ENRICHMENT OF SOME HEAVY METALS IN TOPSOILS AROUND A Pb-Zn SMELTER IN MITROVICA, KOSOVO

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Abstract

The results of a study on the spatial distribution of different elements in surface soil (0-5 cm) in the Mitrovica region, Kosovo, are reported. The investigated region (300 km^2) was covered by a sampling grid of 1.4×1.4 km and a total of 159 soil samples. Inductively coupled plasma-mass spectrometry (ICP-MS) was applied for the determination of 36 elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Th, Ti, Tl, U, V, W and Zn). For data evaluation, parametric and non-parametric statistics methods were used. The content of elements such as Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl and Mo in soil samples appeared as an anthropogenic association of elements due to the mining and processing activities. Thus, the average content of Pb was 19.6-fold higher than European averages; Cd 11-fold and Zn 4.5-fold higher. In the close vicinity of the city of Mitrovica, the contents of these elements were even higher than the corresponding intervention values according to the New Dutch list and were exceed in 152 km^2 of the investigated area.

Introduction

Mining and metallurgic activities in Kosovo have a long history. The Trepča Mine Limited in Mitrovica was built in 1927 and produced lead, arsenic and cadmium from the 1930s until 2000. The smelter close to Zvečan commenced work in 1939. Because of the smelter and three huge tailing dams of the factory, environmental pollution in Mitrovica increased dramatically. The smelter had worked sporadically since the 1999 conflict in Kosovo. However, an environmental audit ordered by UNMIK and conducted in March and April 2000, warned that it should be closed as an "unacceptable" source of air pollution (Palariet, 2003; Frese et al., 2004; OSCE, 2009). 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; OSCE, 2009). The effect of mines and mining industries on the environment in Kosovo is difficult to ascertain as few data exist. 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; Arditsoglou and Samara, 2005; Borgna et al., 2009).

The main objectives of this investigation were to present the results of the first systematic study of spatial distribution of different chemical elements in surface soil in the K. Mitrovica region in the Republic of Kosovo, known for its long-term lead and zinc mining and metallurgical activities in the recent past and to establish the enrichment factors of some elements in soils from the broad area of K. Mitrovica and to assess the size of the area affected by the smelter plant situated nearby.

Material and methods

Study Area

The K. 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.

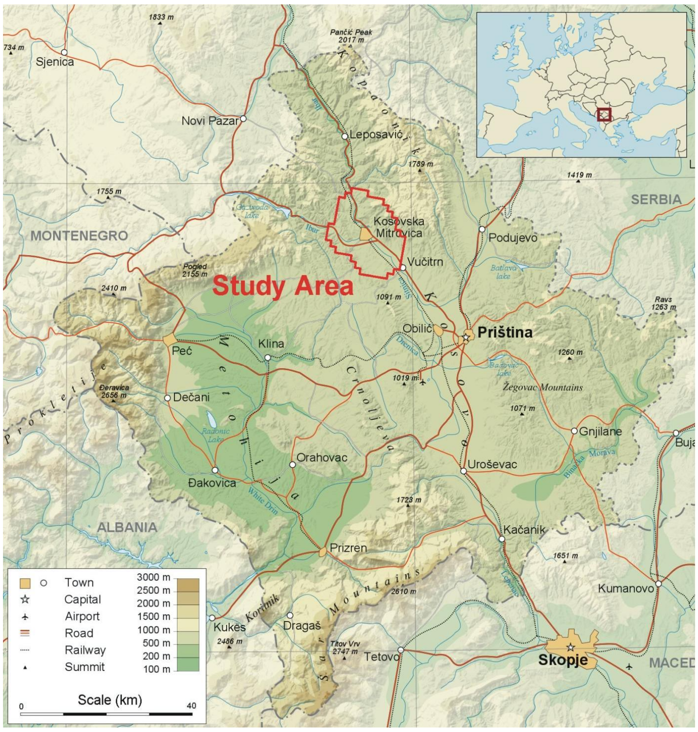

Fig. 1. Location of the study area

The investigated area belongs to the Vardar Zone (Bogdanović, 1978; Bogdanović at 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.

