International Journal of Pure & Applied Chemistry 5(4), (October-December 2010) pp. 351-357

Distribution of Zinc in Surface Soils in K. Mitrovica Region, Kosovo

Milihate Aliu[1], Robert, Šajn[2] and Trajče Stafilov[3*]

[1]Faculty of Medicine, Prishtina University, Prishtina, Kosovo
[2]Geological Survey of Slovenia, Dimièeva ul. 14, 1000 Ljubljana, Slovenia
[*3]Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, POB 162
1001 Skopje, Republic of Macedonia

ABSTRACT: The results of study the spatial distribution of zinc in topsoil (0-5 cm) over the K. Mitrovica region, Kosovo, are reported. The investigated region (300 km^2) is covered by a sampling grid of 1.4×1.4 km. In total 159 soil samples from 149 locations were collected. Inductively coupled plasma – mass spec-trometry (ICP-MS) and inductively coupled plasma – atomic emission spectrometry (ICP-AES) were applied for the determination of zinc. Data analysis and construction of the map were performed using the Statistica (ver. 9), AutoDesk Map (ver. 2008) and Surfer (ver. 9) software. It was found that the average content of zinc in the topsoil for the entire study area is 520 mg/kg (with a range of 721–11900 mg/kg) which exceeds the estimated European Zn average of topsoil by a factor of 7.6. It is evident that the content of zinc is very high in the topsoils from the areas of the lead and zinc smelter plant, as well as in the topsoils from the part of the city of K. Mitrovica. In the region of Zvečan and K. Mitrovica several topsoil samples with extremely high content of zinc are present. The main polluted area covers 40 km^2 with the average concentration of zinc is 1127 mg/kg (from 721 to 11900 mg/kg).

Keywords: Soil, zinc, pollution, ICP-MS, ICP-AES, K. Mitrovica, Republic of Kosovo

Introduction

The main sources of pollution with heavy metals are heavy industries. These heavy industries tend to increase the deposition of heavy metals in the environment. There are many different sources of heavy metal contaminants including chemical and metallurgical industries [1]. When considering these different kinds of contaminants, heavy metals are especially dangerous because of their persistence and toxicity [2]. Heavy metals are known to have adverse effects on the environment and human health. They are significantly toxic even in small amounts and can cause diseases in humans and animals as they cause irreversible changes in the body especially in the central nervous system [2].

It is obvious from the articles published recently that lead and zinc mines and smelter plants activities lead to enormous soil contamination [3-8]. Mining and metallurgic activities in Kosovo have a long history. Trepèa Mine Limited in Mitrovica was built in 1927 produced lead, zinc, arsenic and cadmium from the 1930s until 2000. The smelter close to Zveèan 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 [9-11].

The total production of Trepèa from 1931 to 1998 is estimated at 34,350,000 t run-of-mine ore at grades of 6 % Pb, 4 % Zn, 75 g/t Ag and 102 g/t Bi. The ore was beneficiated in the Prvi Tunel (Tuneli Pare) flotation with the capacity of 760,000 t/y. The lead concentrates were brought to the lead smelter of Zvecan (capacity 80,000 t/y), the zinc ones to the zinc smelter of Mitrovica (capacity 50,000 t/y); there was also a unit for the production of

---

To whom correspondence be made:
trajcest@pmf.ukim.mk

fertilizers using the sulfuric acid by-product of the hydrometallurgy, and lines of battery production and battery recycling. The metal production was 2,066,000 t Pb, 1,371,000 t Zn, 2,569 t Ag and 4,115 t Bi. Gold production is estimated at 8.7 t from 1950 to 1985, i.e. and average of 250 kg/y; the Cd production is estimated at 1,655 t from 1968 to 1987. Traces of Ge, Ga, In, Se and Te in the run-of-mine ore have been also reported, which were valorized at the level of the smelters [9-11].

The effect on the environment of mines and mining industries in Kosovo is difficult to ascertain as little data exist since 1999. The problems are wide from hazardous material to air/soil/water pollution. Several reports indicate that current levels of lead exposure were extremely high in soil and in the air as well [12-16].

The main objectives of the present investigation were to determine the content of zinc, essential elements but toxic in higher concentrations, which minerals are present in the lead and zinc ore from these region [17-23], to establish its spatial distribution in soils from the broad are of K. Mitrovica (Figs. 1 and 2) and to assess the size of the area affected by the smelter plant situated nearby.

