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REGULAR ARTICLE

THE LEVEL OF PLANT CONTAMINATION BY MERCURY FROM THE RUDŇANY MINES IMMISION AREA

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ABSTRACT

In the present work we focused on the monitoring of total mercury in forest ecosystem Volovské mountains, in the middle of the file which has been subjected to long-term emission burden metalworking plant in Rudňany. Sampling sites located between Rudňany and Krompachy in regular, well-defined distances. From every point of delivery, we sampled the soil and forest, respectively, pasture growth. In all samples, we conducted analyzes to determine mercury content on dedicated absorption spectrometry AMA 254 companies from Altech. The results of total mercury content in the soil show higher values compared with the limit value, especially at a distance of 5 km from the emission source (0.6888 to 10.0279 ug.g^{-1}). Such high levels of mercury content in the soil creates an increased risk of contamination of biota, but this assumption does not apply, as shown by the results of analyzes the content of Hg in the stand.

Keywords: forest soil, forest plants, mercury, immision

INTRODUCTION

Mercury (Hg) is one of the most hazardous environmental pollutants, but its toxicity is dependent on its chemical form. MethHg compounds, the main mercury species in seafood, are considerably more toxic than elemental Hg and inorganic Hg salts. During the last decade improvements in analytical techniques as well as reaction oriented environmental research have considerably improved the knowledge on the Hg biogeochemical cycling and the impact of Hg exposure on human health (**Wilson - Pyatt, 2007)**. To reduce the risks of mercury intoxication, limits of Hg levels in fish as well as consumption advisory limits have been compelled by EU, USA and Canada amongst others. Hair is a suitable indicator for the monitoring of human exposure by mercury, especially resulting from dietary intake **(Harkins – Susten, 2004)**.

Mercury in soil, depending on the redox conditions can occur in three main valence states: Hg^0, Hg^+ and Hg^{2+}, the first two are essential components of the soil ecosystem **(Ďurža - Khun, 2002)**. Many authors indicate that mercury in its inorganic form is well adsorbed by soil organic matter - humus. Sorption of Hg is largely dependent on the pH, while the largest is in the range 4 - 5 Due to the high affinity of Hg to organic carbon **(Suchar - Sucharová, 2005)** consists of Hg in soils stabil complexes with organic compounds. Therefore, Hg in neutral, humus soils quickly bound into complexes and it also corresponds to the low availability of Hg for plants **(Štefanidesová *et al.*, 2000)**.

Approximetly 2 - 3% of the Hg in the soil microorganism activity "methylate" **(Suchar - Sucharová, 2005)**. This process occurs mainly under anaerobic conditions, but certainly groups of microorganisms are able to make even a relatively high partial pressure of oxygen in the soil air. Methylated compounds of mercury ($CH3Hg^+$-R^-) in soil represented only up to 2% of the total Hg in the soil have a higher vapor pressure and are well volatile, but a major proportion of metallic Hg from the soil evaporates into the atmosphere and subsequent wet deposition are brought back the soil **(Bencko *et al.*, 1995)**.

The median Hg contents in soils of Slovakia stands at 0.08 $mg.kg^{-1}$ in the humic horizon, with the highest levels of moving areas of geochemical anomalies, which include the area of interest central Spiš where almost 70 years mercury mined and processed **(Vilček *et al.* 2012)**.

The most risky in terms terrestrial ecosystems are forests **(Schwesig - Matzner, 2000)**. An important source of Hg in forest soils is litter assimilation organs and the highest concentrations of mercury are found in rock layers of forest soils, emphasizing the importance of transport processes occurring between the organic and mineral horizons. Transport of mercury compounds from the organic layer of forest soils may be the first step is mobilization of Hg in forest catchments and is important in the release of mercury compounds, especially MetHg in aquatic ecosystems, where they represent a significant risk of contamination of the human food chain.

