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ASSESSMENT OF THE POTENTIAL RISK ELEMENTS AT METAL POST-MINING SPOIL HEAPS

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Abstract Motivation/Background: Metallic minerals mining and smelting are connected with the environment degradation, including spoil heaps arising. Even after processing, spoil still contains high levels of the metals, metalloids as well as other potential risk elements and became a potential source of air, water and soil metalliferous contamination for dozens of years. Eastern Slovakia is well known for its mining history and presence of old mining excavation, yet the spoil heaps represent almost the third of them.

Method: We surveyed potential risk elements, including metals and metalloids in the substratum from overall nine spoil heaps (study sites) within the metal post-mining areas of Krompachy (KR) and Zlatá Baňa (ZB), located in Eastern Slovakia. The paper deals with characterization of substratum metalliferous contamination, with lay emphasis on the environmentally most relevant pollutants.

Results: At all study sites, iron and aluminium were in the highest content, at both localities, Fe exceeded permissible limits and background values almost 43-times. Overloading of permissible limits as well as background levels of arsenic, cadmium, lead and mercury was noticed too. Clustering indicates the identical origin of risk elements, since iron and aluminium are supposed to be purely lithogenic and the rest of them are in increased concentrations as a consequence of mining activities.

Conclusions: On the basis of results obtained, both of the areas could be characterized as highly polluted by environmentally relevant elements including arsenic, cadmium, copper, lead and especially mercury, i.e. heavy metals and metalloids found to be highly toxic even at low concentrations.

Keywords: heavy metals, mining activities, pollution

INTRODUCTION

Areas of Krompachy (KR) and Zlatá Baňa (ZB), located in Eastern Slovakia, are both well-known for their mining history. Intensive gold, silver, copper and also iron mining with consequential smelting activities started at the 13th century in Krompachy. At the 16th century, gold, antimony and colored metals mining started at Zlatá Baňa area, which is also well-known for the largest and the oldest opal deposits in the Europe. Although mining and smelting activities are significantly limited nowadays at both of localities, huge amounts of waste from the excavating related activities are presently deposited in a form of spoil-heaps. Spoil heaps are found to be environmental loads due to being potential source of water, air and soil contamination with potentially risk elements including heavy metals and metalloids. Negative consequences for local ecosystems persist for dozens of years, even after the cessation of mining operations. Yet, the spoil heaps represent almost the third from the 17.000 old

mining excavations which could be found in Slovakia [1], [2], [3]. Metals are of the natural origin and several of them are found to be biologically essential components. But, if their levels increase after anthropogenic activities, wide spectrum of negative impacts are observed: heavy metals affect fauna behaviour, physiology or morphology; metalliferous pollution inhibits plants growth, cause chlorosis and plant death, decelerate photosynthesis, biomass production and nutrient assimilation; change quantity and species spectrum composition of affected flora and fauna; soil enzymatic production and activity are negatively correlated with heavy metal pollution too. Different flora and fauna groups are differently tolerable to metalliferous pollution. Humans intoxication is manifested by a wide range of carcinogenic, teratogenic or mutagenic diseases [4], [5], [6], [7], [8], [9], [10]. Just the communities within metal post-mining spoil heaps and in the surrounding environment are chronically exposed to potentially lethal dozens of environmental hazardous elements including heavy metals and metalloids. Thus, regular monitoring of risk elements sources is essential.

MATERIALS AND METHODS

Potential risk elements, including metals and metalloids were determined in the substratum from overall nine spoil heaps i.e., study sites: four spoil heaps were situated within the metal post-mining areas of Krompachy and five spoil heaps situated within Zlatá Baňa. Heaps are under different stages of vegetation succession, uncovered, with the dominance of bare-naked substratum and the occurrence of sparse trees as *Betula pendula* L. and mosses.