Experimental

Study Area

The Kosovska Mitrovica (Figs. 1 and 2) is a city located in the north of Kosovo (Fig. 1) approximately 40 kilometers north of Prishtina (capital of Kosovo). It is bordered by Vučitrn and Serbica to the South, Zvečan and Zubin Potok to the West and Podujevo to the East. The complete investigated region (300 km^2) was covered by a sampling grid of 1.4 x 1.4 km^2 (Fig. 2).

Sampling

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. 2). In total 159 samples were collected from 149 locations, including locations near mining centers of K. Mitrovica. The samples were located using Global Positioning System (GPS) and topographic maps at scale of 1:25,000. 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 composite of each sample (about 1 kg) was placed into plastic self-closing bags and bring to the Laboratory for atomic spectroscopy at the Institute of Chemistry, Faculty of Science, the University of Skopje, Republic of Macedonia, where they were prepared for analysis.

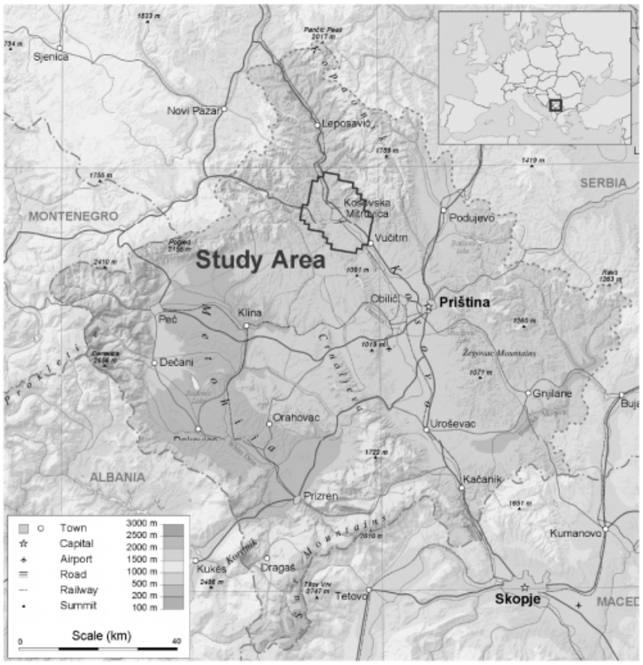

Figure 1: Location of the Study Area

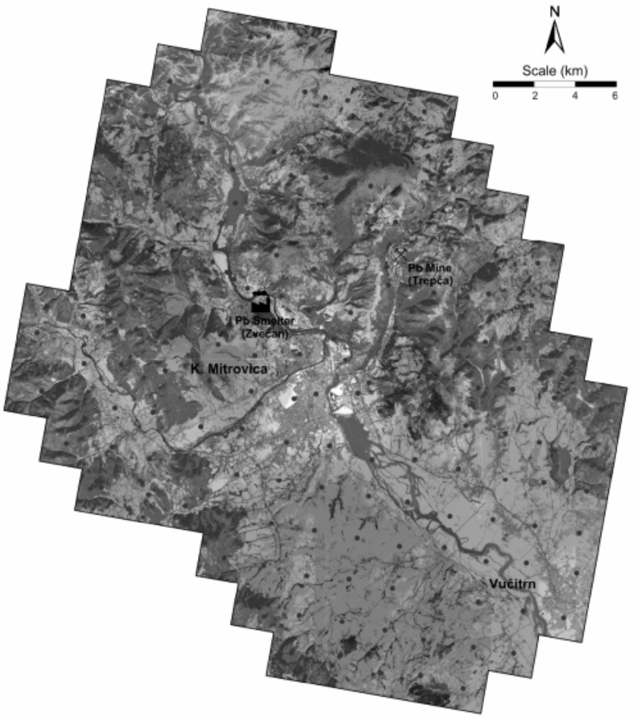

Figure 2: Sampling Locations

Sample Analysis

After being returned to the laboratory, 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 (Tracepur, 69% m/V, Merck), HF (Tracepur, 48% m/V, Fluka), $HClO_4$ (p.a., 70% m/V, Alkaloid) and HCl (Tracepur, 36% m/V, Merck) according to ISO 14869-1:2001(E) method.

