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DISTRIBUTION OF CADMIUM IN SURFACE SOILS IN K. MITROVICA REGION, KOSOVO

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A b s t r a c t: The results of the study of spatial distribution of cadmium 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 spectrometry (ICP-MS) and inductively coupled plasma – atomic emission spectrometry (ICP-AES) were applied for the determination of cadmium. Data analysis and construction of the map were performed using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software. It was found that the average content of Cd in the topsoil for the entire study area is 3.25 mg/kg (with a range of 0.10–46.8 mg/kg) which exceeds the estimated European Cd average of topsoil by a factor of 27. It is evident that the content of cadmium 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 cadmium are present. The main polluted area was found that covers 5.9 km^2 with the average concentration of Cd is 14 mg/kg (from 12 to 47 mg/kg).

Key words: soil; cadmium; ICP-MS; ICP-OES; K. Mitrovica; 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 (Kabata-Pendias and Pendias, 2001). When considering these different kinds of contaminants, heavy metals are especially dangerous because of their persistence and toxicity (Goyer, 1996). 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 (Goyer, 1996).

It is obvious from the articles published recently that lead and zinc mines and smelter plants activities lead to enormous soil contamination (Li et al., 2005; Li et al., 2006; Tembo et al., 2006; Cappuyns et al., 2006; Stafilov et al., 2008, 2010). Mining and metallurgic activities in Kosovo have a long history. Trepča Mine Limited in Mitrovica was built in 1927 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 total production of Trepča 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 Zvečan (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 fertilizers using the sulfuric acid by-product of the hydrometallurgy, and lines of battery production and battery recycling. The metal produced 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 ((Palariet, 2003: Frese et al., 2004; OSCE, 2009).

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 (Di Lella et al., 2003; Jia et al., 2004; Arditsoglou and Samara 2005; Prathumratana et al., 2008; Borgna et al., 2009).

The main objectives of the present investigation were to determine the content of cadmium, very toxic element which minerals are always present in the lead and zinc minerals (Lieber, 1973, 1975; Féraud, 1974, 1979; Dušanić et al., 1982; Pruthi and Kastrati, 2002; Monthel et al., 2002), to establish its spatial distribution in soils from the broad area of K. Mitrovica (Figs. 1 and 2) and to assess the size of the area affected by the smelter plant situated nearby.

MATERIAL AND METHODS

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 Priština (capital of Kosovo). It is bordered by Vučitrn and Serbica to the couth, 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 × 1.4 km^2 (Fig. 2).

