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Original Research

The Soil-to-Herbs Transfer of Heavy Metals in Spruce Ecosystems

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Abstract

The pollution of soils with Pb, Cd, and Hg, and the transfer of these elements into the above-ground organs of 4 dominant herb species was studied in spruce ecosystems situated along the vertical transects Muráň (Skeli-Humic Podzols) and Hliníky (Dystric Cambisols) in the protected zone of Slovenský raj National Park (eastern Slovakia). The maximum amounts of Pb (62-86 $mg \cdot kg^{-1}$ d.m.) and Cd (0.48-1.03 $mg \cdot kg^{-1}$ d.m) found in Ooh horizons of Podzols were substantially lower than the calculated limit values. The concentrations of Hg (1.59-2.09 $mg \cdot kg^{-1}$ d.m) in both soils were very similar, and in comparison with the limit values A1 substantially higher. The concentrations of Pb (1.54-8.05 $mg \cdot kg^{-1}$ d.m) and Cd (0.15-1.92 $mg \cdot kg^{-1}$ d.m), found in *Vaccininium myrtillus*, *Dryopteris dilatata*, *Luzula luzuloides*, and *Rubus idaeus* species were within the toxicity range. Substantially higher as 1 were only transfer coefficients of Cd in the case of *D. dilatata*, *R. idaeus*, and L. *luzuloides* species.

Keywords: spruce ecosystems, acid soils, atmospheric pollution, heavy metals, herb species

Introduction

Global contamination of the environment has resulted in increasing amounts of heavy metals in both the air and soil [1]. Acid atmospheric pollutants damage assimilatory organs of plants, which results in partial loss of their assimilatory surface, disturbance of their physiological conditions, and decrease of their vitality [2]. In the central Spiš region (eastern Slovakia), the highest amounts of pollutants get in atmosphere from the factory chimneys processing wood and mineral raw materials (Rudňany, foundry and metal industry Krompachy, limekiln Margecany). In addition, there are also present local heating systems. The main pollutants are oxides of sulphur (SO_x), nitrogen (NO_x), CO and heavy metals (Zn, Hg, Cu, As, Cd, and Pb).

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The growth of plants is determined by properties of climate and soil, but the plants have also considerable impact on soil [3]. The resistance of different plant species to airborne and soil-accumulated toxic elements is not the same, which is reflected in their growth, survivability, and occurrence along pollution gradients [4]. The higher contents of heavy metals in soil can be backed up by geochemical anomalies or can be the result of air pollution [5-7]. From the aspect of physiology, the amounts of heavy metals accumulated by the plants from the soil, as well as their distribution patterns in the plants, are important [8, 9]. From an ecological point of view, the most dangerous are cadmium, lead, and mercury, because these elements can be accumulated in and damage living organisms [10, 11].

The aim of this paper is to evaluate the extent of soil contamination with some heavy metals and the transferability of these contaminants into above-ground organs of 4 dominant herb species in spruce ecosystems.

Table 1. Ecological characteristics of the studied spruce ecosystems.

Locality	Muráň		Hliníky	
Spruce stand	A – damaged	B – undamaged	C – damaged	D – undamaged
Altitude (m)	1,110	1,080	960	950
Parent rock	polymict conglomerates	violet-grey shist	quartz conglomerates	
Soil subtype	Skeli-Humic Podzol		Dystric Cambisol	
Soil depth [cm]	70	110	90	75
pH_{H_2O}	3.22-4.52	3.52-4.11	3.55-4.49	3.65-4.50
pH_{KCL}	2.53-3.75	2.60-3.57	3.00-4.25	3.07-4.15
C/N in surface humus (%)	40-46	38-50	34-50	37-51
C/N in mineral soil layers (%)	12-20	10-39	10-17	9-17

Materials and Methods

The research was realized in 4 spruce geobiocoenoses situated along a vertical transect crossing the localities Muráň (48º52'N, 20º28'E, Skeli-Humic Podzols, *Fageta abietino-piceosa*) and Hliníky (48º51'N, 20º31'E, Dystric Cambisols, *Abieti-Fageta inferiora*) in the buffer zone of Slovenský raj National Park [12]. The locations are situated in the cool climatic region, with the mean temperature in July 12-16ºC. The mean annual temperature is 4-5ºC, and average annual precipitation reaches 700-800 mm [13]. The other ecological characteristics are presented in Table 1.