Procedure: Weigh precisely 0.500 g of the milled soil sample and placed in a Teflon digestion vessel and add 10 mL of nitric acid. Place the dish on the asbestos net plate at ring at 100 °C and evaporate until approximately 1 mL of nitric acid remains. Note that several successive additions of nitric acid may be necessary until the emission of nitrous vapors ceases to remove all organic matter. After the last addition of nitric acid, remove the dish from the hot plate and cool to room temperature before undertaking the digestion. After cooling add 10 mL hydrofluoric acid and 3 mL of perchloric acid to the pretreated portion. Heat this mixture on the hot plate until the dense fumes of perchloric acid and silicon tetrafluoride cease. Do not allow the mixture to evaporate to complete dryness. Remove the vessel from the hot plate allow cooling, adding 2 mL of hydrochloric acid or 2 mL of nitric acid and approximately 5 mL of water to dissolve the residue. Transfer this solution quantitatively to the 50 mL volumetric flask, fill to the mark and mix well.

Preparations of Solutions

Stock standard Zn solution (1000 mg/L) supplied by Merck was used for calibration. Working standards were prepared by appropriate diluting of stock solution. During the preparation and measurements great care was taken to prevent contaminating any of the solutions. Deionized water was always used for the dilutions and for final rinsing of glassware. The concentrations of standard solutions for calibration are 1 µg/ml, 10 µg/ml and 200 µg/ml. All the chemicals used were of analytical reagent grade.

Instrumentation

An optical emission spectrometer with inductively coupled plasma, ICP-OES, (Varian 715-ES) was employed to determine Zn concentration using argon plasma. The instru-men-ta-tion and operating conditions

Table 1
Instrumentation and Operating Conditions for ICP-AES System

RF Generator	
Operating frequency	40.68 MHz free-running, air-cooled RF generator.
Power output of RF generator	700–1700 W in 50 W increments
Power output stability	Better than 0.1%
Introduction Area	
Sample Nebulizer	V- groove
Spray Chamber	Double-pass cyclone
Peristaltic pump	0-50 rpm
Plasma configuration	Radially viewed
Spectrometer	
Optical Arrangement	Echelle optical design
Polychromator	400 mm focal length
Echelle grating	94.74 lines/mm
Polychromator purge	0.5 L min^{-1}
Megapixel CCD detector	1.12 million pixels
Wavelength coverage	177 nm to 785 nm
Wavelength for Zn measurement	231.604 nm

Conditions for program			
RFG Power	1.0 kW	Pump speed	25 rpm
Plasma Ar flow rate	15 L min^{-1}	Stabilization time	30 s
Auxiliary Ar flow rate	1.5 L min^{-1}	Rinse time	30 s
Nebulizer Ar flow rate	0.75 L min^{-1}	Sample delay	30 s
Background correction	Fitted	Number of replicates	3

for this ICP-AES system are given in Table 1. Also all collected soil samples were shipped to ACM Analytical Laboratory in Vancouver, Canada. Analyses were conducted using mass spectrometry with inductively coupled plasma (ICP-MS) after Aqua Regia Digestion (1DX1 and DISP2 method).

Results and Discussion

The main mineral present in the ore resources of Zn is sphalerite (ZnS), but it is very often associated with other chemical elements (such as chlorides, oxides, sulphides and sulphates). The most important anthropogenic sources of Zn are the metallurgy industry, burning of fossil fuels, mines and Zn ore processing. Most of Zn is used in car industries, alloys, and galvanization procedures, industry of colours, lacquers and ointments. Zn is often present in urban regions where it is mostly generated from industrial activities and traffic [24].

Zn is an essential element for most living organism (plants, animals and humans) with important role in enzymes processes and cellular metabolism [25], in immune function, protein synthesis, DNA synthesis, and cell division [26]. Zinc also supports normal growth and development during pregnancy, childhood, and adolescence [27]. A daily intake of zinc is required to maintain a steady state because the body has no specialized zinc storage system [28]. Even the toxicity of Zn is relatively low, there are cases when poisoning with Zn can occur in both acute and chronic forms. Acute adverse effects of high zinc intake include nausea, vomiting, loss of appetite, abdominal cramps, diarrhea, and headaches [26]. The chronic effects are expressed as low copper status, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins [28] or in raising the possibility that chronically high intakes of zinc adversely affect some aspects of urinary physiology [30].

