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Biomonitoring of heavy metals contamination by mosses and lichens around Slovinky tailing pond (Slovakia)

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ABSTRACT

Three moss (*Pleurozium* spp., *Polytrichum* spp., and *Rhytidiadelphus* spp.) and two lichen (*Hypogymnia physodes* and *Pseudevernia furfuracea*) taxons covered in the bags were used to monitor air quality. Bags were exposed at the different distances from the tailing pond because of insufficient security and source of heavy metal pollution. Moss/lichen bags were exposed for six weeks at 0-, 50-, 100-, 150- and 200-m distances from Slovinky tailing pond, in the main wind direction (down the valley). Accumulation ability of heavy metals expressed by relative accumulation factor (RAF) increases in the order of *Polytrichum* spp.< *H. physodes* <*Pleurozium* spp.<*P. furfuracea* <*Rhytidiadelphus* spp. Moss/lichen species showed different accumulation capacity for individual heavy metals. *Rhytidiadelphus* spp. was found to possess the significantly highest ($P < 0.01$) ability to accumulate Cd, Zn, Ni, Mn and Fe. The highest RAF values of Pb, Zn, Ni and Fe were determined in samples exposed at 200-m distance from pollution source.

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Introduction

Among human activities, mining is responsible for soil, water and air contamination in huge areas of the globe.[1,2] The mining impact on the environment varies greatly, depending on the methods used for material extraction, the adequate pollution control, the waste management and proper reclamation.[3] Mining bodies, which remain unchanged years after the mining closure, disrupt the landscape structure and became the source of undesirable substances.[4] The presence of tailing ponds, heaps of waste material and open mines as the sources of high concentrations of heavy metals, represent serious environmental problems.[5] The surface of tailing ponds, consisting of small particles, can be eroded by wind and transported to long distances.[6,7] Metals volatilized into the air can be carried into the land surface via precipitation and dry fallout. Spreading the toxic substances by air can affect the large areas, contaminate other environmental components and affect the health of humans.[8]

Traditional air pollution monitoring techniques include automatic sampling stations and biomonitoring, i.e., the use of organisms and biomaterials to obtain quantitative information on the quality of the environment.[9]

At present, the most widely used atmosphere pollution bioindicators in the world are mosses and lichens.[10] In few studies,[11] this method has also been used to investigate water pollution. Mosses and lichens were found as suitable bioindicators of atmospheric pollutions because they retain and accumulate a portion of the elements that reach them via atmospheric deposition. In addition, as they do not have a root system, there is a small possibility of contamination through this way.[12]

Moss and lichen bag technique, introduced by Goodman and Roberts,[13] represents a simple and cost-effective alternative to monitor air quality,[14] especially in the places, where the presence of native moss is limited or absent.[15] The method has been developed over the last decades for monitoring hazardous pollutants such as heavy metals.[16,17] Moss and lichen bag technique has been used to determine the extent of environmental pollution in several regions [18,19] and has been used to estimate the environmental concentrations [20] of contaminants.

The aims of the study were to: (1) assess spreading of toxic elements from tailing pond towards the valley using moss and lichen bag techniques; (2) determine the level of accumulation of heavy metals at different distances from the tailing pond, and (3) compare the ability of different moss and lichen species to accumulate heavy metals.

Materials and methods

Study area

The study was performed in the Slovinky village, which, as part of the former mining middle Spiš area, is well known since the 13th century for intensive mining activities. Slovinky tailing pond [48° 53′ 15.29′′ N; 20° 52′ 09.88′′ E] is

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located in the northeastern part of the Slovinky cadaster (Fig. A1).

With the dam height of 113 m, it is considered the highest located pond in Slovakia. The upper part of the pond is composed of slag material, and in deeper horizons, the flotation sludge from processing of siderite-sulfidic ores was stored. Since 1993, this tailing pond is closed, without any remediation procedures. The upper part of the tailing pond has powder consistency, and small particles are transported by wind in north-west direction (along the valley, which follows the dam),[21] which cause heavy metal pollution to the environment.