The soils were classified according to World Reference Base for Soil Resources 1994 [14], the forest geobiocoenoses were determined according to Zlatník [15] and the names of plant taxa were given according to Dostál [16].

Soil samples taken from surface humus and mineral soil layers were air dried and sieved through a sieve with a mesh size of 2 x 2 mm. The contents of Pb and Cd in soil samples were determined in extract of 2M HNO_3 (proportion of soil to 2M HNO_3 1:10 w/v) by electrothermal atomization atomic absorption spectroscopy (ETA-AAS) using Varian Spectr. AA 300/400. The highest allowable values of risk elements (A1) for standard soil (25% of clay fraction, 10% of organic matter) given in the Decision of the Ministry of Agriculture of the Slovak Republic [17] (Pb 30.0, Cd 0.3, and Hg 0.3 $mg \cdot kg^{-1}$) have been re-calculated according to the actual parameters of the soils we studied.

The herb material was obtained by random sampling from an area of 400 m^2. There were collected green twigs or shoots growing out from creeping stems of *Vaccinium myrtillus* L. and *Rubus idaeus* L. species, leaves growing out from polycormon of *Dryopteris dilatata* (Hoffm.) A. Gray species and shoots of *Luzula luzuloides* (Lam.) Dandy et Willm species. All plant samples were dried at 80ºC for 48 hours and homogenized with a Fritsch planetary micro mill (<0.001 mm). The contents of Pb and Cd were determined after microwave mineralization of non-washed herb samples in concentrated HNO_3 by inductively coupled plasma-atomic emission spectrometry (AES-ICP) using a LECO 3000. The amounts of Hg in soil and plant samples were determined in solid samples with LECO AMA 254 Advanced Mercury Analyzer.

The transfer coefficients were calculated as a ratio of metal concentration in the herb to the concentration of the same metal in the soil, as follows:

$$TC = \frac{\text{content of heavy metal in plant } (mg \cdot kg^{-1})}{\text{content of heavy metal in soil } (mg \cdot kg^{-1})}$$

The differences in mean transfer coefficients of risk elements among spruce plots and herb species were tested by Kruskal-Wallis analysis (Statistica 7).

Results and Discussion

The contents of heavy metals found in the soil samples are presented in Figs. 1-3. Maximum of lead was found in the Ooh surface humus horizons of Podzols (62-86 $mg \cdot kg^{-1}$ d.m.) and in Ool and Oof surface humus horizons of Cambisols (16-60 $mg \cdot kg^{-1}$ d.m.). In mineral layers of both soil types the amounts of lead were mildly decreasing from topsoil (17-23 $mg \cdot kg^{-1}$ d.m. in Podzols; 37-41 $mg \cdot kg^{-1}$ d.m. in Cambisols) toward subsoil (4-6 $mg \cdot kg^{-1}$ d.m. in Podzols; 0.7-1.6 $mg \cdot kg^{-1}$ d.m. in Cambisols). They were relatively low and represented 1-66% from the maximum amounts of Pb detected in Ooh soil horizons.

The limit values A1 [17] calculated for Pb reached 150 $mg \cdot kg^{-1}$ d.m. in surface humus and 54-65 $mg \cdot kg^{-1}$ d.m. in mineral soil layers. The contents of lead found in studied soils were substantially lower and reached from 41-47% (in surface humus) to 1-76% (in mineral layers).

The contents of cadmium found in surface humus of the studied soils ranged between 0.3-1.0 $mg \cdot kg^{-1}$ d.m., and they were somewhat higher in Podzols increasing from Ool horizons of surface humus to A horizons. The contents of Cd in mineral layers were lower, usually below 0.12 $mg \cdot kg^{-1}$ d.m. In comparison with the limit values A1 (2.5 mg Cd kg^{-1} d.m. in surface humus and 0.4-0.7 mg Cd kg^{-1} d.m. in mineral layers) the amounts of Cd found in studied soils represented usually less than 20%, exceptionally 58% (in A horizon of Podzol on spruce plot A). In soils of uncontaminated areas of eastern Poland Królak [18] found 0.15 mg Cd kg^{-1} d.m., while in the samples collected in contaminated areas of Upper Silesia up to 5.1 mg Cd kg^{-1} d.m. Bowen [19] considers as natural the values between 0.01-2.0 mg Cd kg^{-1} d.m.