Data from the descriptive statistics of measurements of zinc by both techniques (ICP-MS and ICP-AES) in topsoil from whole investigated region are given in Table 2 and its spatial distributions with the results obtained by ICP-MS and ICP-AES are presented on Figs. 3 and 4, respectively. As it can be seen, in general the obtained average and median values obtained by ICP-MS are very similar with those obtained by ICP-AES. Namely, the correlation factor between the results from both methods are 0.99 (for normal distribution), 0.95 (for logarithmic) and 0.94 (for rank). On Fig. 5 the logarithmic correlation between both data sets is given. These results confirms

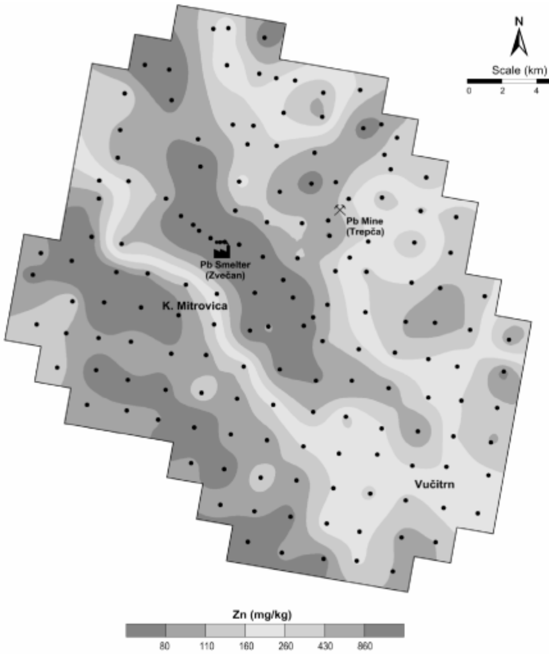

Figure 3: Spatial Distribution of zinc in K. Mitrovica Area from the Results Obtained by ICP-MS

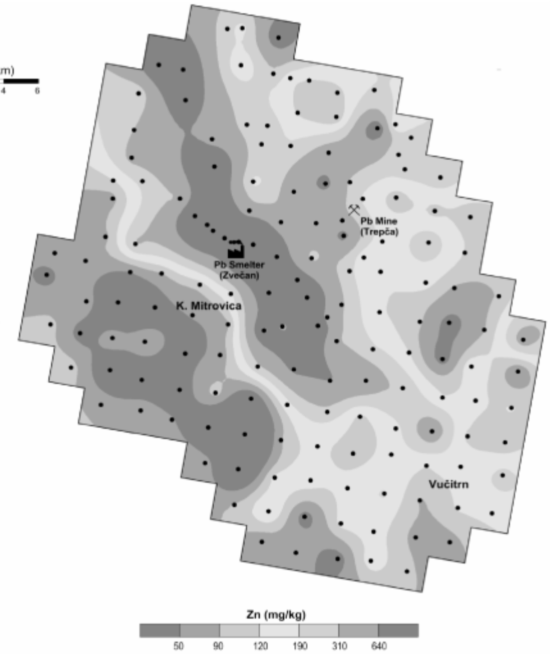

Figure 4: Spatial Distribution of zinc in K. Mitrovica Area from the Results Obtained by ICP-AES

Table 1
Descriptive Statistics of Measurements for Zinc in Soil (Values given in mg/kg)

Technique	N	Dis.	X	s	Xg	sg	Md	P10	P90	Min	Max
AES-MS	156	Log	520	1141	239	2.99	173	76	1178	32	11900
AES-ICP	156	Log	369	791	174	3.00	141	49	1008	9.0	8310

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

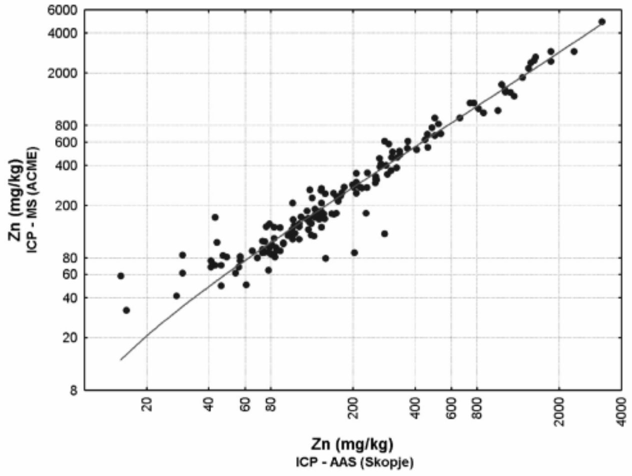

Figure 5: Scatter-plot Diagram between Data Obtained for Zn by ICP-MS (ACME) and ICP-AES (Skopje)