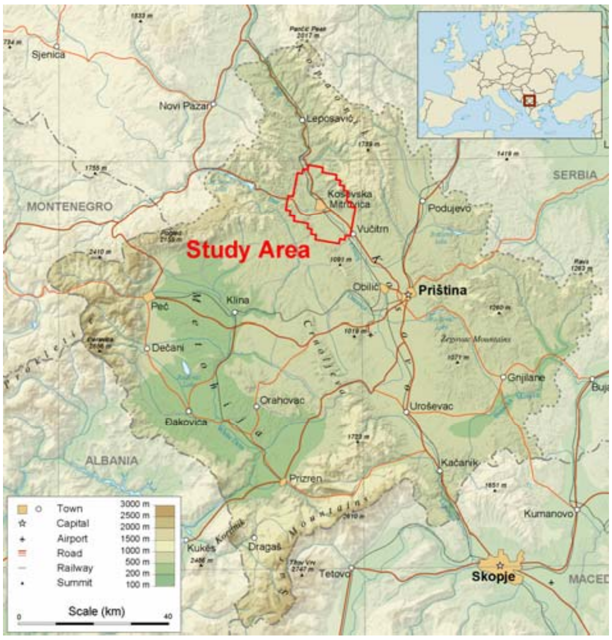

Fig. 1. Location of the study area

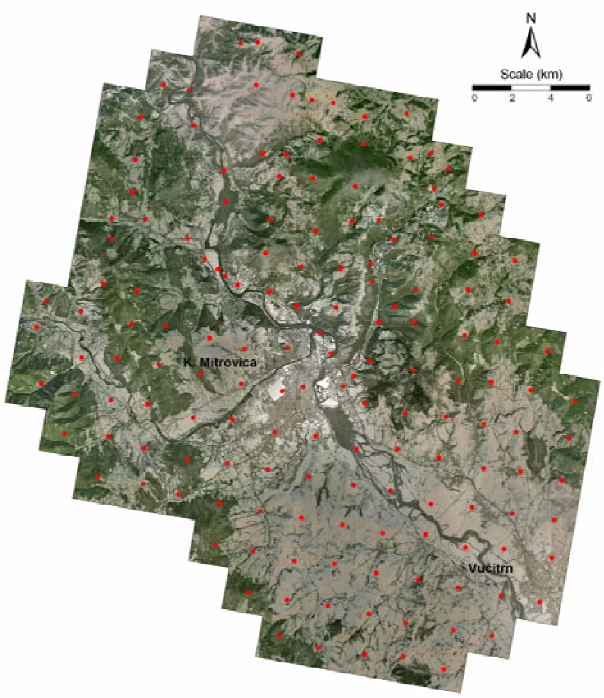

Fig. 2. Sampling locations

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 10 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.

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 Cd 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 Cd concentration using argon plasma. The instrumentation and operating conditions 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

Data from the descriptive statistics of measurements of cadmium 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 low than those obtained by ICP-AES. Namely, the correlation factor between the results from both methods are 0.94 (for normal distribution), 0.73 (for logarithmic) and 0.72 (for rank). The reason for these differences is the limit of detection of ICP-AES (1.0 mg/kg) which lead in statistical calculation to higher average and median values (missing values below 1.0 mg/kg). On Fig. 5 the logarithmic correlation between both data sets is given.

The average amount of Cd in soils in the world is 0.35 mg/kg (Bowen, 1979), in the European topsoil is 0.12 mg/kg (Salminen et al., 2005). The average amount of Cd in the topsoil for the entire study area is 3.25 mg/kg, with a range of 0.10–46.8 mg/kg (Table 1). This means that the Cd average for the whole area exceeds the estimated European Cd average of topsoil by a factor of 27.

It is evident from the obtained results (Table 2, Figs. 3 and 4) that the content of cadmium 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 (Fig. 6).

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 Cd measurement		214.439 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

Table 2

Descriptive statistics of measurements for cadmium in soil (values given in mg/kg)

Technique	*N*	*Dis.*	*X*	*s*	*X*g	*s*g	*Md*	P_{10}	P_{90}	Min	Max
AES-MS	156	Log	3.25	5.25	1.64	3.05	1.40	0.40	10.0	0.10	46.8
AES-ICP	157	Log	5.5	4.4	4.5	1.8	4.3	2.1	10	1.0	43.0