MATERIAL AND METHODS

In the present work, we focused on monitoring contamination levels in the middle Spiš. Interest will be located in the district of Spišská Nová Ves in Volovské hills (mountains between Rudňany and Krompachy) west of the emission source. All samples (n = 10) of soil and plant material represents the forest ecosystem, which is located in the catchment area of the emission source (ES) - ron-ore processing company Rudňany mine, which until 1993 year issued by about 4,64 to 6,5 tons of metallic mercury into the environment by gaseous air pollutants **(Hronec et al, 1992)**.

The soil samples were collected with a well-defined sampling point using a handheld navigation device Garmin 60 Cx, with an accuracy of ± 2 m, the theoretical determination of the point of delivery. We then carried out at the place of soil sample to a depth of 0.10 to 0.20 m, depending on the depth of soil.

In all soil samples was performed analyzes for the detection of basic chemical parameters that greatly influence the mobility of heavy metals in soil environment (active pH, exchangeable pH, humus content) and analysis to determine total mercury single-purpose spectrometer AMA 254 (Altech - Czech Republic). Functional diagram of the apparatus is shown in Fig. 1

To assess levels of heavy metals observed transition, we investigated the contents of the plant matter, which were taken from the same sampling sites as land. The composition of plant samples was determined by local conditions that we provide the delivery point (assimilation litter, wild fruits, edible mushrooms). Plant material was analyzed after drying the AMA 254 instrument according to the methodology defined by the STN 465735.

Table 1 Basic characteristics of the sampling sites and the basic chemical parameters in pooled samples of soil

Sampling points	VGS 84 coordinates	Distance by ES (km)	Soil - parcel				
			Sample charakteristic	Cadaster	pH-H_2O	pH-$CaCl_2$	Humus (%)
Spiš 03	48°54,113 20°40,105	1	Pasture	Matejovce n/H	6,05	3,97	3,33
Spiš 11	48°54,142 20°40,924	2	Forest	Matejovce n/H	8,40	7,52	3,63
Spiš 19	48°54,171 20°41,742	3	Forest	Chraťn/H	6,78	6,19	4,60
Spiš 27	48°54,201 20°42,556	4	Forest	Chraťn/H	7,74	7,01	7,26
Spiš 35	48°54,229 20°43,377	5	Forest	Vitkovce	7,61	7,08	17,55
Spiš 43	48°54,258 20°44,194	6	Forest	Olcnava	7,68	7,02	11,26
Spiš 51	48°54,315 20°45,826	8	Forest	Olcnava	5,80	4,88	4,42
Spiš 59	48°54,373 20°47,461	10	Forest	Spiš. Vlachy	7,70	7,05	10,41
Spiš 67	48°54,429 20°49,091	12	Forest	Spiš. Vlachy	8,04	7,27	7,62
Spiš 75	48°54,485 20°50,726	14	Forest	Krompachy	7,29	6,69	2,42