Sludge sampling and analysis

Sewage sludge samples were collected from 12 randomly selected places in the surface of the pond at the volume of 0.2 kg. After homogenization, samples were manually crumbled, air dried in the laboratory conditions, sieved through 2-mm sieve and stored in polyethylene bags. Prior to analysis, all samples were well mixed to one representative sample, which was in three replicates used for heavy metal analyses. The total content of heavy metals was determined after mineralization in Aqua regia mixture of 2.5 mL 65% HNO_3 (Suprapur, Merck, Darmstadt, Germany) and 7.5 mL 37% HCl (Suprapur). Mineralization was performed using microwave digestion system Mars Xpress 5 (CEM Corp., Matthews, NC, USA). After mineralization, the digested substance was filtered through filter paper Filtrak 390 (Munktell & Filtrak GmbH, Bärenstein, Germany) and filled up with deionized water to a volume of 100 mL.

Moss and lichen selection and preparation

Two lichen (*Hypogymnia physodes* (L.) and *Pseudevernia furfuracea* (L.)) and three moss (*Pleurozium, Polytrichum*, and *Rhytidiadelphus*) taxon, commonly occurring in Slovakia, were chosen for bag biomonitoring. Lichen and moss samples were obtained in May 2015 in Čergov hills (Slovakia) at a minimum of 500-m distance from main forest road. Samples were transported in paper bags to laboratory, where they were manually separated from the brown tissue, cleaned of soil particles, homogenized, washed three times in deionized water and air-dried in an oven at 120°C for 24 h (Venticell 111, BMT, a.s., Czech Republic). Finally, the bags were vacuum packed and stored at −20°C until exposure.

About 5 g of the moss was packed in 10 × 10 cm nylon net bags with 2-mm mesh size. One part of the moss was stored as background sample (non-exposed). Four bags of each moss/lichen were exposed to the ten sampling points, which were deployed on both the sides of the tailings pond dam, as shown in Figure A1. A total number of 100 samples were exposed for a six-week period in a downward direction to the village, in 0-, 50-, 100-, 150- and 200-m distance from the tailing pond. Bags were tied in trees at a height of 1.5–2.0 m in each sampling site. After six weeks of exposure, samples were collected and stored at −20°C until analyses. After the exposure, the moss and lichen samples were air dried at 40°Cin a hot air oven Venticell 111 (BMT, a.s., Czech Republic) and homogenized using a ceramic mortar.

Heavy metal analysis

Homogenized samples (0.5 g, corrected to four decimal places accuracy) were mineralized in a closed system of microwave digestion using Mars Xpress 5 (CEM Corp.) in a mixture of 5 mL 67% HNO_3 (Suprapur) and 5 mL deionized water (0.054 μS cm^{-1}) from Simplicity 185 (Millipore SAS, Molsheim, France). The mineralized solutions were subsequently filtered through a quantitative filter paper Filtrak No. 390 (Munktell & Filtrak GmbH) and filled up to a volume of 50 mL with deionized water. The content of heavy metals was determined using flame atomic absorption spectrophotometry: F-AAS: Zn, Cr, Ni, Mn and Fe on the SpectrAA 240FS (Varian Inc., Mulgrave, VIC, Australia) and electrothermal atomic absorption spectrophotometry: GF-AAS (Cd and Pb) with Zeeman background correction [22] on the SpectrAA 240Z (Varian Inc.). Detection limits for F-AAS were 0.6, 3.0, 8.0, 3.0 and 5.0 $\mu g\ kg^{-1}$for Zn, Cr, Ni, Mn and Fe, respectively, and GF-AAS: 10.0 and 10.0 ng kg^{-1} for Cd and Pb, respectively.

Data processing and statistical evaluation

To assess the heavy metal accumulation of the studied moss and lichen species, relative accumulation factor (RAF; Equation 1) was calculated by subtracting the moss/lichen content of each element before exposure ($C_{initial}$) from the element content after exposure ($C_{exposed}$) and then by dividing the element content before exposure ($C_{initial}$):

$$\mathrm{RAF} = \left(C_{exposed} - C_{initial}\right)/\,C_{initial} \qquad (1)$$

All statistical operations were performed using R studio.[23] Differences in RAF values for each heavy metal between 5 studied moss/lichen species were tested using ANOVA and Kruskal–Wallis test for normally and non-normally distributed data, respectively. The same differences in RAF values of studied elements between 5 distances from pollution source were noted. Tukey post hoc test was used to detect species with significantly different heavy metal accumulation ability, from the same distance with the highest RAF values. Spearman's correlation analysis was used to determine correlation relationship between different heavy metal RAF values. Spearman's correlation coefficient and ANOVA test were considered statistically significant if *P* values were less than 0.05 and 0.01. Cluster analysis (squared Euclidean distance) was used to identify groups of species with a similar ability to accumulate heavy metals.

