ENVIRONMENTAL CONTAMINATION BY HEAVY METALS IN REGION WITH PREVIOUS MINING ACTIVITY

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ABSTRACT

Extreme use of raw materials and their processing dramatically increases the loading of all environmental components by heavy metals, which is then reflected in also in the human health. At present there are 7 environmentally loaded areas in Slovakia. In this study the north part of Volovske Mountains is monitored which is located between two major emission sources of Rudniansky loaded region. Iron ore mines in Rudnany was in the past the most important source of Hg (in 1978-1979 over 4000 kg Hg were emitted into the atmosphere per year) due to the mining of Cu and Fe ore. Smelter factory Krompachy with the previous copper production is another major emission source in this region. Studied area is also characterized by geochemical anomalies.

The study is focused on determination of the loading level of forest ecosystems by Zn, Cd, Cu, Pb, Hg originated from iron-ore mines Rudnany and smelter factory Krompachy. In the investigated area of about 156 km^2 samples of forest soil and vegetation from 45 predetermined sampling sites were collected. In soil samples the exchangeable soil reaction, content of humus and heavy metals were determined (total content of heavy metals - in soil extract by aqua regia, mobile forms of heavy metals - in soil extract by NH_4NO_3, c = 1 mol/dm^3). Samples of plant material (permanent grassland) were mineralized by microwave decomposition. Content of heavy metals in soil and plant material was determined using by AAS method. The threshold values proposed by Directive 86/278/EEC were exceeded for total soil content for Zn (Cd, Pb, Hg and Cu, resp.) in 26 (44, 18, 42 and 19, resp.) sampling sites. In terms of ecotoxicity Hg is the most risky metal. The determined soil Hg content ranged from 0.28 to 414.85 mg/kg, while the limit value was exceeded more than 800 times (average 65-fold). Average value of total Cd content exceeded the limit value nearly three times (0.65-6.73 mg/kg). Contents of Zn, Pb and Cu (mg/kg) were in range 33.10-952.50, 26.50-165.00 and 11.00-912.50, respectively. From the point of view of mobile forms content lead seems to be the most risky. The critical value, given by Law 220/2004 (0.1 mg/kg soil) was exceeded at 35 sampling sites, while the average Pb content was almost three times higher than the hygienic limit. The determined contents of Zn, Cd and Cu compared with the critical values (2.0, 0.1 and 1.0 mg/kg, respectively) were higher in 14, 11 and 4 (resp.) sampling sites. The maximal allowed amounts of Cd, Pb and Hg in feed given by Government Decree 438/2006 valid in the Slovakia were exceeded in 1, 2 and 12 samples of permanent grassland, respectively.

Although there is no statistically significant dependence between the content of the mobile forms monitored risky metals in the soil and in the permanent grassland, the obtained data indicate significant levels of forest ecosystem contamination by heavy metals. This fact can be reflected also at the level of other environmental component loading.

Keywords: contamination, heavy metals, environment, hygienic state

1. Introduction

Heavy metals are major contaminants with negative impact on environment. They occur in soil in various concentration and forms (Bystricka and Tomas, 2009). Soils contaminated by heavy metals have raised serious concerns in recent decades. Main concerns include potential risk to human health through the direct intake, bioaccumulation through food chain (Naveedullah *et al.*, 2013). Their high concentrations are toxic to the liver, kidneys, lungs, have a negative impact on gastroenterology, accumulate in the body and can cause collapse (Hailemariam and Bolger, 2014; Hronec *et al*., 2002; Makovnikova *et al*., 2006; Nriagu, 2011).

According to numerous studies, the pollution sources of heavy metals in environment are mainly derived from anthropogenic sources (Wei and Yang, 2010), The main sources include emissions from smelters. Slovakia is well tainted by mining and related processing of iron ores of the Middle Spis. The smelter for processing raw materials for copper production located in Krompachy has been operating with several breaks since 1843. According to data, in 1952 there were almost 12,000 t of solid pollutants emitted by smelter in Krompachy (Banasova and Lackovicova, 2004; Hronec *et al.*, 2010). In recent years this activity has stopped and all mines have been closed (Krokusova and Cech, 2010). The production of mercury in Iron mines Rudnany was the most serious source of pollution in this region. According to the producer data, the highest annual emission of solid pollutants was measured in 1988 (2406 tons, of which 6.40 t was Hg). Nowadays the mining activity is stopped, closed mines and enterprises were liquidated (Hronec *et al.*, 2010; Krokusova and Cech, 2010).

The aim of this study was to determine the level of forest ecosystem loading by chosen heavy metals (Hg, Cd, Cu, Ni and Cr) originated from Smelter in Krompachy and Iron mines Rudnany in the area of Volovske Hills in Middle Spis region.

