SPATIAL DISTRIBUTION AND ACCUMULATION OF HEAVY METALS IN AGRICULTURAL AND FOREST SOIL FROM FORMER MERCURY MINING AREA, SLOVAKIA

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ABSTRACT

The contamination level of the environment in the past few decades is largely influenced by the anthropogenic activity. The territory of Slovakia has been characterized by high level of the development of mining, ores processing and metallurgical industry, which is currently reflected in the deteriorated quality of all components of the environment. Central Spiš region belongs to the most burdened areas affected by the remains of the mining and ores processing industry. Mercury-containing ore (cinnabar and tetraedrite) was processed here since the middle of 20th century to 1993. About 500 meters from the main processing plant there is a tailing pond containing landfilled flotation sludge with the mercury content of more than 46 mg/kg. In the present paper, we focused on the assessment of the level of contamination of the topsoil (0-0.1 m) of agricultural and forest soil in the cadastral territory of Markušovce, where the former mercury smelters and the tailing pond are located. We determined 28 sampling points by GPS. All soil samples have been subjected to analyses for the detection of the active and the exchange of the soil reaction, total organic carbon (%), total mercury content and the contents of Cd, Pb, Cu and Zn (mg/kg) in the aqua regia extract. The results proved an extremely high level of contamination of these elements in the soil. Mercury concentration was in the range of 0.69-90.7 mg/kg, while the median value exceeded the standard established by applicable legislation more than 30 times. The content of other heavy metals closely correlated with contaminant concentration, which varied in wide intervals as evidenced by high standard deviations (Cd: 1.62±0.61 mg/kg; Pb: 37.6±15.2 mg/kg; Cu: 37.8±5.8 mg/kg Zn: 108±38.5 mg/kg). The results indicate that heavy metal concentrations represent a high level of the soil contamination in the study area, which might reflect in the contamination of other components of environment and food chain.

Keywords: mercury, soil contamination, heavy metals, mercury smelter

1. Introduction

The level of environmental contamination with heavy metals represents a significant risk in relation to the quality of the food chain (Adriano, 2001). In the last decades, a significant increase in the concentration of contaminating elements such as cadmium, mercury and arsenic in all components of the environment was reported (Granero and Domingo, 2002; Li *et al*., 2008). Non-ferrous metal production contributed to 15.5% of the Hg emission into the atmosphere globally (UNEP, 2013). It is mainly due to continuous increase of industrialization of human society (Huang *et al*., 2007; Govil *et al*., 2008; Li *et al*., 2008). Increasing demands for raw materials result in adverse interventions in nature. Increasing concentrations of certain trace elements, especially their mobile forms can cause serious environmental concern about the contamination and their accumulation in soil, vegetation, animals, and/or surface and ground waters (Chopin and Alloway 2007). In addition to the production of metals, industry is a very important source of environmental contamination with metals and burning of fossil fuels, especially coal. Burning municipal waste and pollution effluents containing increased levels of toxic metals is becoming an increasingly important source of environmental pollution with heavy metals. Soil contamination exceeded the limit value of at least one risky substance. In case of the risk elements we talk about their overall concentration. The available data regarding the total content (after the soil decomposition using potent mineral acids, especially aqua regia used in the Slovak Republic since 2004) may give us the necessary information in accordance with the valid legislation (including the approved maximum content of the risk elements and the level of contamination). Analyses of the transport of the risk elements to the plants and the interactions between soil and plant are especially crucial and studied by several authors (Árvay *et al*., 2014; Castaldi *et al*. 2009). On the other hand, low concentrations of the risk elements in soils, e.g. in acid soils, are related to their exceeded limits in plants (Kobza *et al*. 2007).

2. Materials and methods

The paper focuses on determining the level of contamination of soil cover in the cadastral territory of Markušovce. There is an old environmental burden (tailing pond, area of the former mercury smelter and heaps of pyrites) in the southern part of the territory The main mercury smelter was launched into operation in 1969. The summary of Hg emissions from all sources was 142 tonnes during the years 1963-1993 (Svoboda *et al.* 2000). The substrate consists of naturally high concentration of mercury, copper, lead, zinc and cadmium. The study area with the emission source and sampling points is shown in Figure 1.