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

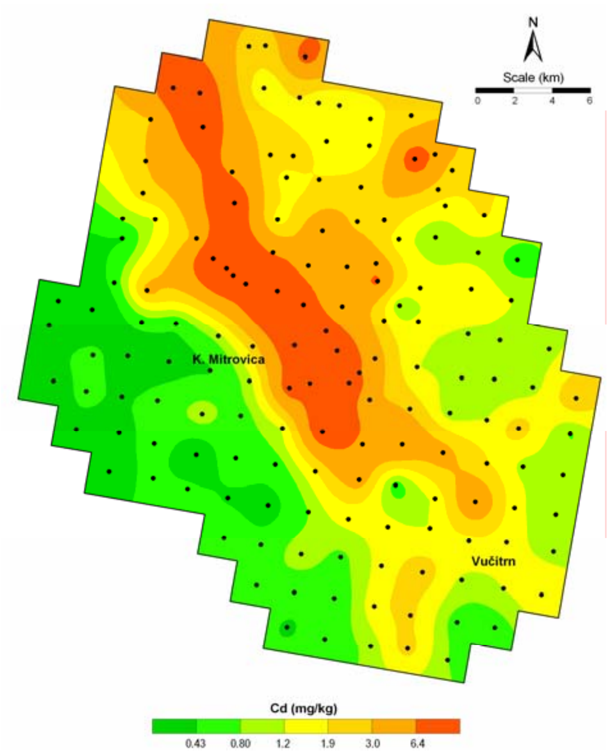

Fig. 3. Spatial distribution of cadmium in K. Mitrovica area from the results obtained by ICP-MS

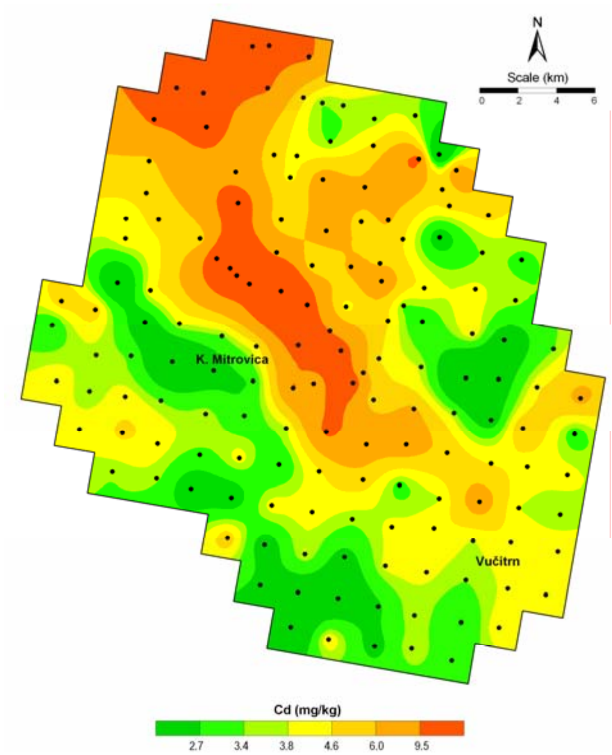

Fig. 4. Spatial distribution of cadmium in K. Mitrovica area from the results obtained by ICP-AES