Figure (1): Spoil heaps at Krompachy and Zlatá Baňa study areas

A mixed substratum sample was taken once at every study site. The sample consisted of three sub-samples, randomly taken within the sampling plot of approximately 15 x 15 meters, located as near as possible to the centre of spoil heaps and from the depth of 5-15 cm [11]. Following elements were determined using Agilent ICP-OES spectrometer: aluminium (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb) and zinc (Zn) in mg/kg. Prior to analysis, substratum was mineralized using microwave digestion Mars Xpress 5 in a mixture of 5 mL 67% HNO₃ and 5 mL deionized water. The mineralized solution was filtered and subsequently filled up with deionized water. Determined contents of potential risk elements were compared to permissible limits [12], [13] and background values [14], [15]. Contents of potential risk elements in substratum were used to determine:

(1.) Cd-degree of contamination indicating (a) low ($Cd < 8$); b) moderate ($8 < Cd < 16$); c) considerable ($16 < Cd < 32$) and d) very high ($Cd > 32$) degree of contamination; (2.) Cf-contamination factor indicating (a) low ($Cf < 1$); b) moderate ($1 < Cf < 3$); c) considerable ($3 < Cf < 6$) and d) very high ($Cf > 6$) contamination [34]; (3.) GeoI – Geo-accumulation index indicating (a) unpolluted area ($GeoI \leq 0$); (b) unpolluted/moderately polluted area ($0 < GeoI \leq 1$); moderately polluted area ($1 < GeoI \leq 2$); moderately/heavily polluted area ($2 < GeoI \leq 3$); heavily/extremely polluted area ($3 < GeoI \leq 4$); extremely polluted area ($4 < GeoI \leq 5$) (4.) PLI - Pollution load index indicating (a) no pollution ($PLI < 1$), b) moderate pollution ($1 < PLI < 2$), c) heavy pollution ($2 < PLI < 3$) and d) extreme pollution ($PLI > 3$) [16], [17], [18], [19], [20].

Mentioned factors were not proposed for the Ag and Mo because of missing background values and for Sb and Se because of the zero values at some of the sites. Mean values of the potential risk element's contents of the entire study area of Krompachy and Zlatá Baňa were determined using univariate statistic, potential risk elements were clustering used Ward's method and mutually correlated using Spearman's correlation analysis in the PAST [21].

RESULTS AND DISCUSSION

At every from spoil heaps in Krompachy as well as in Zlatá Baňa included in the study, the highest content of iron was noticed from the elements determined in the substratum (Table 1, Figure 2).

Table 1: Permissible limit levels (PL) in mg/kg and background values (BV) in mg/kg of potential risk elements used within study and determined contents (mg/kg) of selected elements in the substratum from four spoil heaps were situated within the metal post-mining areas of Krompachy (KR 1-4) and five spoil heaps situated within Zlatá Baňa (ZB 1-5).

Table 1: Permissible limit levels (PL) in mg/kg and background values (BV) in mg/kg of potential risk elements

	PL	BV	KR-1	KR-2	KR-3	KR-4	ZB-1	ZB-2	ZB-3	ZB-4	ZB-5
Al	10	900	7 992	7 321	6 701	8 215	10 870	11 798	9 968	7 888	9 053
As	30	7	17.74	351.8	96.41	55.34	9.916	75.90	74.30	70.88	280.1
C	1	0.3	2.130	4.149	2.929	1.506	2.662	2.183	3.138	3.277	1.455
Co	15	25	9.029	12.39	13.12	5.227	3.694	1.775	2.162	6.102	0.371
Cr	60	10	12.78	9.418	17.81	11.58	47.36	64.54	11.08	4.541	5.864
C	50	25	15.30	3123	688.7	105.6	18.66	18.40	20.12	15.03	18.74
Fe	550	550	20 422	35 517	26 627	11 915	25 969	21 787	28 996	26 696	13 784
H	0.5	0.0	434.8	36.65	1.611	0.742	1.278	24.69	0.356	1.369	14.55
M	488	530	392.2	1268	915.0	329.1	79.32	41.99	38.69	383.7	48.07
Ni	50	25	19.14	39.64	15.19	10.85	5.017	1.645	2.074	3.216	0.353
Pb	70	25	1.726	11.96	21.61	51.25	11.51	10.04	9.586	70.66	513.5
Sb	1	0.6	0	3.769	0.947	0	2.568	1.653	1.942	0.628	2.047
Zn	150	70	26.66	110.3	92.13	106.3	26.21	18.54	20.39	107.3	70.41

