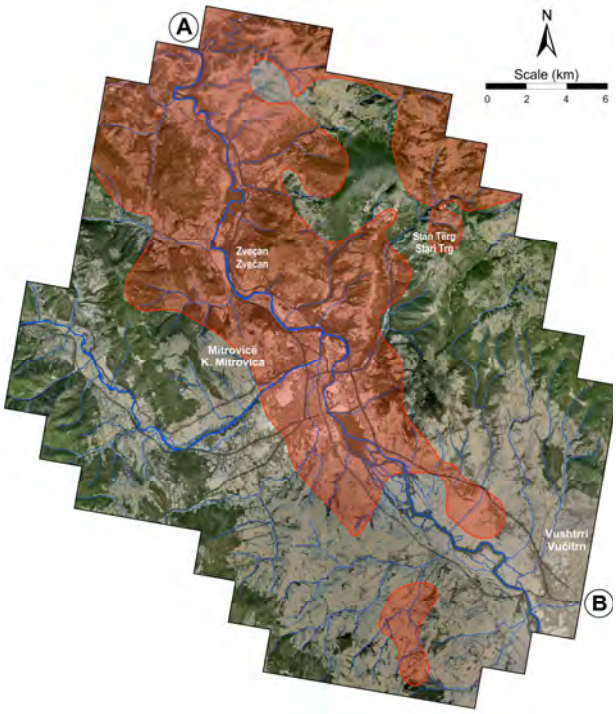

Fig. 6. Critically polluted area with lead in Mitrovica surface soil according to New Dutchlist

Conclusion

The results obtained in this study increase our knowledge of the Pb content in surface soils (0-5 cm) of the Mitrovica region, Kosovo. The Pb content in surface soils was found to range from 34 to 35,000 mg kg^{-1} with an average of 450 mg kg^{-1}. By comparing the obtained results with the data of the European lead average it appears that lead average in soils of Mitrovica region exceeds European lead average by a factor of 20. The highest Pb content was related to industrial zones and can be associated to the presence of anthropogenic sourses. In the region of Zvečan and Mitrovica several soil samples with extremely high

content of lead are present. The spatial distribution of lead content in surface soils of Mitrovica region shows a extremely polluted area of 113 km^2 with the Pb average of 891 mg kg^{-1} (from 530 to 35,000 mg kg^{-1}). Therefore, it may be concluded that there is significant degree of lead pollution in the examined soils. Due to the extremely high Pb content found in soils, lead present a serious ecological and health risk in this site must be considered.

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