Results and discussion

Content of heavy metals in sludge samples

The results of heavy metal analysis of sludge samples from the tailing pond are summarized in Table 1. Content of heavy metals was extremely high and exceeded several times the limit values for hazardous substances in sewage sludge.

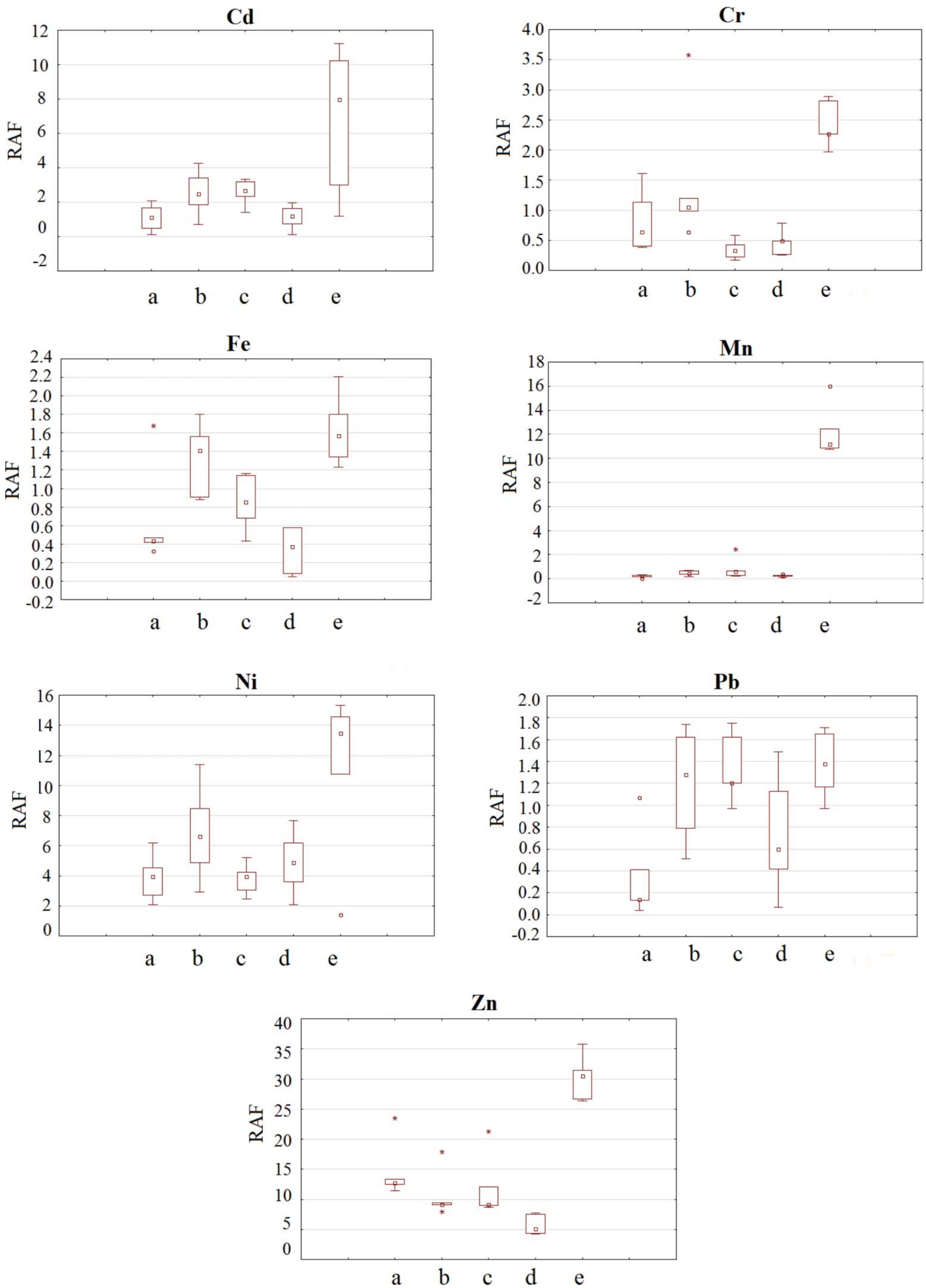

Figure 1. Mean RAF values of heavy metals (measured at different distances) in moss and lichen taxon (a) *H. physodes*, (b) *P. furfuracea*, (c) *Pleurozium* spp., (d) *Polytrichum* spp., (e) *Rhytidiadelphus* spp.; *outlying value, min-max, □ median, [] 25 – 75%, ┬ maximum; ┴ minimum).