Sampling and sample preparation

The complete investigated region (301.5 km^2) was covered by a basic sampling grid of 2x2 km^2, but in the diagonal cross-section of each entire grid cell, one more sample was added (Fig. 2). Altogether, 156 locations were defined. In each sampling point, topsoil samples (0-5 cm) were collected. 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. Soil samples were air dried indoors at room temperature for about two weeks. Then, they were gently 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.

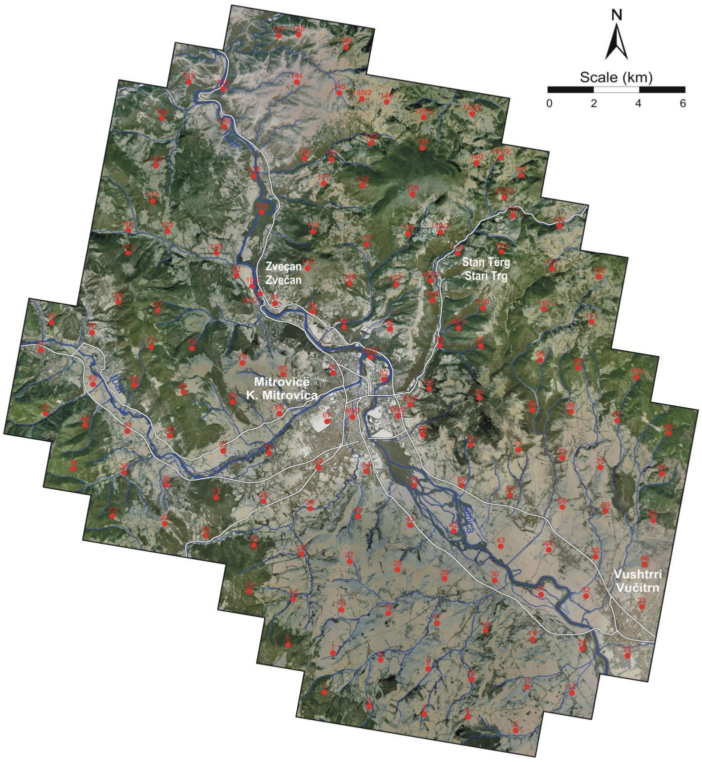

Fig. 2. Soil sample locations in the study area

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 (Fig. 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 Zvečan was covered by 5 sampling sites, K. Mitrovica by 11 sampling sites, and Vučitrn by 8 sampling sites (Fig. 3).

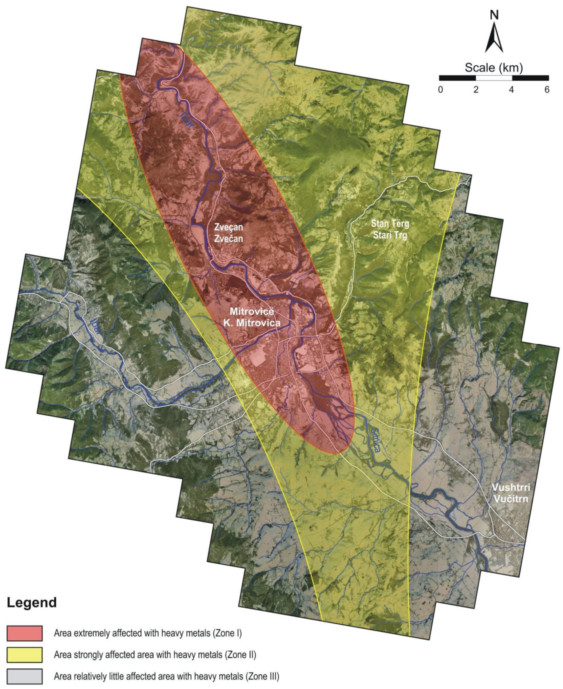

Fig. 3. Determinate polluted zones in the study area

Chemical analysis

The ICP-MS determinations of 36 elements were performed after aqua regia digestion (mixture of HCl, HNO_3 and water at 95°C - 1DX method). The following 36 elements were analysed: Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mn, Na, Mg, Mo, Ni, P, Pb, S, Sb, Sc, Se, Sr, Th, Tl, Ti, U, V, W and Zn. The sensitivity in terms of the lower limit of detection was adequate for 32 out of 36 determined chemical elements. Four elements (B, Bi, S and Se) were removed from further statistical analysis since their contents in the majority of analysed samples were below the lower detection limit of the analytical method.

