Carpathian Journal of Earth and Environmental Sciences February 2023, Vol. 18, No. 1, p. 225 – 229; DOI:10.26471/cjees/2023/018/253

PHYTOACCUMULATION OF MERCURY INTO VASCULAR PLANTS AT AREA OF ABANDONED Hg-ORE DEPOSIT MALACHOV (CENTRAL SLOVAKIA)

Pavol MIDULA[1], Peter ANDRÁŠ[2], Janka ŠEVČÍKOVÁ[2], & Oliver WICHE[3]

[1]Jan Evangelista Purkyně University, Pasteurova 1, 400 01, Ústí nad Labem, Czech Republic, pavol.midula@ujep.cz
[2]Matej Bel University in Banská Bystrica, Tajovského 44, 974 01, Banská Bystrica, Slovakia, peter.andras@umb.sk; janka.sevcikova@umb.sk
[3]Technische Universität Bergakademie Freiberg, Leipziger Str. 29, 09599, Freiberg, Germany, Oliver.Wiche@ioez.tu-freiberg.de

Abstract: The study is focused on Hg content in topsoil of dump-field Veľká Studňa, nearby former mining area Malachov and its accumulation by selected plants, which consisted of the local representatives of grass, herb, and wood species. The study area was divided into several parcels, based on physiognomic features of plant communities. In the order to predict the Hg distribution for the whole study area, the interpolation methods were used in GIS. The plant material consists of 4 plant species: *Calamagrostis epigejos*, *Lotus corniculatus*, *Leontodon hispidus* and *Picea abies*. The samples were dried, grained, dissolved in HNO_3 and HCl solution and consequently measured by inductively coupled plasma mass-spectrometry (ICP-MS) for Hg content. The results show a mass contamination of the dump top-soil horizon by mercury. The values in soil variable from 16 to 910 mg kg^{-1}. The bioaccumulation potential of some investigated plant species can be considered as significant as well. The highest concentration of Hg was found in *Picea abies* ─ 24 mg kg^{-1}. With the regard to presented data, the dump-field could be assigned as the risk enclave for the local environment and therefore its study is demanding. Applying proper techniques for investigations of bioavailable forms of mercury in the topsoil samples should be also considered.

Keywords: mercury, phytoaccumulation, Malachov, ore deposit, bioavailability

1. INTRODUCTION

In term of landscape ecology, the mine deposits are unnatural components with disturbing effect on the natural environment. They also represent a suitable object for the study of not only the pedogenetical processes but also the processes of natural succession and evolution of phytocenoses (Banásová, et al., 2012).

Mercury is well known for its toxic character in plants – it strongly inhibits photosynthesis by interacting with metal ions (DalCorso, 2012). The availability of Hg into the plants is generally considered as very low. Similarly, as in the cases of other potentially toxic elements, roots are the first barrier to Hg uptake into the other parts of plant body from soil, thus they show the first signs of the toxicity. The significant role in plant uptake also plays the content of Hg^0 in local air (Lindberg, et al., 1979).

The dump-field Veľká Studňa presents the remnant of one of the most frequent mining activities in Slovakia for the last century. In urban area of Malachov, where the dump is situated, Hg mine industry is very well known. In the past, Malachov was one of the most important Hg-deposits in the world. The main ore source of mercury on this site was mineral cinnabar (HgS). The mining activity was dated here to almost 600 years ago and finally finished in 1993 (Maťová et al., 2008).

Municipality Malachov is situated in Central Slovakia, approximately 2 km from Banská Bystrica city in the Kremnické vrchy Mts. Mercury deposit Veľká Studňa (GPS 48°42'54,519"N 19°1'42,416"E) could be found in the western direction from the urban area. The dump enclave consists mainly of the waste rock material, accumulated in the period of very last mining activity at the site. The field has a considerable degree of incline from west to east and

is approximately 300 m long, with the area of 57,000 m^2. Some parts of the dump area were recultivated recently after the last mining attempt by covering the tailing material with a backfill. Nowadays, the area of dump-field presents the site with a diversified flora. The primary and secondary succession processes are quite fast, what results in the occurrence of several types of vegetation with a relatively high diversity of plant taxa. A couple of anomalies in the plant physiology, caused probably by the contaminated soil substrate is noticeable.