In general, mean values of Fe for both entire localities exceeded permissible limits and background values almost 43-times. Aluminum was the second highest represented element at every from the spoil heaps studied. Provided elements clustering showed the individual position of Fe and Al in comparison to the rest of monitored potential risk elements. We suppose that detected potential risk elements became from identical source; however, iron and aluminum are purely lithogenic, till the increased concentrations of the rest of them are conditioned by mining activities.

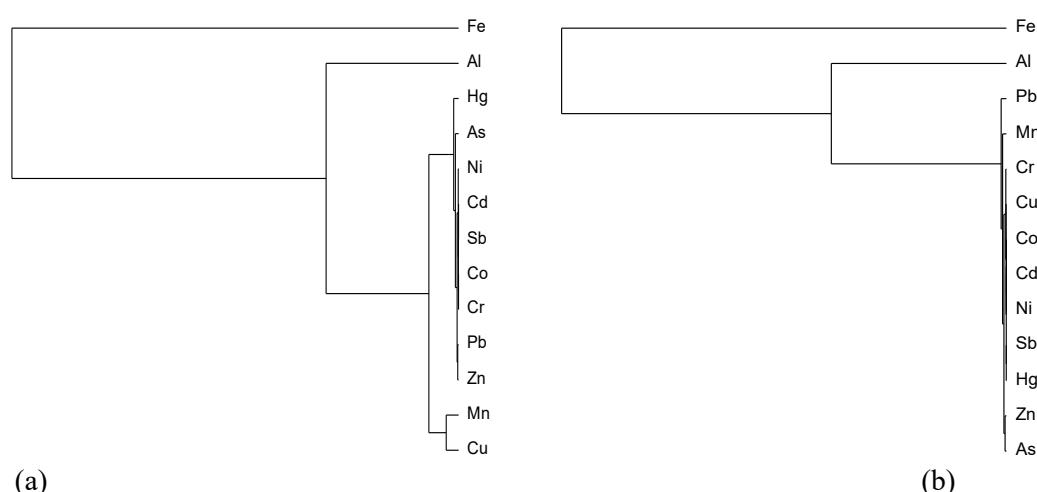


Figure 2: Dendrogram of monitored elements at Krompachy (a) and Zlatá Baňa (b) study areas based of their contents in substratum, provided using clustering, Ward's method in the PAST [17].

Concerning As, Cd, Cu, Hg and Pb elements, which are found to be environmentally relevant, the most risk and highly toxic even at low concentrations [22], arsenic limit level was exceeded with the

exception of KR1 and ZB1 at every from the spoil heaps and, As background limit even every time. The most expressive it concerned KR2 and ZB5 spoil heaps when content of arsenic was higher than the permissible limit level more than 11 and 9 times consequently. Previous studies [1], [14], which reported arsenic environmental pollution of the Central Spiš area, relate it not only to the anthropogenic impact but also to the geochemical effects of the mineralized zones.

Cadmium content exceeded permissible as well as background at every sample from spoil heaps studied, the most expressive at KR2. At the same study site equally content of copper was more than 62 times as high as permissible limit. High content of Cu was also observed on the other from spoil heaps in Krompachy, KR3 and KR4, in spite of their mutual distance. Taken into account evaluating factors, entire post mining area of Krompachy could be found as considerable polluted by copper, or as hotspot of copper contamination [23], [24], (Table 2)..

Table 2: Values of Cd-degree of contamination, Cf-contamination factor, Geo-accumulation index and PLI - Pollution load index for the separate spoil heaps and entire study area of Krompachy.