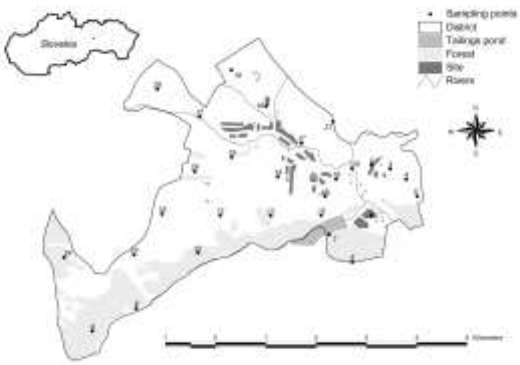

Figure 1: The study area with the emission source (sampling point No. 1) and sampling points.

Soil samples (n=28) were taken by sampling probe from a depth of 0.0-0.1 m in 2013. Sampling points were determined using GPS navigation device at regular intervals of 1 km from the emission source (sampling point 1). The samples were dried to constant weight and sieved through a 2 mm pore sieve. An analysis was carried out to determine the active and exchange soil reaction, humus content, total concentration of mercury and total concentration of monitored heavy metals (Cd, Pb, Cu and Zn) in extract of aqua regia. Mineralization of soil samples was done by 10 cm^3 of aqua regia (2.5 cm^3 HNO_3 and 7.5 cm^3 HCl, *Merck*, Germany) using microwave digestion unit Mars X-press 5 (*CEM Corp*., USA) in closed PTFE vessels. Metal determinations were performed in a Varian AA240Z (*Varian*, Australia) atomic absorption spectrometer with Zeeman background correction. The graphite furnace technique was used for the determination of Cd and Pb. The content of copper and zinc were determined by Flame Atomic Absorption Spectrometry AA240FS Varian (*Varian*, Australia). The total mercury concentration was determined in the homogenized dried soil samples (0.005-0.01 g) using a cold-vapour AAS analyser AMA 254 (*Altec*, Czech Republic) with a detection limit of 0.5 ng/g. Mean difference between duplicates were up to 5% (Svoboda *et al*., 2006). All statistical analyses were carried out using the statistical software Statistica 12.0 *(Statsoft,* USA). We used Pearson correlation coefficients at significance level of $p<0.05$ (weak statistical significance) and $p<0.001$ (very strong statistical significance) to compare the impact of the monitored parameters. The obtained data on the concentration of heavy metals we have compared with the limit values that define the legislative norm (Act No. 220/2004).

3. Results and discussion

According to our findings, relatively small study area of cadastral territory Markušovce (19.2 km^2) is in all parameters significantly heterogeneous. Active soil reaction at the level of the median value varied in the range 6.40±6.28 (median±SD). Soil reaction in $CaCl_2$ solution with c=0.01 mol/dm^3 was at the level of the median value in the range 6.07±22.2. Our findings show that 3.51 km^2 of land (18.3%) is strongly acidified (pH<4.5), which can affect the increased mobility and subsequent bioavailability of the monitored contaminants (Kocher *et al*. 2005). The humus content varied in wide range (2.72%±87.9), which is caused by the different nature of the samples. Statistically significant effect of soil parameters on the level of topsoil contamination with heavy metals is also confirmed by Pearson correlation coefficients (p<0.05, <0.001) and these results are shown in Table 1. Statistically high positive impact on the lead content R=0.70 (p<0.001) of humus content but also other monitored contaminants is confirmed by the findings of the authors Turer and Maynard (2003), who found a strong positive statistical dependence between the content of $C_{ox.}$ and the content of heavy metals in soil. The total mercury concentration in the study area varied in wide range. The level of the median value was 2.91±23.1 mg/kg. From the hygienic point of view, it is necessary to emphasize that in an area of more than 15 km^2 (78.5%) an excess of the limit value of 0.5 mg/kg was detected. The results of mercury concentration in the soil closely correlate with the results of other authors, who pointed to the high level of contamination of all environments (Dombianová 2005; Bobro *et al*. 2006; Takáč *et al*. 2008). It represents a significant risk of possible contamination of agricultural production and food and feed chain (Vilček *et al*. 2012). The cadmium concentration of the study area varied in the range 1.62±34.2 mg/kg. Exceeding of the limit value of 0.70 mg/kg was recorded at the level of the median value more than two times. We can state that the study area is contaminated with heavy metals. The limit values were exceeded for almost 96% of the study area. The lead concentration exceeds the limit value of 75 mg/kg at two sampling sites. The lead concentration is varied in the median value in the range 37.6±60.7 mg/kg. The concentration of heavy metals exceeded the limit value by 10.3% of the total area. It does not pose any risk of contamination of the agricultural products, because it is a forest soil. There is a high positive correlation between the lead concentration of the topsoil and the humus content (Table 1) and it shows a high level of affinity of the monitored parameters, what is confirmed by the results of other authors Brehuv *et al.* (2005). The concentration of copper and zinc in the topsoil was compared to the level of mercury. It does not represent a significant risk. The level of contamination of the study area is showed in Figure 2. Detected concentration of copper (37.8±76.1 mg/kg) and zinc (108±92.3 mg/kg) point to a high variability of the monitored contaminants in the study area (Figure 2). In the case of all contaminants, there was a local pollution observed in the vicinity of the emission source, which is confirmed by the findings of Angelovičová and Fazekašová (2014). Our findings show that the study area is contaminated with copper and zinc on 19.8% and 69.9%, respectively.