The bioavailable content of mercury in ecosystems presents a big risk to the environment due to the potential toxicity of the element as well as to the potential to be accumulated in the organisms through the trophic chain. The ore-deposit of Veľká Studňa represents a suitable area for investigation of Hg potential to be accumulated in vascular plants. This work is primarily aimed on the characterization of spolic technosol in presented dump-field from the viewpoint of Hg content; and investigate the phytoaccumulation potential of representatives of natural occurring vegetation. Monitoring of the Hg content in topsoil of the former mining sites as well as the understanding of its impact on plants is an essential part of understanding of bioavailability and transport mechanism of this specific potentially toxic element.

2. MATERIAL AND METHODS

The study area was investigated during dry and sunny periods from early spring to late summer. The dump-field was divided into several polygons are representing individual plant habitats, specific in composition, density, abundance, and dominance of plant species (Figure 1A).

In total, 18 sampling sites were selected on the area of dump-field (16) and reference areas (2). As figure 3 shows, the samples were taken from most of the identified habitats. The soil samples were taken from the depth of 10 cm (main rooting horizon). The soil material was dried at 40°C, grained and stored in plastic bags in the cold.

The plant material taken from the study area consisted of 4 autochthonous, widely represented *plants of the dump: Calamagrostis epigejos (grass), Lotus corniculatus*, *Leontodon hispidus* (herbs) and *Picea abies* (wood) – 3 individuals for each species. The samples consisted of all parts of the upper ground plant body (shoots and leaves/needles). The leaves and tillers were dried at 80°C for one day, weighted and stored.

In order to determine the Hg distribution for whole area of dump-field (Figure 1B), interpolation method Spline was used in geoprocessing program ArcGIS 10.2.1. The calculation was used according to polygons, representing the physiognomic types (habitats).

2.1. Analyses of Hg content in soil and plants

Analytical part of work took a place in the laboratories of Institute of Biosciences at the Technische Universität Bergakademie Freiberg in Saxony (Germany).

The dry soil and plant samples were ground to a fine powder. A subsample of 100 mg of investigated material was used for microwave digestion (Ethos plus 2, MLS) with nitric and hydrochloric acid according to Krachler et al., (2002). The concentration of Hg was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The concentrations of mercury in soil sample were correlated with two physiochemical soil parameters – pH and soil organic matter (SOM). The

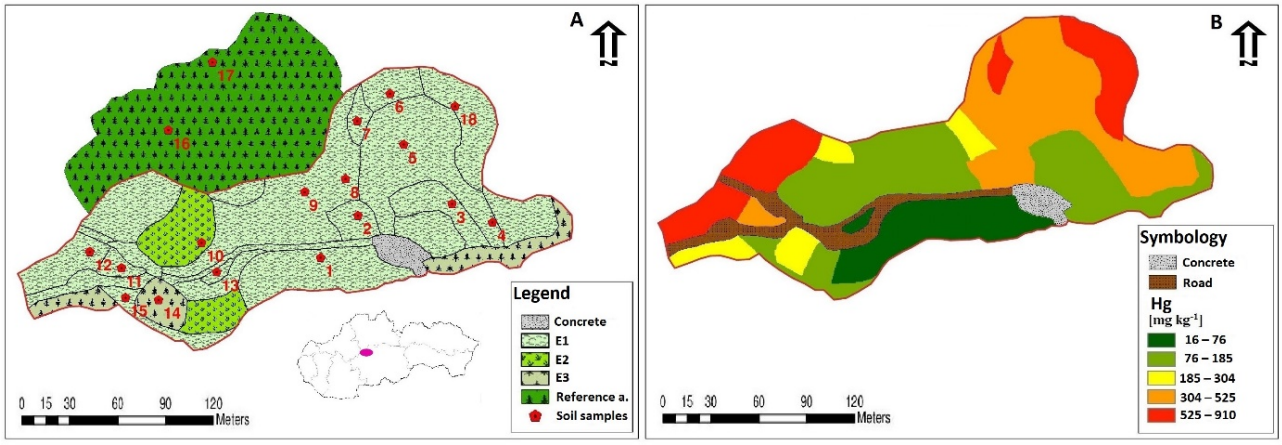

Figure 1. **A**: The study area of Veľká Studňa dump-field with marked sites of sampled topsoil and vertical diversification of natural vegetation (E3 – tree layer, E2 – shrub layer, E1 – herb layer); **B**: Interpolation model of Hg distribution within the topsoil of study area.

soil reaction (pH) was measured according to Sobek et al., (1978). 10 g of fresh soil samples were mixed with 100 ml distilled water into a suspension and shaken for 1 h. The pH values were measured directly from the centrifuged solutions. In the order to define the organic matter content, a specific amount of soil sample was weighted and consequently heated to 550°C for 2 hours. The percentage of humus was calculated from the combustion residues.