Data processing

Parametric and non-parametric statistical methods were used for data processing (Snedecor and Cochran, 1967; Le Maitre, 1982). The enrichment ratio provided a much better measure for comparison. This ratio was calculated by dividing the contents of chemical elements in the topsoil of Zone I (areas extremely affected with heavy metals) by the contents in the topsoil of Zone III (areas relatively little affected with heavy metals).

Results and discussion

The distributions of elements that reflect natural processes are indicated by elements that rarely or never include industrial processes. Their contents usually change gradually across the landscape and depend on geological background. The most characteristic association is that of the high contents of Co, Cr, Fe, Ni, Mg and Sc; geochemical association consisted of Ba, La, Mo, Th, Tl and U; association of Al, Ga, K and of V and Ca and Sr. These associations represent chemical elements that are little affected by anthropogenic activities and closely dependent on the lithology. Their sources are mainly natural phenomena, such as a rock weathering and chemical processes in soil.

However, the association consists of Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl and Mo represents chemical elements that are the most probably anthropogenically distributed (Pb-Zn mining, ore processing and smelting operations). Figure 4 shows the enrichment ratio of the 31 selected elements, according to the obtained results vs. average European topsoil (Salminen et al., 2005). Figure 5 shows the enrichment of heavy metals in the topsoil of Zone I vs. Zone III.

The obtained data for the content of some elements in topsoil shows high enrichment comparing with the European values. Thus, the average content of Pb was 19.6-fold higher than European averages; Cd 11-fold and Zn 4.5-fold higher that European average values (Fig. 4). Additionally, the obtained data for the content of the anthropogenetic elements in topsoil according to the determined zones show that the highest contents were in Zone I, the extremely contaminated parts of the study area (Fig. 5). As expected, the contents decreased from Zone I to the Zone III. For these elements, the enrichment ratios were calculated between the contents of elements in the topsoil in the area of Zone I, vs. Zone III. High contents and enrichment ratios in the topsoil were noticeable. Typical enrichments were from 3.7-fold (Tl) to 10-fold (Zn), 12-fold (Cd, Bi), 16-fold (Pb), 20-fold (Sb) and 27-fold (Ag).

It was also concluded that the contents of As, Cd, Cu, Hg, Pb and Zn, set out in the New Dutch List recommendations (http://www.contaminatedland.co.uk/std-guid/dutch-l.htm). Anthropogenic pollution, the consequence of Pb-Zn mining, processing and smelting operations, was associated with high contents of As, Cd, Cu, Hg, Pb and Zn. The high contents of the abovementioned elements exceeded the optimum values in the entire study area (302 km^2). The action values of these elements were exceeded in 122 km^2 in topsoil.