2. Material and methods

The samples of soil and plant material were collected from 45 sampling sites (SS) (2 SS - intravilan, 34 SS - forest, 8 SS - pastures, 1 SS - permanent grassland) at acreage territory of approximately 156 km^2 in Volovske Hills in Middle Spis region. The sampling sites (SS) determination for soil and plants: source of air pollution in Rudnany was the basic point for determining the SS. The exact SS location was given by the radius penetration (1, 2, 3, 4, 5, 6, 8, 10, 12, 14 and 16 km, resp.) with vectors (N, E, S, NE, NE, NW, SE, ESE and SSE, resp.). Soil samples were taken at 0-10 cm horizon, plant samples were collected from the same SS).

2.1. Soil samples

Analysis of soil samples: content of organic carbon (C_{OX}, %) volumetric method (H_2SO_4: Merck, Germany, $K_2Cr_2O_7$: Merck, Germany; $(NH_4)_2Fe(SO_4)_2 \bullet 6H_2O$: Merck, Germany); content of humus (Hum, %) calculated from value of C_{OX} content; values of active soil reaction (pH/H_2O) and exchange soil reaction ($pH/CaCl_2$, $CaCl_2$: CentralChem, Slovakia; 691 pH Meter Metrohm, Swiss); these parameters were determined according to Fiala *et al.* (1999); content of heavy metals: the content of mobile forms of Zn, Cd, Pb and Cu was determined in soil extract by NH_4NO_3 (c = 1mol/dm^3, NH_4NO_3: Merck, Germany); total content of Zn, Cd, Pb and Cu, including all metal forms with exception of silicate forms, was determined in soil extract by *aqua regia* (HCl: CentralChem, Slovakia, HNO_3: Merck, Germany); total Hg content was determined using AAS method with cold Hg vapor detection.

2.2. Plant samples

In plant samples contents of Zn, Cd, Pb, Hg and Cu were determined; samples were mineralized by microwawe digestion using HNO_3 (Merck, Germany) before determination of HMs content.

Analysis of plant samples: content of heavy metals in soil and plant samples were determined using AAS (atomic absorption spectrometry) method: Cd, Pb: GF-AAS; Zn and Cu: F-AAS (VARIAN AASpectr DUO 240FS/240Z/UltrAA equipped with a D2 lamp background correction system, using an air-acetylene flame, Varian, Ltd., Mulgrave, Australia) and Hg: CV-AAS (AMA 254, Altec, Czech Republic). The measured results were compared with multielemental standard for GF AAS (CertiPUR®, Merck, Germany).

Contents of heavy metals determined in soil samples were compared with limit and critical values according to Act No. 220/2004 and proposals of threshold values for investigated metals in soils (OJEC, 1986). Contents of heavy metals determined in plant samples were evaluated according to maximal allowed amounts given by Government Decree 438/2006.

2.3. Statistical analysis

The descriptive statistic, regression and correlation analysis (Microsoft Excel) was used for the evaluation of correlation between contamination of soil and plants by heavy metals.

3. Results and discussioun

3.1. Soil

The informations about investigated location were gained based on results of soil sample analysis evaluated using descriptive statistics. The observed parameters are used as criteria for evaluation of agricultural soil properties. This evaluated soil group includes pastures, permanent grassland (PG) and intravilan, i.e. 11 SS (see Table 1).

Table 1: Selected parameters of soil quality

	C_{OX} (%)	Hum (%)	pH/H_2O	pH/$CaCl_2$
Minimum	1.02 (1.05)	1.75 (1.82)	4.16 (4.42)	3.08 (3.97)
Maximum	20.08 (5.90)	34.61 (10.17)	8.40 (7.73)	7.54 (7.08)
Average	4.33 (2.69)	7.46 (4.63)	6.29 (6.14)	5.64 (5.67)
Median	3.09 (2.11)	5.33 (3.63)	6.17 (6.05)	5.59 (5.59)
STDEV	3.44 (1.67)	5.93 (2.88)	1.14 (1.02)	1.23 (1.15)
Mode	2.04 (-)	3.51 (-)	7.61 (-)	7.08 (6.87)

Note: ( )* - values determined in soil samples from sampling sites with PG, from pastures and intravilan

The evaluated soils have low (1.0-2.0%, 1 SS) till very good humus supply (higher than 5.0%, 3 SS), extremely acid (pH/$CaCl_2$ < 4.5, 3 SS) till neutral soil reaction (pH/$CaCl_2$ = 6.6-7.2, 3 SS) (Declaration 338/2005). Soil reaction is one of factors which most affects behaviour of heavy metals in soil.
Various forms of heavy metals, determined in two soil extracts, were compared with the limit values for Slovakian soils. The obtained results are presented in Table 2.