2.2. Statistical evaluation

Statistical work was performed in software application IBM SPSS Statistics 19. Spearman Rank Correlation coefficients were calculated in order to identify significant relationships between two numerical parameters. Results with p-values < 0.1 were considered as statistically significant.

3. RESULTS AND DISCUSSION

High content of mercury in the soil samples was proved (Table 1). Average concentration for whole dump-field is 370,28 mg kg^{-1} (min. 16.16, max 910.80 mg kg^{-1}). According to regulation issued by Ministry of Agriculture in Slovakia (Decree No. 508/2004), where the limit for agriculture soil is 0.5 mg kg^{-1}, the topsoil on the study site could be specified as highly contaminated. Average pH (7.36) indicates almost neutral soil reaction, the content of soil organic matter reached 9.94 % in average (min. 0, max. 23.5). The results from reference areas also indicate conditions of Hg pollution (24.42 mg kg^{-1} in av.), however in the comparison with the dump itself this value could be considered as low. Such a high Hg content in this area could be also related to the very close position of mining shafts, where most of the activities and material-cumulation works were performed.

Supporting this statement, the highest content of Hg, shown on the interpolation model (Figure 1B) indicates a large pool on western sites, where the main entrance of the shaft is situated. An interesting fact is, that the other large pool is on the eastern side, where are the habitats with the lowest elevation, situated just on the opposite side of the mining shafts.

The primary source of mercury content is cinnabar, which is the only Hg-mineral at the deposit (Dadová et al., 2015). Cinnabar is slightly soluble under strong alkaline conditions (Steinnes, 2013), however, since the scale of measured pH values show nearly neutral conditions in the topsoil, there can be assumed that Hg is not primarily released into the soil by this process or the basic reactions deeper in the dumped material affect the Hg content in the upper levels of soil horizons.

Table 1. Total concentrations of mercury, pH and soil organic content (SOM) in topsoil of Veľká Studňa dump-field. The marginal sites considering as the reference are marked by dash lines; the highest and lowest values are in bold.

Sample	**Hg** [mg kg^{-1}]	pH	SOM
1	**16.16**	**6.50**	13.50
2	380.70	7.08	13.50
3	155.60	7.45	5.00
4	323.80	7.12	13.00
5	359.70	7.47	7.50
6	525.00	7.02	10.00
7	864.30	7.20	4.00
8	335.40	7.32	13.50
9	130.60	7.92	6.00
10	143.10	**8.25**	6.50
11	481.10	8.10	7.00
12	**910.80**	7.59	**0.00**
13	26.23	7.03	8.50
14	223.40	7.44	**23.50**
15	140.30	7.49	15.50
16	37.83	6.52	23.00
17	11.00	5.10	11.00
18	908.30	7.25	12.00
s. d.	298.76	0.44	5.59

The correlations of Hg content and other investigated parameters (pH, SOM) were detected, but according to p values, these results could not be considered as highly significant (Figure 2). The figure 5 shows that Hg content correlates with pH what could be caused by high mobility of the metal in acid conditions. The correlation of pH values and soil organic matter was neutral. Those results could be also caused by low variability of pH values.

3.1. Hg contents in plants

The analyses of plant material proved, that Hg cumulates in plant tissues. Significant amounts are detected in tissues of *Leontodon hispidus* (5) and mainly in *Picea abie*s (3; 10; 12). It is evident then, that the bioavailable Hg forms are present in the topsoil of dump-field. The bioavailable abilities for Hg among the investigated plant species decrease as follows: *Picea abies* > *Leontodon hispidus* > *Lotus corniculatus* > *Calamagrostis epigejos*. As table 2 shows, the highest content was found in spruce on site 10, where the content of Hg in soil is one of the