	Cf				GeoI				Cd
	KR-1	KR-2	KR-3	KR-4	KR-1	KR-2	KR-3	KR-4	
Al	8.879	8.135	7.446	9.128	2.566	2.439	2.311	2.605	33.59
As	2.534	50.26	13.77	7.906	0.756	5.067	3.199	2.398	74.47
Cd	7.101	13.83	9.763	5.020	2.243	3.205	2.702	1.743	35.72
Co	0.362	0.496	0.525	0.209	-2.054	-1.598	-1.515	-2.843	1.591
Cr	1.278	0.942	1.781	1.158	-0.231	-0.672	0.248	-0.373	5.159
Cu	0.612	124.9	27.55	4.224	-1.293	6.379	4.199	1.494	157.3
Fe	37.13	64.58	48.42	21.67	4.630	5.428	5.012	3.852	171.8
Hg	5435	458.2	20.13	9.273	11.82	8.255	3.746	2.628	473.8
Mn	0.740	2.392	1.726	0.621	-1.019	0.673	0.203	-1.272	5.479
Ni	0.765	1.586	0.608	0.434	-0.970	0.081	-1.303	-1.789	3.393
Pb	0.069	0.478	0.864	2.052	-4.442	-1.649	-0.795	0.451	3.462
Sb	-	-	-	-	-	-	-	-	-
Zn	0.381	1.576	1.316	1.519	-1.978	0.071	-0.189	0.018	4.792
PLI	4.097	2.742	1.752	2.609					

Concerning lead, permissible and background limits overload were noticed only at ZB5 sites, with the more than 7-times higher value. We noticed exceptionally high mercury content: with the exception of ZB3 spoil heap, permissible limit was exceeded at every from the study sites. It could be supposed, that increased contents of Pb is connected with the solid waste from the copper production [25].

We also noticed exceeded permissible limits and background values by manganese, antimony, selenium and chromium (Table 3).

Table 3: Values of Cd-degree of contamination, Cf-contamination factor, Geo-accumulation index and PLI - Pollution load index for the separate spoil heaps and entire study area of Zlatá Baňa.

	Cf					GeoI					Cd
	ZB-1	ZB-2	ZB-3	ZB-4	ZB-5	ZB-1	ZB-2	ZB-3	ZB-4	ZB-5	
Al	12.08	13.12	11.08	8.765	10.06	3.010	3.128	-14.69	-9.901	2.746	55.09
As	1.417	10.84	10.62	10.13	40.01	-0.083	2.854	9.891	9.553	4.737	73.01
Cd	8.873	7.277	10.46	10.924	4.851	2.565	2.278	7.236	7.853	1.693	42.38
Co	0.148	0.071	0.086	0.244	0.015	-3.344	-4.401	-3.579	-3.516	-6.659	0.564
Cr	4.736	6.454	1.108	0.454	0.586	1.659	2.105	-2.795	-1.298	-1.355	13.34
Cu	0.747	0.736	0.805	0.601	0.750	-1.007	-1.027	-1.759	-3.046	-1.001	3.638
Fe	47.22	39.61	52.72	48.537	25.06	4.976	4.723	-5.358	-5.778	4.062	213.1
Hg	15.97	308.7	4.456	17.112	181.91	3.413	7.686	1.571	3.512	6.922	198.1

Mn	0.150	0.079	0.073	0.724	0.091	-3.325	-4.243	-7.374	-6.471	-4.048	1.117
Ni	0.201	0.066	0.083	0.129	0.014	-2.902	-4.511	-4.407	-4.849	-6.731	0.492
Pb	0.460	0.402	0.383	2.826	20.54	-1.704	-1.902	-4.177	-3.544	3.775	24.61
Sb	4.280	2.755	3.236	1.047	3.411	1.513	0.877	3.413	6.295	1.185	14.73
Zn	0.374	0.265	0.291	1.533	1.006	-2.002	-2.502	-2.455	-1.301	-0.577	3.47
PLI	1.389	1.457	1.014	1.679	1.386						

No significant correlations were observed between the elements at Krompachy area, at Zlatá Baňa, several correlations were observed as indicated in Table 4.

Table 4: Mutual correlations between elements in Zlatá Baňa detected using Spearman's Rs correlation test in PAST.