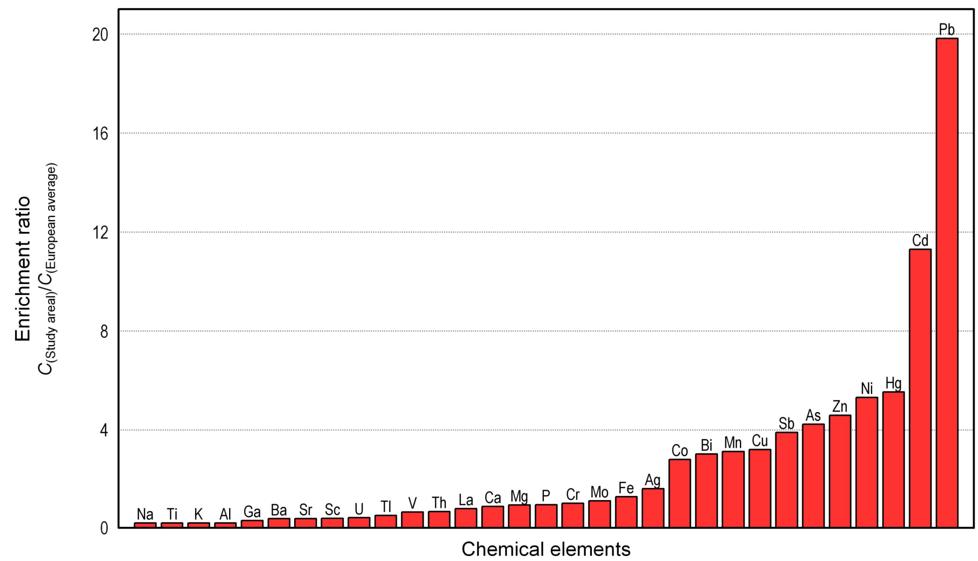

Fig. 4. Enrichment ratios of the study area topsoil vs. average European topsoil

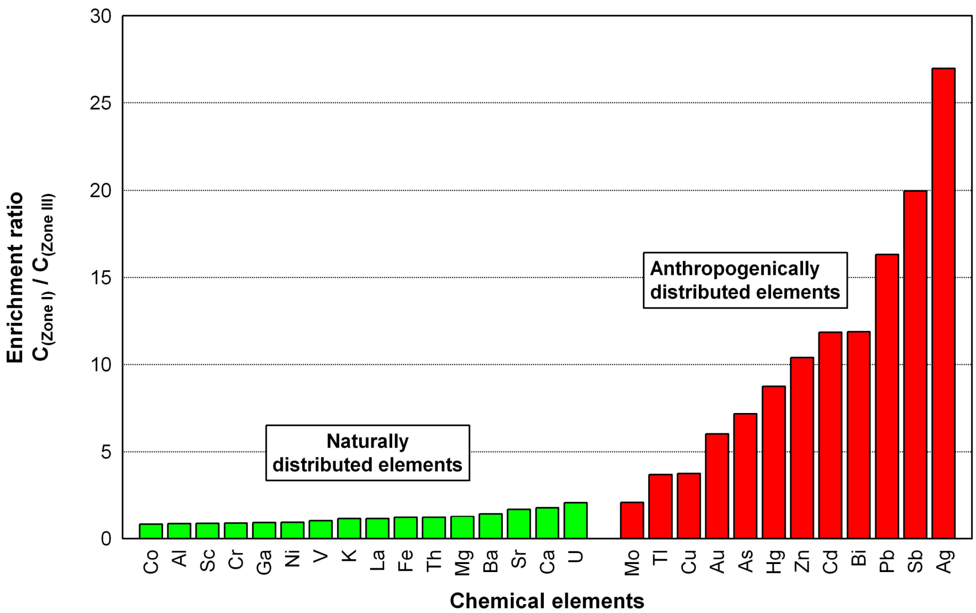

Fig. 5. Enrichment ratio of the study area topsoil comparing the results for Zone I vs. Zone III

Conclusion

The obtained results of the study of the distribution of chemical elements in the surface soil over of the Mitrovica region, Republic of Kosovo, show that the content of some elements, such as Ag, Pb, Sb, Bi, Zn, Cd, As, Cu, Hg, Au, Tl and Mo, in soil samples appeared as an anthropogenic association of elements due to the mining and processing activities around the lead and zinc mines and smelter plants. Thus, the average content of Pb was 19.6-fold higher than European averages; Cd 11-fold, Hg 5.4-fold, Zn and As 4.5-fold and Cu 3.2-fold higher. In the close vicinity of the cities of Zvečan and Mitrovica, the contents of these elements were even higher than the corresponding intervention (critical) values according to Dutch standards (the New Dutch list) and were exceed in 152 km^2 of the investigated area.

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