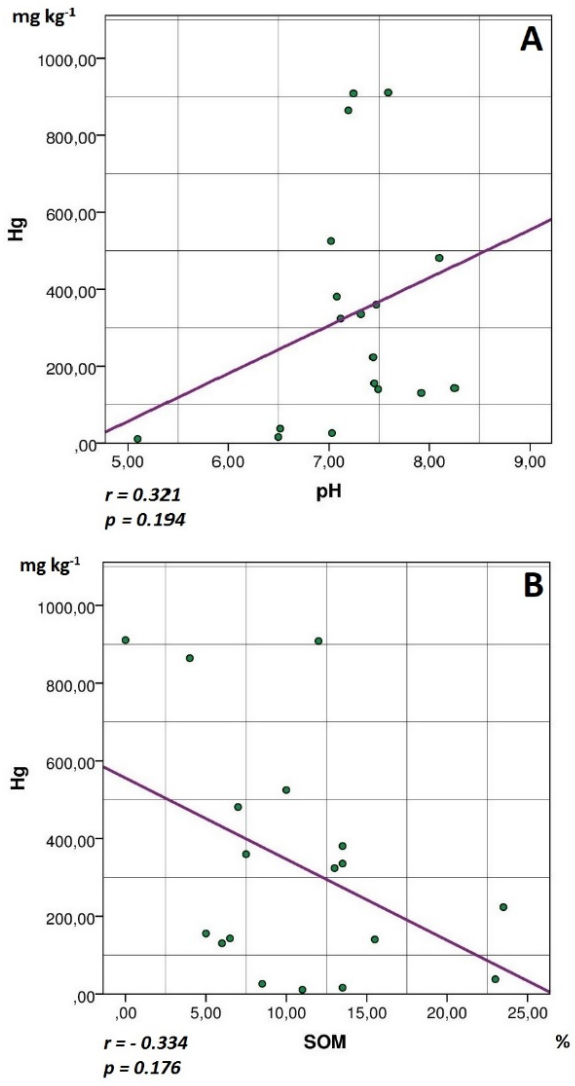

Figure 2. The correlations of mercury concentrations in topsoil soil with pH (**A**) and soil organic matter – SOM (**B**).

lowest. According to Law Decree describing the heavy metal contents in agricultural crops for Slovak Republic (2006), the content of mercury in plants used for food production should be lower than 0.05 mg kg^{-1}. Considering the average contents in investigated species at the area, none truly fulfil the norm limits. On the top-area of Veľká Studňa dump-field, there could be observed numerous juvenile spruce trees remarkably affected by growing deformations and chlorosis. As mentioned in the work of Lackovičová (1993), on dump-fields, heaped after a polymetallic-ore mining activity, it is possible to find representatives of *Picea abies*, with unnatural body shape and small and uneven annual increment, however, the mercury cation Hg^{2+} is not primary phytotoxic at normal conditions (Han, et al., 2006).

Considering the high Hg concentrations in plant tissues (Table 2), there can be expected higher content of bioavailable forms in deeper soil horizons, transported to plants by symbiotic mycelium. However, this is also questionable, since the highest Hg content in soils is concentrated also in humus horizon, bound to organic matter (Hlodák, 2015; Hygueraz, et al., 2003). Since there was not investigated Hg bound to soil organic matter and regarding the high Hg concentrations in plant tissues, there can be assumed that bioavailable contents are present in this form. The interesting, but possible pathway of mercury (in the form of elemental Hg^0) could be the uptake through transpiration system in above-ground plant parts (Lindberg, et al., 1979). High concentrations of mercury in wild mushrooms at the investigated area is well described in work of Andráš et al., (2022).

Table 2. The contents of Hg in selected plant species on Veľká Studňa dump-field (The highest values are in bold).

Species	**Site**	**Hg** [mg kg^{-1}]	**Average content of Hg** [mg kg^{-1}]
Calamagrostis epigejos	9	0.033	0.065
	10	**0.154**	
	13	0.008	
Lotus corniculatus	2	**0.487**	0.244
	3	0.214	
	5	0.031	
Leontodon hispidus	4	0.821	1.779
	5	**4.476**	
	6	0.040	
Picea abies	3	1.450	**10.493**
	10	**24.150**	
	12	5.880	

4. CONCLUSIONS

Dump-field Veľká Studňa at Malachov presents a significant source of Hg contamination in the region. Mercury occurs here in the forms, available for the bioaccumulation in plant species, thereby it possibly can enter the biotic parts of the ecosystem. *Picea abies* was identified as the species with the highest bioavailable ability for Hg, what could be also the reason of its physiological anomalies on this site. The further research demands the detailed characterisation of Hg in soil of the dump and its surroundings and should be particularly aimed on the bioavailable forms of this potentially toxic element, that are obviously present in topsoil of the dump field.