Table 1: Pearson correlation coefficient between heavy metals and chemical parameters in soil

	Hg	**Cd**	**Pb**	**Zn**	**Cu**
pH – H_2O	-0.08	**0.46***	0.24	**0.39***	0.25
pH – $CaCl_2$	-0.17	**0.41***	0.15	**0.42***	0.27
$C_{ox.}$ (%)	**0.42***	0.20	**0.70****	0.19	0.07
Hg		0.02	0.11	-0.09	**0.72****
Cd			**0.61****	0.31	0.30
Pb				**0.55****	0.24
Zn					0.23

*p<0.05 – statistical significant of the correlations

**p<0.001 – very strong statistical significant of the correlations

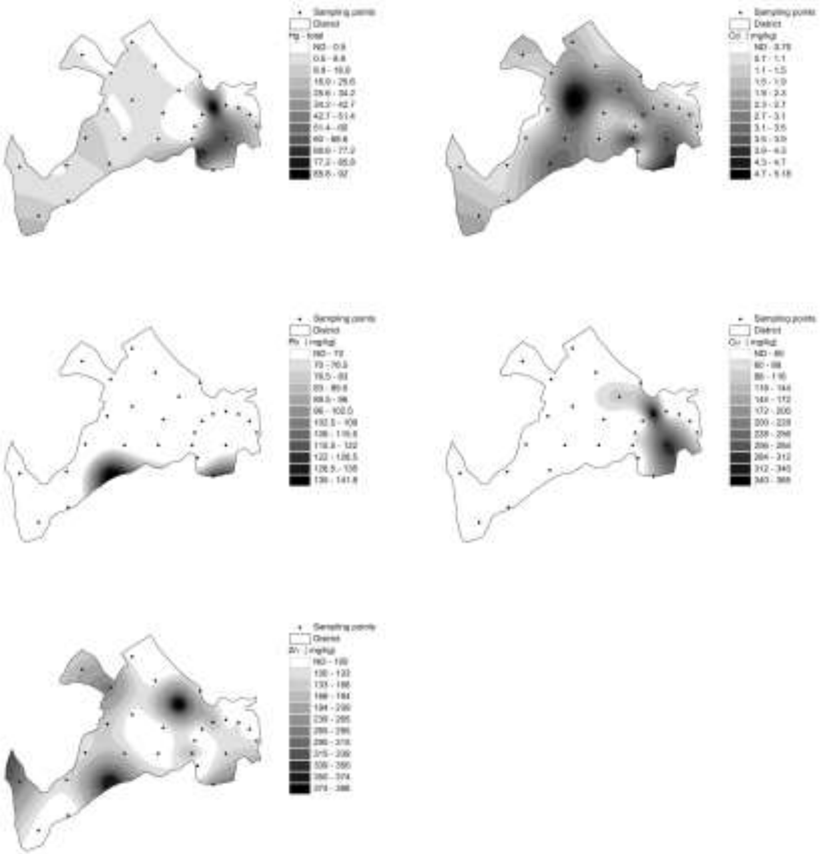

Figure 2: Spatial interpolation of total concentrations of Hg, Cd, Pb, Cu and Zn. White area – the limit value (mg/kg) was not exceeded

4. Conclusions

In the present paper, we aimed at detection of the level of burdened topsoil in the area of the former metallurgical company, which in 1993 was processing ore with a high content of Hg and other monitored elements. According to the results, it can be concluded that the area within 5 km from the emission source is heavily contaminated with monitored heavy metals, thus permitting passage of contaminants from abiotic environment to food chain, which in turn reflected the deterioration of health of the local population and thus to increased mortality.