the fact that zinc in the polluted area is present in the form of sphalerite, as the most present mineral in the ore [17-23], and zinc oxide or zinc sulfate obtained during the metallurgical processes of roasting of zinc concentrates [9-11, 31-33] as well as that they are soluble in both acidic solution which were applied in this study [31, 34-36].

The average amount of Zn in world soils is 90 mg/kg [36] and in European topsoil is 68 mg/kg [32]. The average amount of Zn in the topsoil for the entire study area is 520 mg/kg, with a range of 32–11,900 mg/kg (Table 1). This means that the zinc average for the whole area exceeds the estimated European Zn ave-rage of topsoil by a factor of 7.6. It is evident from the obtained results (Table 2, Figs. 3 and 4) that the content of zinc is very high in the topsoils from the areas of the lead and zinc smel-ter plant, as well as in the topsoils from the part of the city of K. Mitrovica (Fig. 6).

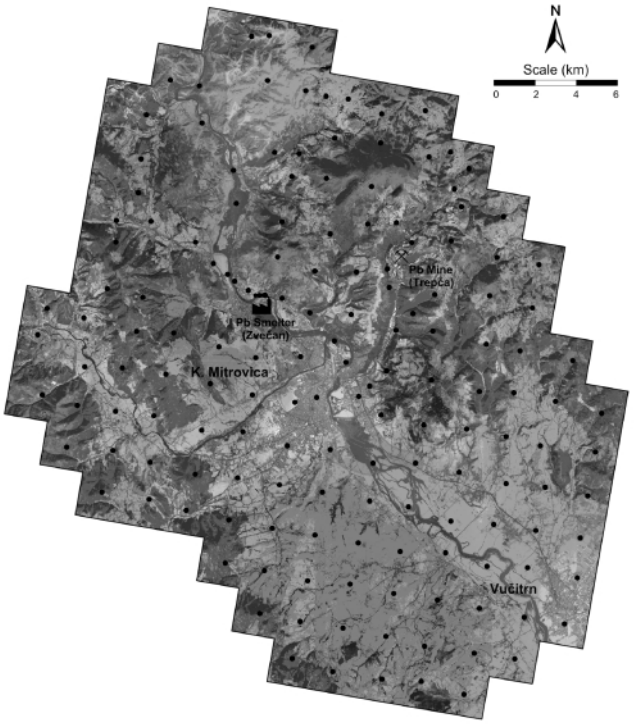

Figure 6: Critically Polluted Topsoil with Zinc in K. Mitrovica Area According to New Dutchlist

In the region of Zvečan and K. Mitrovica several topsoil samples with very high content of zinc are present. It should be noted that sample No. 93 with the content of 11,900 mg/kg is 175 times higher than the European topsoil average of 68 mg/kg [37]. The main polluted area was established by marking the sites with the content over the intervention value of 720 mg/kg according to New Dutchlist [38]. It was found that this main polluted area covers 40 km^2 (Fig. 3) with the average concentration of Zn is 1127 mg/kg (from 721 to 11900 mg/kg) which is about 17 times higher than the European Zn average (Table 3).

Table 3
Statistical Data for the Main Polluted Area

	Area	Average	Min	Max
Zn	40 km^2	1127 mg/kg	721 mg/kg	11900 mg/kg

Conclusion

The results of the study of spatial distribution of zinc in topsoil (0-5 cm) over the K. Mitrovica region, Kosovo show that the average content of Zn in the topsoil for the entire study area is 520 mg/kg (with a range of 32–11,900 mg/kg) which exceeds the estimated European zinc average by a factor of 7.6. It is evident that the content of zinc is very high in topsoils from the areas of the lead and zinc smelter plant, as well as in the topsoils from the part of the city of K. Mitrovica. In the region of Zvečan and K. Mitrovica several topsoil samples with extremely high content of zinc are present. The main polluted area was found that covers 40 km^2 with the average concentration of Zn is 1,127 mg/kg (from 721 to 11,900 mg/kg) which is about 17 times higher than the European Zn average.