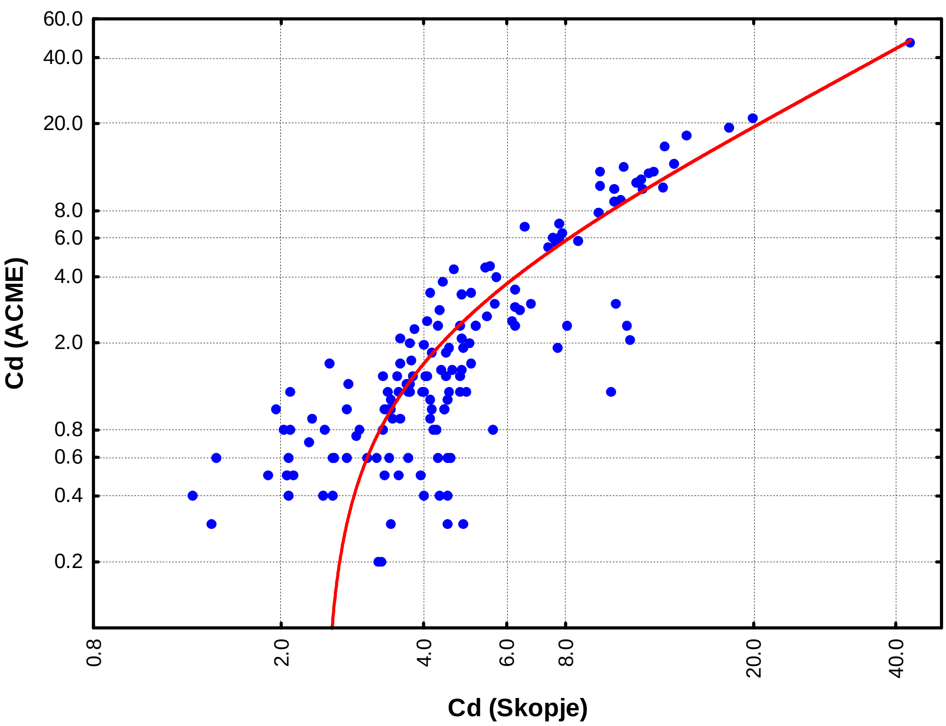

Fig. 5. Scatter-plot diagram between data obtained for Cd by ICP-MS (ACME) and ICP-AES (Skopje)