Mercury belongs to very dangerous toxic elements. Common range of this element in soils ranges between 0.01-0.5 mg Hg·kg^{-1} d.m. [19]. The mean amounts of Hg (0.71-0.89 mg·kg^{-1} d.m.) found in studied soils exceeded the limit values A1 (0.21-0.23 mg Hg kg^{-1} d.m.), but the critical values (0.3-5.0 mg Hg kg^{-1}) stated by Kabata-Pendias and Pendias [20] were not exceeded.

Lead and cadmium can be moderately or medium toxic for plants [21]. General symptoms of Cd toxicity are leaf chlorosis, leaf and root necrosis, and decreasing growth rate [22]. The content of these elements in plant samples is an indicator of loading by airborne pollutants.

The amounts of lead (Fig. 1) in dry matter of the *Vaccinium myrtillus*, *Dryopteris dilatata*, and *Luzula luzuloides* species exceeded from 1.8 to 8 times the content of Pb in "reference plants" – 1.0 mg·kg^{-1} d.m., reported by Markert [23]. Facek [24] considers toxic for plants the content between 3.0-5.0 mg·Pb kg^{-1} d.m. According to

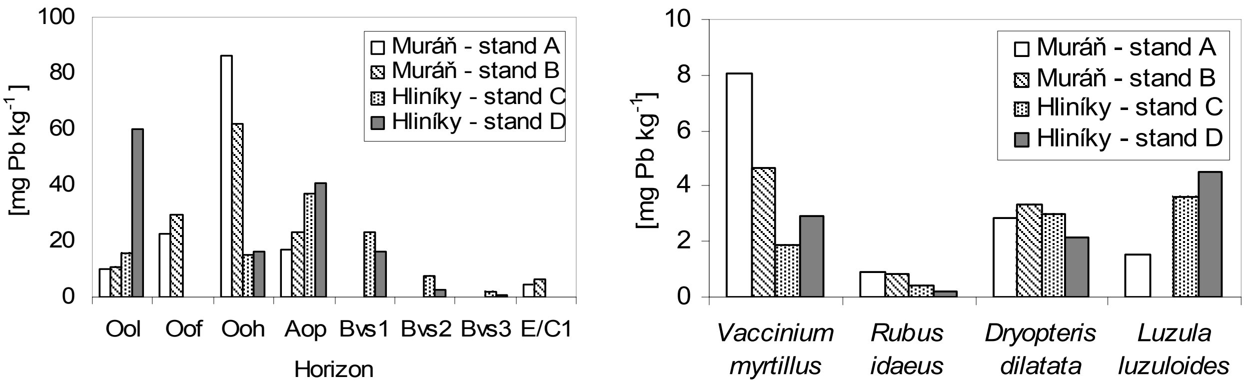

Fig. 1. Mean Pb content in soils and dominant herb species of spruce ecosystems situated along the vertical transect Muráň-Hliníky (n=3).

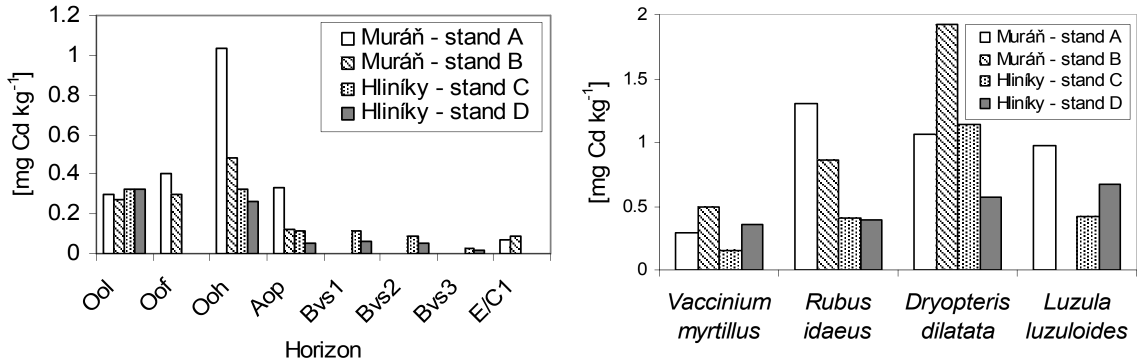

Fig. 2. Mean Cd content in soils and dominant herb species of spruce ecosystems situated along the vertical transect Muráň-Hliníky (n=3).