Table 1. Mean values of total content of heavy metals (mg kg^{-1}) in sludge samples ($N = 3$) from Slovinky tailing pond.

	Cd	Pb	Zn	Cr	Ni	Mn	Fe
Content in the sludge	1.1	1900	46000	2700	250	720	27
Limit value*	**10**	**750**	**2500**	**1000**	**300**	–	–

*Limit values for hazardous substances in sewage sludge according to Act no.188/2003 Coll. of laws.

Total content of Pb, Zn, and Cr exceeded limit value [24] 2.5, 18 and 2.6 times, respectively. Cadmium slightly exceeds limit value, and the value of iron was below limit. Usually, because of insufficient security and the absence of remediation actions, toxic elements from tailing ponds penetrate into groundwater and contaminate air and surrounded soils by wind transmission.[25,26] Due to their accumulation in environment, they can induce a potential contamination of food chain and endanger the ecosystem safety and human health.

RAF values of evaluated elements in different moss and lichen samples

Mean values of RAF of 7 elements (measured at different distances from pollution source) in three mosses and two lichen species are shown in Figure 1. The concentration of metals in *Hypogymnia* spp. and *Pseudevernia* spp. bags (expressed by RAF) is in the following order: Zn>Ni>Cd>Cr>Fe>Pb>Mn. Salo,[27] who used *H. physodes* for air pollution biomonitoring in Finland, found it as effective accumulator that can be applied to monitor spatial and temporal distribution of pollution effects. Mosses species *Pleurozium* spp. and *Polytrichum* spp. also accumulate heavy metals in the order of Zn>Ni>Cd>Pb; however, best accumulation ability for manganese (after Zn) was found only for *Rhytidiadelphus* spp.

One-way ANOVA (Table 2) test detects whether there are some significant differences between moss/lichen species in accumulation ability of different heavy metals. The significantly highest ($P < 0.01$) ability to accumulate Cd, Zn, Ni, Mn and Fe was found for *Rhytidiadelphus*. The lowest RAF values of Cd and Cr were found for *Polytrichum* spp.

Table 2. One-way ANOVA for the comparison of RAF values of heavy metal between different species and between distances.

RAF	Factor	Df	F value	*P*
Cd	Species	4	5.67	0.003**
Pb		4	4.94	0.006**
Zn		4	24.35	1.91e-07 **
Cr		4	9.809	0.000147 **
Ni		4	4.522	0.00916 **
Mn		4	121.3	1e-13 **
Fe		4	8.265	0.000419 **
Cd	Distance	4	0.867	0.501
Pb		4	2.351	0.089
Zn		4	0.767	0.559
Cr		4	0.87	0.499
Ni		4	1.94	0.143
Mn		4	0.043	0.996
Fe		4	1.645	0.202

**$P < 0.01$.

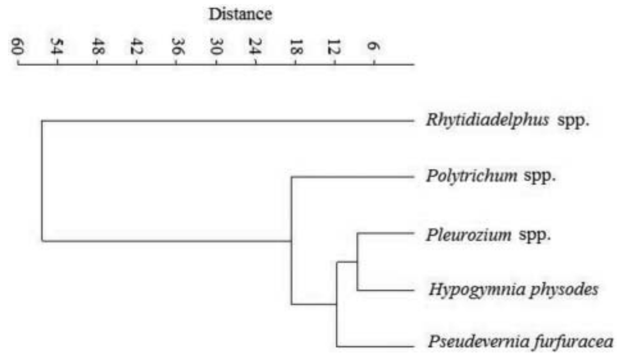

Figure 2. Dendrogram obtained by cluster analysis for RAF values in moss and lichen samples.

($P < 0.05$) and of Zn and Fe for *Hypogymnia* spp. ($P < 0.05$). The highest values of RAF for Pb and Cr were determined in *P. furfuracea* samples, but a significant difference was not confirmed. Tremper et al.[28] compared *Pleurozium schreberi* and *Rhytidiadelphus squarrosus* and found higher concentrations of contaminants(Cu, Pb and Zn) in *P. schreberi*.

According to Spagnuolo et al.,[29] lichens (*P. furfuracea*) exhibited better resistance to environmental stress compared to the moss *Hypnum cupressiforme*; they preserve or recover their vitality during biomonitoring. Giordano et al.,[30] who compared lichen *P. furfuracea* with moss *H. cupressiforme*, have also characterized the lower capacity of lichens to intercept and accumulate the most airborne elements compared with mosses. Moreover, they confirmed better ability to accumulation of heavy metals for *P. furfuracea* during the rainy period.