	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Zn
Al	0												
As	0	0											
Cd	-0.4	-0.7	0										
Co	-0.3	-0.9*	0.9*	0									
Cr	1*	0	-0.4	-0.3	0								
Cu	0.1	0.3	-0.3	-0.5	0.1	0							
Fe	-0.2	-0.6	0.9*	0.7	-0.2	0.1	0						
Hg	0.2	0.6	-0.6	-0.5	0.2	-0.5	-0.8	0					
Mn	-0.5	-0.5	0.3	0.6	-0.5	-0.7	-0.1	0.1	0				
Ni	0	-1*	0.7	0.9*	0	-0.3	0.6	-0.6	0.5	0			
Pb	-0.6	0.2	-0.3	-0.1	-0.6	-0.3	-0.6	0.4	0.7	-0.2	0		
Sb	0.3	-0.1	-0.5	-0.3	0.3	0.6	-0.3	-0.3	-0.1	0.1	0.1	0	
Zn	-0.9*	-0.2	0.3	0.4	-0.9*	-0.3	0	-0.1	0.8	0.2	0.8	-0.1	0

CONCLUSIONS AND RECOMMENDATIONS

In spite of the significant limitation of smelting activities in the study areas of Krompachy and Zlatá Baňa post metal-mining spoil heaps remain a strong source of the environmental contamination with potential risk elements, including heavy metals and metalloids, which, as non-biodegradable, remain accumulated in the substratum for years [26], [27]. Especially it concerns environmentally the most risk, highly toxic As, Cd, Cu, Hg and Pb elements, which contents exceeded permissible limits several times. Spoil heaps as the contamination sources are very, *spatially*, variable – different content of the same element at different spoil heaps in spite of the localisation within the same study area and low mutual distance; as well as, *time*, variable, as the element's contents are changing during the time [2]. As the risk elements could be spread to the surrounding environment [4] and recultivation and remediation are technically demanding, it seems important to avoid erosion of the spoil-heaps body by f.e. timber harvesting in the vicinity as much as possible.

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REFERENCES

- [1] Hronec, O., Vilček, J., Tóth, T., et al. Heavy metals in soils and plants of contaminated area Rudnany-Gelnica. Acta regionalia et environmentalica. 2008; 1: 24-28.