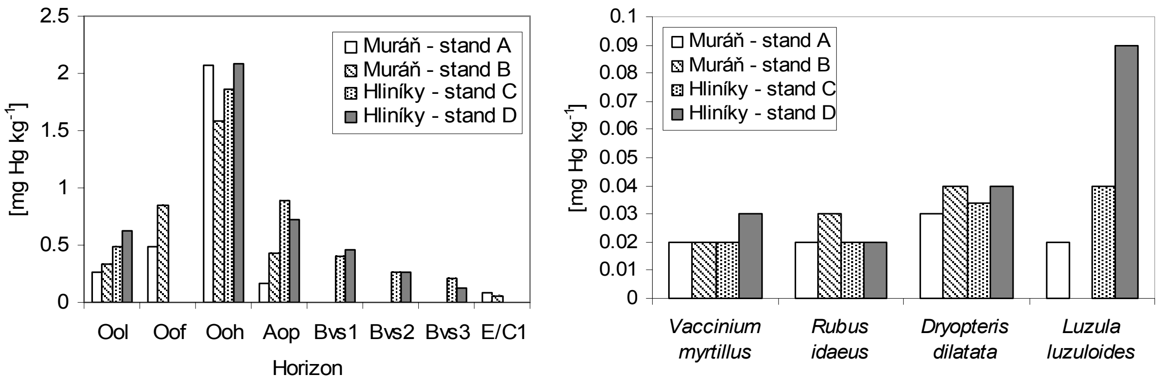

Fig. 3. Mean Hg content in soils and dominant herb species of spruce ecosystems situated along the vertical transect Muráň-Hliníky (n=3).

Table 2. Significance of differences in mean transfer coefficients (TC) compared between locations (mg·kg^{-1} d.m.; Kruskal-Wallis analysis).

Locality		Muráň		Hliníky		Sample size	Significance level
Spruce stand		A	B	C	D		
Soil		Skeli-Humic Podzols		Dystric Cambisols			
Herb species	Risk element	[TC arithmetic mean±standard error]					
Vaccinium myrtillus	Pb	0.44±0.15	0.22±0.08	0.09±0.04	0.10±0.04	14	0.102
	Cd	0.72±0.15	2.14±0.67	0.46±0.08	3.15±1.93	14	0.018*(C-D)
	Hg	0.06±0.02	0.04±0.01	0.03±0.01	0.03±0.01	14	0.779
Dryopteris dilatata	Pb	0.15±0.05	0.15±0.05	0.14±0.07	0.07±0.03	14	0.630
	Cd	2.60±0.55	8.36±2.62	3.46±0.56	5.13±3.14	14	0.123
	Hg	0.10±0.04	0.07±0.02	0.05±0.02	0.05±0.02	14	0.753
Rubus idaeus	Pb	0.05±0.01	0.04±0.01	0.02±0.01	0.01±0.01	14	0.081
	Cd	3.22±0.69	3.76±1.18	1.21±0.19	3.50±2.15	14	0.241
	Hg	0.06±0.02	0.06±0.02	0.03±0.01	0.02±0.01	14	0.375
Luzula luzu-loides	Pb	0.08±0.03	-	0.17±0.08	0.15±0.06	10	0.566
	Cd	2.42±0.52	-	1.27±0.20	5.98±3.66	10	0.137
	Hg	0.07±0.02	-	0.07±0.03	0.11±0.03	10	0.581

*α <0.05

Kozanecka et al. [25], plants from unpolluted environment contain 2.1-3.6 mg·Pb kg^{-1} d.m.

Accumulations of Pb in phytomas of studied herbs growing on Podzols (0.8-8.1 mg·kg^{-1} d.m.) represented only 1.0-9.4% of the maximum Pb amounts detected in their Ooh horizons. The same species growing on Cambisols contained a little more – 1.1-30.0% of the Pb amounts detected in their Ooh horizons.

The cadmium contents (Fig. 2) found in studied herbs were in the range of the limit values in plants (0.1-2.4 mg Cd kg^{-1} d.m.) reported by Bowen [19]. On the other hand, these values are from 3 to 26 times higher than the reference value 0.05 mg·kg^{-1} d.m. reported by Markert [23].

The contents of Cd accumulated in phytomas of herb species growing on Podzols (0.29-1.92 mg·kg^{-1}) were relatively high and represented 28-186% of the maximum Cd amounts detected in their Ooh horizons. The same species growing on Cambisols contained 47-356% of the Cd amounts detected in their Ooh horizons. This fact points out the easy mobility and availability of Cd to plants growing in acid soils [11, 18, 27, 28].