Comparing accumulation ability of evaluated mosses and lichens regardless the species, no statistical differences were found in heavy metal accumulation. One-way ANOVA test confirmed that only manganese is better accumulated by mosses ($P < 0.05$) than by lichens.

By comparing average RAF values, we can conclude that the ability to accumulate heavy metals increases in the order of *Polytrichum* spp.<*H. physodes*<*Pleurozium* spp.<*P. furfuracea* <*Rhytidiadelphus* spp.

Cluster analysis was used to identify groups of moss/lichen species with similar RAF values. Results are shown in a dendrogram (Fig. 2), where two groups are identified. Group 1 includes only *Rhytidiadelphus* spp., which was characterized by the highest accumulation ability of most of the evaluated metals, which was also confirmed by one-way

Table 3. Correlation relationship between RAF values of heavy metals and between RAF values of heavy metals and the distance from the pollution source.

	Cd	Pb	Zn	Cr	Ni	Mn	Fe
Distance	0.39*	0.54**	0.18	−0.10	0.65**	0.01	0.24
Cd		0.69**	0.42*	0.8	0.62**	0.55**	0.55**
Pb			0.30	0.21	0.61**	0.59**	0.61**
Zn				0.63**	0.33	0.61**	0.69**
Cr					0.31	0.59**	0.71**
Ni						0.36	0.49*
Mn							0.78**

*$P < 0.05$; **$P < 0.01$.

Table 4. Comparison of mean values of RAF (± SD) of heavy metals in moss/lichen species with respect to the distance from pollution source.

		Distance from pollution source [m]				
		0	50	100	150	200
RAF	Cd	1.07 moss 1.07	2.67 ± 2.73	3.80 ± 3.29	4.12 ± 3.62	2.42 ± 1.22
	Pb	0.58 ± 0.45	0.81 ± 0.55	1.02 ± 0.45	1.07 ± 0.54	1.53 ± 0.25
	Zn	13.02 ± 7.43	12.98 ± 9.09	13.68 ± 8.95	12.43 ± 7.52	21.23 ± 9.03
	Cr	1.77 ± 1.28	1.08 ± 0.94	0.87 ± 0.74	0.69 ± 0.66	1.16 ± 0.62
	Ni	2.30 ± 0.61	5.64 ± 4.53	6.65 ± 2.49	7.69 ± 4.13	8.22 ± 4.17
	Mn	3.16 ± 4.74	3.49 ± 6.24	2.64 ± 4.35	2.35 ± 4.19	2.54 ± 4.17
	Fe	0.93 ± 0.63	0.78 ± 0.36	0.98 ± 0.53	0.62 ± 0.40	1.48 ± 0.57

ANOVA results. Group 2 includes all other species, but especially *Pleurozium* spp. and *Hypogymnia* spp. were found as the most similar in terms of their accumulation ability.

Correlation relationship between elements determined in moss/lichen samples

It has been reported [31] that positive correlations among heavy metals suggested a common source for them. Correlation relationships between RAF values of heavy metals are listed in Table 3. Cadmium gave significant positive correlation with all evaluated heavy metals except Mn. Spearman's correlation coefficient at a significance level of $P < 0.01$was also found for the following pairs: Cr-Fe, Cr-Mn, Pb-Fe, Pb-Mn, Pb-Ni, Mn-Fe, Zn-Cr, Zn-Fe, Zn-Mn and at a significance level of $P < 0.05$ only for Ni-Fe. Presence of all mentioned heavy metals in the study area was confirmed by several authors as a remnant of the polymetallic ore mining and processing activities.[32–34]

RAF values of different heavy metals with respect to the distance from pollution source

Wind transport is an important factor influencing the spreading of pollution.[35,36] Moss and lichen bag technique was predominantly used with regard to transport [37] or industrial emissions [38] and their spatial distribution or in relation to the spread of volcanic emissions.[39] In most of the cases investigated, pollutants have a similar spatial distribution pattern over the entire study area.