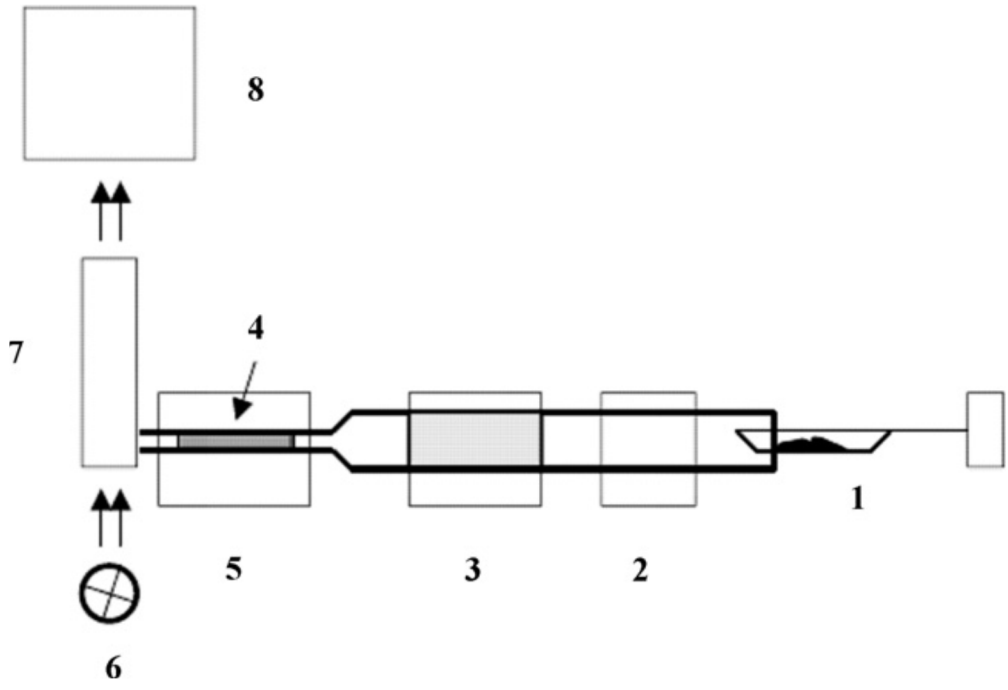

Figure 1 Scheme of the AMA 254 spectrometer. (1) Sampling boat, (2) decomposition furnace, (3) catalytic column, (4) gold amalgamator, (5) releasing furnace, (6) mercury cathode lamp, (7) optical cell system, and (8) detector (**Spěváčková et al., 2004**).

RESULTS AND DISCUSSION

Values and active soil exchange reactions in soil samples varied in a relatively wide range, indicating different quality parameters of samples, which is also reflected on the level of contamination and subsequent bioaccumulation of mercury in biota **(Poty et al., 2012)**. The value of the active soil reaction ranged level averaging 7.65 ± 0.85 and exchange at pH 7.02 ± 1.15. The relatively high value of the standard deviation indicates the high variability of the measured value, which means that words can assess the situation as slightly acidic to neutral. Such an environment creates favorable conditions for low mercury transition from inanimate to the living environment. Another important parameter that significantly affects the mobility of the heavy metal content is humus content. Mean humus content in this case was at the level of 5.93 ± 4.70, while such values indicate extremely high levels of organic matter in the soil environment monitored site, but the data are not unrealistic, since it contains humus matter in forest soils moving significantly higher levels than soils used for agriculture (regular cultivation leads to intense oxidative processes that reduce the content of organic matter in the soil).

Table 2 The content of mercury in the samples soil and plant samples labeled exceeding the statutory limit values

Sampling points	Distance by ES (km)	THg content in soil ($mg.kg^{-1}$)	Hg content in plant material ($mg.kg^{-1}$)
Spiš 03	1	**10,0279**	0,0909
Spiš 11	2	**3,0409**	0,0906
Spiš 19	3	**1,8843**	0,1929
Spiš 27	4	**1,4914**	0,0768
Spiš 35	5	**2,2212**	0,0583
Spiš 43	6	**1,4354**	0,0856
Spiš 51	8	**0,8871**	0,2400
Spiš 59	10	**0,6888**	0,0301
Spiš 67	12	0,3618	0,0920
Spiš 75	14	**0,8709**	0,0516

The content of total mercury (THg) in the top layer of forest soils studied varied over a wide range (from 0.3618 to 10.0279 mg.kg^{-1}). From Table 2 it is seen a high negative correlation between THg content in the soil and distance delivery point from the emission source. The highest concentration (10.0279 mgkg^{-1}) was recorded at the point of delivery "Spiš 03", which is located 1000 m as the crow flies from ES. This high concentration is the limit value (0.5 mg.kg^{-1}) by more than 20 times. This high level of contamination of the sampling point "Spiš 03", along with other the parameters that affect the mobility of Hg (pH - extremely acidic and medium humus content) creates an extremely high risk of mercury bioaccumulation in the biotic environment, but this was not confirmed in our case. Of the ten sampling sites was recorded exceeding the limit values for nine, indicating a high risk of contaminant levels observed area Volovské Hills.