Mercury is an indicator for air pollution, originating both from natural and anthropogenic sources. The natural way this element enters soil is weathering of minerals contained in rocks. This element is a part of a high number of organic and inorganic compounds that are for living organisms toxic even at low concentrations. The Hg contents found in the studied herbs (0.02-0.09 mg·kg^{-1} d.m., Fig. 3) did not exceed the reference value 0.1 mg·kg^{-1} d.m. according to Markert [23]. On the other hand, there are higher than 0.01 mg Hg kg^{-1} d.m., the value considered by Chreneková [26] as background.

The content of Hg accumulated in phytomas of herb species growing on Podzols made 2.4-18.3% of the maximum Hg amounts detected in Ooh horizons. On the other hand, the same species growing on Cambisols contained up to 4.4-10.8% of the Hg amounts detected in their Ooh horizons.

The values of the mean transfer coefficients (TC) presented in Table 2 indicate selective accumulation of risk elements in the herb species. The best Pb accumulator was *Vaccinium myrtillus* species (TC 0.09-0.44) the worst was *Rubus idaeus* species (TC 0.01-0.05). In the case of Cd, corresponding positions are taken by *Dryopteris dilatata* (TC 2.60-8.36) and *Vaccinium myrtillus* species (TC 0.46-3.15). The best accumulators of Hg were *Luzula luzuloides* (TC 0.07-0.11) and *Dryopteris dilatata* species (TC 0.05-0.10), the worst were *Vaccinium myrtillus* (TC 0.03-0.06) and *Rubus idaeus* species (TC 0.02-0.06).

The higher TC of Pb was found at Muráň (more than 1,000 m a.s.l.), where contents of Pb in topsoil mineral layers were lower, in comparison with Hliníky (less than 1,000 m a.s.l.). This fact, together with higher content of Pb in Ool and Oof surface humus horizons (compared with Ooh horizon) on Hliníky, can point to higher input of Pb from polluted atmosphere in recent years.

The maximum TC of Pb (0.05-0.44) and Hg (0.06-0.10) were as a rule found for herbs growing on spruce plot A in the Muráň, only in the case of *Luzula luzuloides* species on spruce plots C (Pb TC 0.17) and D (Hg TC 0.11) in Hliníky. The relatively low TC of Pb correspond with data of Tóth et al. [29] and Markert [30], according

Table 3. Significance of differences in mean transfer coefficients (TC) compared within individual locations (Kruskal-Wallis analysis).

Localities	Risk element	Herb species	TC arithmetic mean ± standard error	Sample size	Significance level
Muráň – A	Pb	*Vaccinium/Rubus*	0.44±0.15/ 0.05±0.01	16	0.050*
	Cd	*Vaccinium/Rubus*	0.72±0.15/ 3.22±0.69	16	0.024*
Muráň – B	Pb	*Vaccinium/Rubus*	0.22±0.08/ 0.04±0.01	12	0.038*
Hliníky – C	Cd	*Vaccinium/Dryopteris*	0.46±0.08/ 3.46±0.56	12	0.023*

*α <0.05

to which the amounts of Pb transported to the above-ground plant parts (including fruits) are low. The maximum TC of Cd were found in herbs growing either on spruce plot B (3.76-8.36) or on spruce plot D (3.15-5.98) in Muráň.

Significantly different were only the mean values of Pb and Cd TC found for *Vaccinium myrtillus* and *Rubus idaeus* growing on spruce plots A and B in Muráň, and TC of Cd found for *Vaccinium myrtillus* and *Dryopteris dilatata* species growing on spruce plot C in Hliníky (Table 3).

Conclusions

Long-term cultivation of spruce monocultures, together with effects of acid atmospheric pollutants, caused the topsoil horizons of Cambisols in the buffer zone of Slovenský raj National Park (Hliníky) to have been acidified similarly to the topsoil horizons of Podsols (Muráň). Distribution of heavy metals in the soil profiles was influenced by the quantity of organic matter and by sampling site altitude. The limit values A1 calculated for humus and mineral soil horizons have been exceeded along the whole vertical transect only in the case of mercury. The contents of lead and cadmium were substantially lower, well below the limit values.

The background values of heavy metals found in above-ground organs of the studied herb species were exceeded only in cases of Pb and Cd, and fluctuated within the toxicity range. The higher herb/soil transfer coefficients for Pb and Hg occurred as a rule on damaged spruce plots with lower stand density. This could be caused by higher input of these elements from polluted atmosphere. In the case of Cd, the higher transfer coefficients were ascertained on undamaged spruce plots, probably resulting from easy availability of Cd for herb species.

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