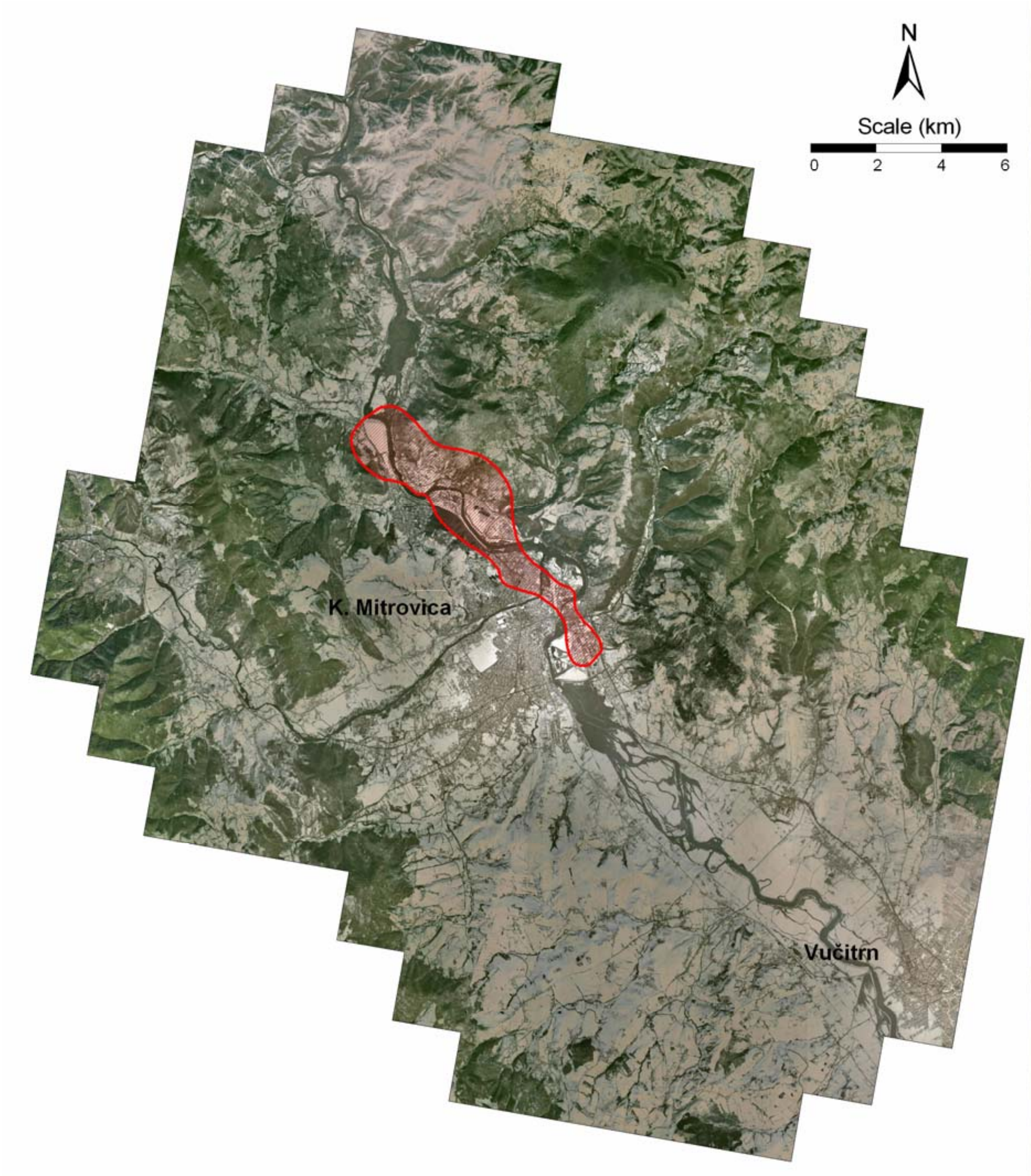

Fig. 6. Critically polluted topsoil with cadmium in K. Mitrovica area according to New Dutchlist

In the region of Zvečan and K. Mitrovica several topsoil samples with extremely high content of cadmium are present. It should be noted that sample No. 93 with the content of 46.8 mg/kg is 390 times higher than the European topsoil average of 0.12 mg/kg (Salminen et al., 2005). The main polluted area was established by marking the sites with the content over the intervention value of 12 mg/kg according to New Dutchlist (http://www.contaminatedland.co.uk/std-guid/dutch-l.htm). It was found that this main polluted area covers 5.9 km^2 (Fig. 6) with the average Cd of concentration 14 mg/kg (from 12 to 47 mg/kg) which is more than 110 time higher than the European Cd average (Table 3).

Table 3

Statistical data for the main polluted are

	Area	Average	Min	Max
Cd	5.9 km^2	14 mg/kg	12 mg/kg	47 mg/kg

CONCLUSION

The results of the study of spatial distribution of cadmium in topsoil (0–5 cm) over the K. Mitrovica region, Kosovo, show that the average content of Cd in the topsoil for the entire study area is 3.25 mg/kg (with a range of 0.10–46.8 mg/kg) which exceeds the estimated European cadmium average by a factor of 27. It is evident that the content of cadmium 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 cadmium are present. The main polluted area was found that covers 5.9 km^2 with the average Cd of concentration 14 mg/kg (from 12 to 47 mg/kg).

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

Р е з и м е

ДИСТРИБУЦИЈА НА КАДМИУМ ВО ПОЧВИТЕ ВО РЕГИОНОТ НА К. МИТРОВИЦА, КОСОВО

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Клучни зборови: почва; кадмиум; ICP-MS; ICP-OES; К. Митровица; Косово

Во трудот се презентирани резултатите од испитувањата на дистрибуцијата на кадмиумот во површинските почви (0–5 cm) од областа на К. Митровица, Косово. На целото испитувано подрачје (300 km^2) поставена е мрежа за земање примероци од 1,4×1,4 km. Земени се вкупно 159 примероци почва од 149 локации. Определувањето на кадмиумот е извршено со примена на масената спектрометрија со индуктивно спрегната плазма (ICP-MS) и атомска емисиона спектрометрија со индуктивно спрегната плазма (ICP-AES). Обработката на податоците и изработката на картите на дистрибуција е извршена со примена на софтверите Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) и Surfer (ver. 8.09). Утврдено е дека средната вредност на содржината на кадмиумот во почвите од испитуваното подрачје изнесува 3,25 mg/kg (од 0,10 до 46.8 mg/kg), што ја надминува средната вредност за содржината на кадмиумот во почвите од Европа за 27 пати. Најдено е дека содржината на кадмиумот е многу висока во површинските почви во околината на топилницата за олово и цинк, како и во почвите во дел од градот. Во областа на Звечан и К. Митровица неколку примероци од почвите имаат екстремно високи содржини на кадмиум. Областа со најголемо загадување опфаќа површина од 5,9 km^2 со средна вредност за Cd од 14 mg/kg (од 12 до 47 mg/kg).