REFERENCES

[1] Kabata-Pendias A. and Pendias H., Trace Ele-ments in Soil and Plants, 3rd edn., CRC Press, Boca Raton, 2001.

[2] Goyer R. A., Toxic Effect of Metals, in Casarett and Doull's Toxicology. The Basic Science of Poisons, 3th ed., Macmillan Publishing Company, New York, 1996.

[3] Li J., Xie Z. M., Zhu Y. G. and Naidu R., Risk Assessment of Heavy Metal Contaminated Soil in the Vicinity of a lead/zinc mine, J. Environ. Sci. China, 17, (2005), 881–885.

[4] Li Y., Wang Y. B., Gou X., Su Y. and Wang, G., Risk Assessment of Heavy Metals in Soils and Vegetables Around Non-ferrous Metals Mining and Smelting Sites, Baiyin, China, J. Envron. Sci. China, 18, (2006), 1124–1134.

[5] Tembo B. D., Sichilongo K. and Cernak J., Distribution of Copper, Lead, Cadmium and Zinc Concentrations in Soils around Kabwe town in Zambia, Chemosphere, 63 (2006), 497–501.

[6] Cappuyns V., Swennen R., Vandamme A. and Niclaes M., Environmental Impact of the Former Pb-Zn mining and Smelting in East Belgium, J. Geochem. Explor., 88, (2006), 6–9.

[7] Stafilov T., Šajn R, Pančevski Z., Boev B., Frontasyeva M. V. and Strelkova L. P., Geochemical Atlas of Veles and the Environs, Faculty of Natural Sciences and Mathematics, Skopje, 2008.

[8] Stafilov T., Šajn R., Pančevski Z., Boev B., Frontasyeva M. V. and Strelkova L. P., Heavy Metal Contamination of Surface Soils Around a Lead and Zinc Smelter in the Republic of Macedonia, J. Hazard. Mater., 175, (2010), 896-914.

[9] Palariet M., Kosovo's Industrial Giant, Trepca, 1965-2000, European Stability Initiatives, June 2003. University of Edinburgh, U.K., 2003.

[10] Frese S. D., Klitgaard R., Pedersen E. K., Rank J. and Klemmensen B., Environmental Management in Kosovo, Heavy Metal Emission from Trepca, II DM - 2003/2004, Institut for Miljø, Teknologi og Samfund, Roskilde University, Roskilde, 2004.

[11] OSCE, 2009: Lead Contamination in Mitrovicë/ Mitrovica Affecting the Roma Community, Background Report, Organization for Security and Co-operation in Europe, OSCE Mission in Kosovo, 2009.

[12] Di Lella L. A., Frati L., Loppi S., Protano G. and Riccobono F., Lichens as Biomonitors of Uranium and other Trace Elements in an Area of Kosovo Heavily Shelled with Depleted Uranium Rounds, Atmos. Environ., 37, (2003), 5445-5449.

[13] Jia G., Belli M., Sansone U., Rosamilia S. and Gaudino S., Concentration, Distribution and Characteristics of Depleted Uranium (DU) in the Kosovo Ecosystem: A Comparison with the Uranium Behavior in the Environment Uncontaminated by DU, J. Radioanal. Nucl. Chem., 260, (2004), 481-494.

[14] Arditsoglou A. and Samara C., Levels of Total Suspended Particulate Matter and Major Trace Elements in Kosovo: A Source Identification and Apportionment Study, Chemosphere, 59, (2005), 669-678.

[15] Prathumratana L., Kim R. and Kim K. W., Heavy Metal Contamination of the Mining and Smelting District in Mitrovica, Kosovo, Proceedings of the International Symposia on Geoscience Resources and Environments of Asian Terranes (GREAT 2008), 4th IGCP 516, and 5th APSEG, November 24-26, 2008, Bangkok, Thailand, 2008.

[16] Borgna L., Di Lella L. A., Nannoni F., Pisani A., Pizzetti E., Protano G., Riccobono F. and Rossi S., The High Contents of Lead in Soils of Northern Kosovo, J. Geochem. Explor., 101, (2009), 137-146.

[17] Lieber W., Trepca (Serbia) and its Minerals. Miner. Record, 4, (1973), 56-61.

[18] Lieber W., Trepca und Seine Mineralien. Der Aufschluss, 26, (1975), 225-235.