Table 2: The content of mobile forms and total content of heavy metals in soil (in mg/kg)

	Zn		Cd		Pb		Hg	Cu	
	MFs	TCs	MFs	TCs	MFs	TCs	TCs	MFs	TCs
Minimum	0.015	33.10	0.029	0.65	0.005	26.50	0.28	0.035	11.00
Maximum	5.425	952.50	0.236	6.73	2.145	165.00	414.85	2.210	912.50
Average	1.329	190.71	0.076	2.97	0.294	60.82	32.84	0.354	108.72
Median	0.720	143.90	0.068	2.63	0.150	52.80	3.04	0.175	41.10
STDEV	1.554	165.01	0.043	1.59	0.411	33.78	93.94	0.510	179.90
Critical value*	2.0		0.1		0.1			1.0	
Threshold value**		100/150 /200		0.5/1.0 /1.5		50/70 /100	0.2/0.5 /1.0		40/50 /100

Note: *soil extract by NH_4NO_3, ** soil extract by *aqua regia,* if: 5 ≤ pH < 6 / 6 ≤ pH < 7 / pH ≥ 7

The critical value for lead (MFs) was exceeded at 33 SS, even at one site by more than 20-fold. Different situation was in the case of Zn, Cd and Cu, but limit values were at several SS exceeded, too (Zn in 14, Cd in 11 and Cu in 4 SS). From the aspect of ecotoxicity Hg is the most hazardous metal. The maximum Hg contents (TCs) were 800 times higher in comparison with limit, while average value 65-fold exceeded the limit value (see Table 2).

The gravity of the situation is confirmed in many studies focused on the monitoring of environmental contamination of this area in Slovakia. Banasova and Lackovicova (2004), Tomas *et al*. (2004), Dobrikova and Salgovicova (2006), Angelovicova and Fazekasova (2014) determined in soil samples from 179.0-720.0 (0.076-3.20, 0.566-110.8, 1.287-1310.0) mg/kg of Zn (Cd, Hg, Cu). In most cases we can talk about exceeding of the hygienic limits for monitored heavy metals in the soil, which do not degrade, but only can be accumulated in soil, water, and sediments (Naveedullah *et al.*, 2013).

Soil heavy metal pollution has become a severe problem in many parts of the world (Facchinelli *et al.*, 2001). Li *et al.* (2014) compared Zn (Cd, Pb, Hg and Cu): China: 1163 (11.0, 641.3, 3.82 and 211.9), Spain: 465.8 (6.59, 881.8, 52.9 and 120.8), Iran: 363.4 (1.49, 1002, 3.13 and 88.40) mg/kg

3.2. Plants

Samples of plant material were collected from the same SS as the soil samples and contents of Zn, Cd, Pb, Hg and Cu were determined. The obtained results are described using the descriptive statistics (see Table 3).

Table 3: Total content of Zn, Cd, Pb, Hg and Cu in plant materials (in mg/kg DM)

	Zn	Cd	Pb	Hg	Cu
Minimum	12.408	0.097	0.088	0.012	3.344
Maximum	158.576	1.628	29.744	12.837	85.712
Average	43.149	0.385	2.605	0.758	9.848
Median	38.456	0.334	0.968	0.051	7.480
STDEV	22.978	0.265	5.075	2.526	12.302
Signif. $F_{MFs/HMp}$	0.135	0.191	0.090		1.472E-03
Signif. $F_{TCs/HMp}$	1.335E-05	0.489	9.064E-03	0.683	0.053

Note: Signif. $F_{MFs/HMp}$ (Signif. $F_{TCs/HMp}$) – correlation between content of mobile forms (total content) of heavy metals in soil and total content of heavy metals in plant materials

Metal concentration found in contaminated soil frequently results in uptake by plants and–their bioavailability can be influenced by change of soil properties (Harangozo *et al.*, 2012; Oves *et al.*, 2012). An increased content of cadmium was determined only in 1 plant sample despite high determined total contents of Cd in all soil samples. High levels of mercury in the soil were reflected in its high accumulation in plants, although no correlation between Hg contents in plants and its soil contents was confirmed. The relation between soil content of metal (MFs, TCs) and its amount in plant (HMp) was evaluated using regression method and correlation analysis (see Table 3).

4. Conclusions

Rich mineral reserves in Volovske Hills in the past led to intensive mining and industrial activity in Middle Spis region. The protected area Volovske Hills became concurrently a locality with the environmental burden due mining and processing of copper and iron ores, and especially none or minimal use of modern technology with a favorable impact on the environment.

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