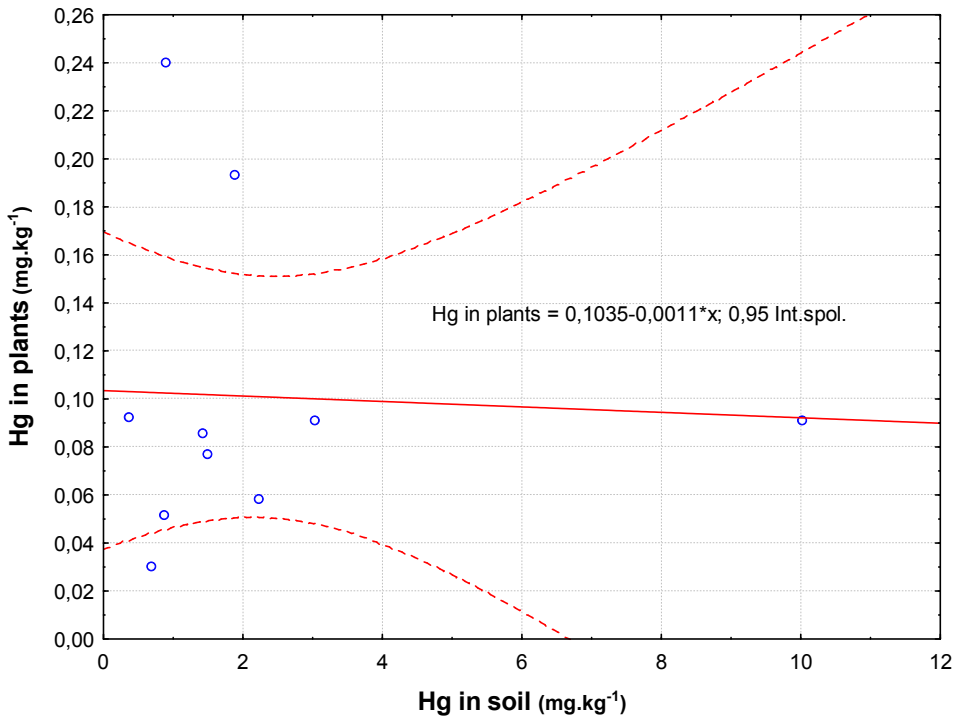

Figure 2 Spot comparison relations of total Hg in soil and its content in plant materials

Relatively high levels of total mercury in the upper soil layer in conjunction with the basic chemical properties that greatly affect the mobility of mercury in the soil - plant showed the expected risk of transition in his stand. The highest THg content in the soil was recorded at the point of delivery "Spiš 03", and this place represented the greatest risk of contamination

of the food chain, since only this place is used to free grazing livestock. However, the content of Hg in plant materials stood at 0.0909 $mg.kg^{-1}$, which does not correlate with each other. The highest concentrations were on the taps "rather 51" and "rather 19", which exceeded the limit of 0.1 $mg.kg^{-1}$ represent the value 140% resp. 93%. Mutual correlation relationships between the individual taps of the total mercury content in soil and its content in plant materials shown in figure 2. Mercury level transition system soil - plant is digressive, confirming the result of the statistical analysis, where R = -0.0493 at confidence level $p < 0.05$.

CONCLUSION

In the present work, we focused on monitoring the level of contamination of forest land and forest, respectively. pasture in relation to the limit of the environmental burden of the past, which was the acquisition and processing of ore with a high content of mercury. Despite the relatively high content of total mercury in soil (exceeding the limit values for 9 sampling sites), we expected excess of the maximum allowable concentration in the plant material recorded, as confirmed by statistical analysis. This fact is probably due to the favorable conditions that create barriers to the expected transition Hg by soil – plant system.

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