In the moss/lichen bags exposed at different distances from Slovinky tailing pond, the highest values of RAF for Pb, Zn, Ni and Fe were found in the samples exposed at 200-m distance (Table 4). Han et al.[40] have found that except for the Ba and Co, all the analyzed heavy metals (Cr, Cu, Mn, Ni, Pb, V and Zn) in the dusts were largely accumulated in the smallest particles (<50 μm), which are able to overcome greater distances downwind. However, some studies have shown [41] no significant differences in heavy metal content between different sized particles.

The highest value of cadmium RAF was found in the samples exposed at 150-m distance. In contrast to the other metals, the highest average value of chromium and manganese RAF were found at 0-m distance and 50-m distance, respectively.

One-way ANOVA test confirmed that there are significant differences between distances ($P < 0.05$) in RAF values only for Pb. The results of Tukey post host test confirmed that values of RAF of Pb were significantly different between 0-m and 200-m distance from pollution source.

Conclusion

Moss–lichen bag technique represents a suitable approach to achieve reliable results about heavy metal pollution. Moreover, the method is simple and cost-effective and could be used in locations where the natural occurrence of mosses and lichens is limited or absent.

Analysis of sewage sludge from Slovinky tailing pond has shown extremely high values and values that exceed the limit of all evaluated heavy metals except iron. The highest values of RAF, which were used to assess the heavy metal accumulation, were found for *Rhytidiadelphus* spp., which showed the significant highest ($P < 0.01$) ability to accumulate Cd, Zn, Ni, Mn and Fe. *P. furfuracea* was found as the best accumulator for Pb and Cr. Comparing heavy metal accumulation ability of mosses and lichens, no differences were found except for manganese, which was significantly better ($P < 0.05$) accumulated by mosses.

Distance of the point of exposure of moss/lichen samples from Slovinky tailing pond was also a key factor influencing amount of accumulated heavy metals. The highest values of RAF for Pb, Zn, Ni and Fe were found in the samples exposed in 200-m distance from the tailing pond. The highest values of chromium and manganese RAF were determined in 0- and 50-m distance from pollution source, respectively. These differences may be caused due to the fact that different heavy metals are associated with different sized soil/dust particles.

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Appendix

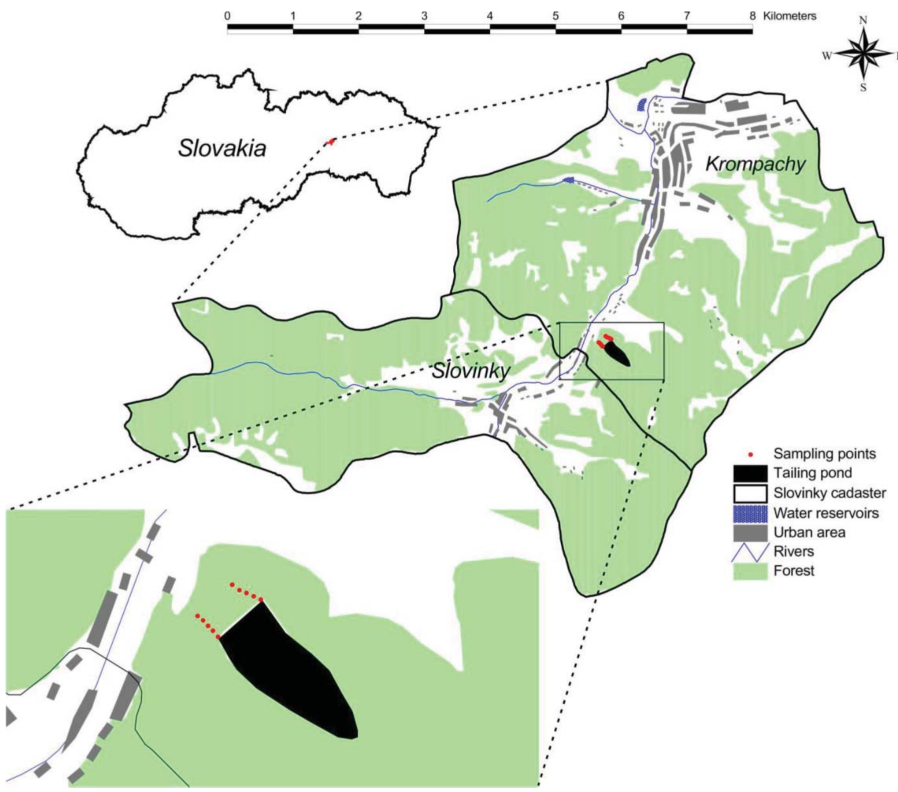

Figure A1. Localization of tailing pond in Slovinky village.