- [2] Demková, L., Jezný, T., Bobuľská, L. Assessment of soil heavy metal pollution in a former mining area – before and after the end of mining activities. *Soil and Water Research*. 2017; 12: 229-236.
- [3] Gabrielvan, A.V., Shahnazaryan, G., Minasyan, S. Distribution and identification of sources of heavy metals in the Voghji river basin impacted by mining activities (Armenia). *Journal of Chemistry*. 2018; Article ID 7172426:1-9.
- [4] Demková, L., Árvay, J., Bobuľská, L., et al. Accumulation and environmental risk assessment of heavy metals in soil and plants of four different ecosystems in a former polymetallic ores mining and smelting area (Slovakia). *Journal of Environmental Science and Health, Part A*, 2017; 52(5): 479-490.
- [5] Tovar-Sánchez, E., Hernandez-Plata, I., Santoyo-Martinez, M., Valencia-Cuevas, L., Mussali Galante, P. Heavy metal pollution as a biodiversity threat. Chapters, in: Hosam El-Din M. Saleh & Refaat Fekry Eid Sayed Aglan (ed.), *Heavy Metals*, IntechOpen. (2018)
- [6] Ali, H., Khan, E., Ilahi, I. Environmental chemistry and ecotoxicology of hazardous heavy metals: environmental persistence, toxicity, and bioaccumulation. *Journal of Chemistry*. 2019; 6730305.
- [7] Demková, L., Árvay, J., Bobuľská, L., et al. Open mining pits and heaps of waste material as the source of undesirable substances: biomonitoring of air and soil pollution in former mining area (Dubník, Slovakia). *Environmental Science and Pollution Research*. 2019; 26: 35227–35239.
- [8] Banášová, V., Pišút, I., Lintnerová, O. Remarks to the specific vegetation of smelter wastes near village Smolník (Slovenské rudohorie Mts., E. Slovakia). *Bulletin of Slovak Botanical Society*. 2003; 25: 135-141.
- [9] Borymski, S., Cycón, M., Beckmann, M., Mur, L.A.J., Piotrowska-Seget, Z. Plant species and heavy metals affect biodiversity of microbial communities associated with metal-tolerant plants in metalliferous soils. *Frontiers in Microbiology*. 2018; 9: 1425.
- [10] Angelovičová, L., Lodenius, M., Tulisalo, E., Fazekašová, D. Effect of heavy metals on soil enzyme activity at different field conditions in middle Spiš mining area (Slovakia). *Bulletin of Environmental Contamination and Toxicology*. 2014; 93: 670–675.
- [11] Fiala, K., et al. *Partial Monitoring System-Soil: Mandatory Statutes*, first ed. SSCRI, Bratislava 1999; 138 p.
- [12] Act No 188/2003 Coll. On application of sewage sludge and bottom sediment into the soil and amendments to Act No 223/2001 Coll.
- [13] Balentine, BL. Permissible limits for metals. Direction of Everett Wilson and revised by: Everett Wilson and Carl Solomon. 7/95 <https://www.occeweb.com/og/metals-limits.pdf> 1995
- [14] Čurlík, J., Šefčík, P., Jambor, P. *Geochemical atlas of the Slovak Republic. Part V: Soils*. Bratislava: Ministry of the Environment. 1999.
- [15] Kabata-Pendias, A. *Trace Elements in Soils and Plants*. New York: CRC Press Taylor & Francis Group. 2011.
- [16] Müller, G. Index of geoaccumulation in sediments of the Rhine River. *The Journal of Geology* 1969; 2:108–118
- [17] Hakanson, L. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research*. 1980; 14(8): 975–1001.
- [18] Tomlinson, D.L., Wilson, J.G., Harris, C.R. & Jeffrey, D.W. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgolander Meeresunters* 1980; 33: 566–575.
- [19] Hashmi, M.Z., Yu, C., Shen, H., et al. Risk assessment of heavy metals pollution in agricultural soils of siling reservoir watershed in Zhejiang Province, China. *BioMed Research International*. 2013; Article ID590306:103–113.
- [20] Loska, K., Wiechuła, D., Korus, I. Metal contamination of farming soils affected by industry. *Environment International*. 2013; 30:159–165.
- [21] Hammer, O., Harper, D.A.T. & Ryan, P.D. PAST: palaeontological statistics software package for education and data analysis, PAST version 2.17c. *Palaeontologica Electronica*. 2001; 4: 9.

- [22] Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K. & Sutton, D.J. Heavy metal toxicity and the environment. In: Luch A. (eds) *Molecular, clinical and environmental toxicology*. Experientia Supplementum. 2012; 101. Springer, Basel
- [23] Lastincová, J., Pospíšilová, L., Matuskova, L., Kaderova, E., Beinrohr E. Determination of total contents of Cd, Pb, Cr, Ni, As, Cu, Zn, Co, V, Mo in some Slovak soils. *Chemical Papers*. 2003; 57: 131–135.
- [24] Wilcke, W., Krauss, M., Kobza, J., Zech, W. Quantification of anthropogenic lead in Slovak forest and arable soils along a deposition gradient with stable lead isotope ratios, *Journal of Plant Nutrition and Soil Science*. 2001; 164: 303–307.
- [25] Michaeli, E., Boltžiar, M. Selected localities of environmental loads in environmentally loaded areas in Slovakia. *Geographica Studies*. 2010; 52: 638–643.
- [26] Merhabi, B., Mehrabani, S., Rafiei, B., Yaghoubi, B. Assessment of metal contamination in groundwater and soils in the Ahangaran mining district, west of Iran. *Environmental Monitoring and Assessment*. 2015; 187: 727–750.
- [27] Mirzaei, R., Teymourzade, S., Sakizadeh, M., Ghorbani, H. Comparative study of heavy metals concentrations in topsoils of urban green space and agricultural land uses. *Environmental Monitoring and Assessment*. 2015; 187: 741–753.