[19] Féraud J, Trepca (Kosovo), Compte Rendu de trois visites Géologiques Individuelles de la mine Effectuées en 1972, 1973 et 1974. Rapport inédit, Lab. Géol. appliquée Univ. Paris VI, 1974.

[20] Féraud J., La mine "Stari-Trg" (Trepca, Yougoslavie) et ses richesses minéralogiques. Minéraux et Fossiles, 59-60, (1979), 19-28.

[21] Dusanic S., Jovanovic B., Tomovic G., Zirojevic O. and Milic D., History of Mining in Yougoslavia. In Cuk L. editor, Mining of Yougoslavia, 11th World Mining Congress, Beograd, 1982, 119-140.

[22] Pruthi V., and Kastrati S., Mineral resources of Kosovo and their use, Proceedings on the Scientific Conference "Consistent Technical-technological Development and the Environment", Prishtina, 2002, 33-40.

[23] Monthel J., Vadala P., Leistel J. M., Cottard F., Ilic M., Strumberger A., Tosovic R. and Stepanovic A., Mineral Deposits and Mining Districts of Serbia; Compilation map and GIS Databases. Ministry of Mining and Energy of Serbia, Geoinstitut Rapport BRGM RC-51448-FR, Beograd, 2002.

[24] Adriano D. C., Trace Elements in the Terrestrial Environment, Springer-Verlag, New York, Berlin, Heidelberg, Tokyo, 1986, p. 533.

[25] Sandstead H. H., Understanding Zinc: Recent Observations and Interpretations. J. Lab. Clin. Med., 124, (1994), 322-7.

[26] Prasad A. S., Zinc: An Overview. Nutrition, 11, (1995), 93-9.

[27] Maret W. and Sandstead H. H., Zinc Requirements and the Risks and Benefits of Zinc Supplementation. J. Trace Elem. Med. Biol., 20, (2006), 3-18.

[28] Rink L. and Gabriel P., Zinc and the Immune System. Proc. Nutr. Soc., 59, (2000), 541-52.

[29] Hooper P. L., Visconti L., Garry P. J. and Johnson G. E., Zinc Lowers High-density Lipoprotein-cholesterol Levels. J. Am. Med. Assoc., 244, (1980), 1960-1.

[30] Johnson A. R., Munoz A., Gottlieb J. L. and Jarrard D. F., High Dose Zinc Increases Hospital Admissions Due to Genitourinary Complications. J. Urol., 177, (2007), 639-43.

[31] Greenwood, N. N., Earnshaw, A. Chemistry of the Elements 2nd ed., Oxford: Butterworth-Heinemann, 1997.

[32] Spero J. M., Devito B., Theodore L., Regulatory Chemical Handbook, CRC Press, New York, 2000.

[33] Porter, F. C., Zinc Handbook, Second Edition, CRC Press, New York, 1991.

[34] Šajn R., Gosar M., Differences in Determination of Chemical Elements in Soil and Attic Dust Samples due to Various acid Treatments, Slovenia, Geologija, 46, (2003), 273-280.

[35] Evans L. J., Fractionation and Aqueous Speciation of Zinc in a Lake Polluted by Mining Activities, Flin Flong, Canada, Water, Air, Soil Poll. 122, (2000), 299-316.

[36] Hita R., Torrent J., Weathering of Pyrite and Sphalerite in Soils Contaminated with Pyritic Sludge, Soil Sci. Soc. Am. J. 69, (2005), 1314-1319.

[37] Bowen H. J. M., Environmental Chemistry of the Elements, Academic Press, New York, 1979.

[38] Salminen R., Batista M. J., Bidovec M., Demetriades A., De Vivo B., De Vos W., Duris M., Gilucis A., Gregorauskiene V., Halamic J., Heitzmann P., Jordan G., Klaver G., Klein P., Lis J., Locutura J., Marsina K., Mazreku A., O'Connor P. J., Olsson SÅ, Ottesen R. T., Petersell V., Plant J. A., Reeder S., Salpeteur I., Sandström H., Siewers U., Steenfelt A. and Tarvainen T., Geochemical Atlas of Europe, Part 1, Background Information, Me-tho-dology and Maps. Geological Survey of Finland, Espoo, 2005.

[39] The New Dutch List (http://www.contaminatedland.co.uk/std-guid/dutch-l.htm)