Acknowledgement

This work was supported by Slovak National Grant Agency KEGA, No.029UMB-4/2021.

REFERENCES

Andráš, P., Midula, P., Grofčík, J., Drímal, M., Vojtech Dirner, V., Rusko, M., Jana Dadová, J., & Turisová, I., 2022. Mercury accumulation in wild mushrooms at abandoned Hg-deposit Malachov (Slovakia), Carpathian Journal of Earth and Environmental Sciences, February 2022, Vol. 17, No. 1, p. 143 – 147; DOI:10.26471/cjees/2022/017/208.

Banásová, V., Ďurišová, E., Nadubinská, M., Gurinová, E. & Čiamporová, M., 2012. *Natural vegetation, metal accumulation and tolerance in plants growing on heavy metal rich soil.* Bio-Geo interactions in metal-contaminated soils. ISBN 978-3-642-23326-5. 233-250.

Dadová, J., Andráš, P., Kupka, J. Krnáč, J., Andráš, P. Jr., Hroncová, E. & Midula, P., 2016. *Mercury contamination from historical mining territory at Malachov Hg-deposit (Central Slovakia).* Environmental Science and Pollution Research, 23, 2914–2927. DOI: https://doi.org/10.1007/s11356-015-5527-y.

DalCorso, G. 2012. *Heavy Metal Toxicity in Plants*. Plants and Heavy Metals. London: Springer, p. 1 – 26.

Decree No. 508/2004 (In Slovakian law): Use and protection of agriculture soil, Ministry of Agriculture and Rural Development of Slovak Republic.

Decree No. 18558/2006-SL., 2006. (In Slovakian Law): Food codex of Slovak Republic regulating the limits of contaminants in food production.

Han, F. X., Su, Y., Monts, D. L, Wagonner, Ch. A., & Plodinec, M. J., 2006. *Binding, distribution, and plant uptake of mercury in a soil from Oak Ridge, Tennessee, USA*. Science of Total Environment, 368, 753-768. DOI: 10.1016/j.scitotenv.2006.02.026.

Hlodák, M., 2015. *Hodnotenie procesov imobilizácie a transformácie ortuti v systéme pôda-rastliny-mikroskopické vláknité huby*. Bratislava: Commenius University.

Hygueraz, P., Oyarzun, R., Biester, H., Lillo, J. & Lorenzo, S., 2003. *A first insight into mercury distribution and speciation in soils from the Almadén mining district, Spain*. Journal of Geochemical Exploration, 80, 95-104. DOI: https://doi.org/10.1016/S0375-6742(03)00185-7.

Krachler, M., Mohl, C., Emons, H. & Shotyk, W., 2002. Influence of digestion procedures on the determination of rare earth elements in peat and plant samples by USN-ICP-MS. Journal of Analytical Atomic Spectrometry, 17(8), 844-851.

Lackovičová, A., 1993. *Rastliny – bioindikátory znečistenia životného prostredia.* Ústredné metodické centrum Ministerstva školstva a vedy SR.

Lindberg, S. E., Jackson, D. R., Huckabee, J. W., Janze, S. A., Levin, M. J. & Lund, J. R., 1979. *Atmospheric emission and plant uptake of mercury from agricultural soils near the Almadén mercury mine*. Journal of Environmental Quallity, 8, 572-578. DOI: https://doi.org/10.2134/jeq1979.00472425000800040026x.

Maťová, V., Fekete, L., Helma, J. & Ferenc, Š., 2008. *Záverečná správa: Komplexné zhodnotenie zatvoreného ložiska Malachov – Veľká Studňa.* Bratislava: Štátny geologický ústav Dionýza Štúra.

Sobek, A. A., Schuller, A. W., Freeman, R. J. & Smith, M. R., 1978. *Field and laboratory methods applicable to overburdens and minesoils*. Environmental protection technology series.

Steinnes, E., 2013. Mercury. Heavy Metals in Soils: trace Metals and Metalloids in Soils and their Bioavailability., p. 411 – 428.

Received at: 31. 01. 2023
Revised at: 16. 02. 2023
Accepted for publication at: 19. 02. 2023
Published online at: 21. 02. 2023