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REFERENCES

1. Act No. 220/2004 (2004), On the Protection and Use of Agricultural Land. National Council of Slovak Republic, 2004 Bratislava, Slovakia. (in Slovak)
2. Adriano D.C. (2001), Trace elements in terrestrial environments, 2nd edition. Springer, New York, 61-90.
3. Angelovičová L. and Fazekašová D. (2014), Contamination of the soil and water environment by heavy metals in the former mining area of Rudňany (Slovakia), Soil and Water Research, **9**, 18-24.
4. Árvay, J.; Tomáš, J.; Hauptvogl, M.; Kopernická, M.; Kováčik, A.; Bajčan, D.; Massanyi, P. (2014), Contamination of wild-grown edible mushrooms by heavy metals in a former mercury-mining area. J. Environ. Sci. Health Part B. **49(11)**, 815-827.
5. Bobro M., Maceková J., Slančo P., Hančulák J. and Šestinová O. (2006), Wastes from mining and metallurgical activities in the water reservoir of Ružín, Acta Metallurgica Slovaca, **12**, 26-32.

6. Castaldi P., Melis P., Silvett, M., Seiana P. and Garau G. (2009), Influence of pea and wheat growth on Pb, Cd and Zn mobility and soil biological status in a polluted amended soil, Geoderma, **151**, 241-248.
7. Dombianová R. (2005), Mercury and methylmercury in plants from different contaminated sites in Slovakia, Plant, Soil and Environment, **51**, 456-463.
8. Granero S. and Domingo J.L. (2002), Levels of metals in soils of Alcala de Henares, Spain: Human health risks, Environmental International, **28(3)**, 159-164.
9. Govil P.K., Sorlie J.E., Murthy N.N., Sujatha D., Reddy G.L. and Rudolph-Lund K. (2008) Soil contamination of heavy metals in the Katedan Industrial Development Area, Hyderabad, India, Environmental Monitoring Assessment, **140(1-3)**, 313-323.
10. Huang S.S., Liao Q.L., Hua M., Wu X., Bi K.S. and Yan C.Y. (2007), Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China, Chemosphere, **67**, 2148-2155.
11. Chopin E.I.B. and Alloway B.J. (2007), Distribution and mobility of trace elements in soils and vegetation around the mining and smelting areas of Tharsis, Riótinto and Huelva, Iberian Pyrite Belt, SW Spain, Water, Air & Soil Pollution, **182**, 245-261.
12. Kobza J., Bezák P., Hrivňáková K., Medveď M. and Načiniaková Z. (2007), The criteria for the identification of risk areas by contamination of agricultural soils, methodologies and their evaluation, The Soil Science and Conservation Research Institute (SSCRI), Bratislava, 31. (in Slovak)
13. Kocher B., Wessolek G. and Stoffregen H. (2005), Water and heavy metal transport in roadside soils, Pedosphere, **15**, 746-753.
14. Li Y., Gou X., Wang G., Zhang Q., Su Q. and Xiao G. (2008), Heavy metal contamination and source in arid agricultural soil in Central Gansu Province, China, Journal of Environmental Sciences, **20(5)**, 607-612.
15. Svoboda L., Havlíčková B. and Kalač P. (2006), Contents of cadmium, mercury and lead in edible mushrooms growing in a historical silver-mining area, Food Chemistry, **96**, 580-585.
16. Svoboda L., Zimmermannová K. and Kalač P. (2000), Concentrations of mercury, cadmium, lead and copper in fruiting bodies of edible mushrooms in an emission area of a copper smelter and a mercury smelter, The Science of the Total Environment, **246**, 61-67.
17. Takáč P., Kozáková Ľ., Vaľková M. and Zeleňák F. (2008), Heavy metals in the middle Spiš soils, Acta Montanistica Slovaca, **13**, 82-86.
18. Turer D. and Maynard B. (2003), Heavy metal contamination in highway soils. Comparison of Corpus Christy, Texas and Cincinnaty, Ohio shows organic matter is key to mobility, Clean Technologies and Environmental Policy, **4**, 235-245.
19. UNEP – United Nations Environment Programme (2013), Technical background report for the global Hg assessment, 2013 Geneva, Switzerland.
20. Vilček J., Hronec, O. and Tomáš J. (2012), Risk elements in soil of burdened areas of eastern Slovakia, Polish Journal of Environmental Studies, **21(5)**, 1426-1436.