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Contamination of vegetation growing on soils and substrates in the unhygienic region of Central Spiš (Slovakia) polluted by heavy metals

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Abstract

The present paper aims at clarifying the long-term impact of mining activities on the contamination of biotic components of the environment. The research was conducted in during 2011-2014 at selected locations of the cadastral territory of former mining towns of Central Spiš (Slovakia) with different ecosystems of permanent grassland, mine waste sites and bankside vegetation. The results of the analysis showed that considerably dominant species at contaminated locations such as *Betula pendula*, *Silene vulgaris*, *Geranium sylvaticum*, *Petasites hybridus*, *Mentha longifolia* could absorb high quantities of heavy metals. The observed contents of heavy metals, especially zinc, copper and mercury in plants significantly exceeded the threshold values determined by law. The highest contamination as compared to the threshold values was found in young plants of *Betula pendula* in the Slovinky tailing pond site, in which zinc content exceeded the threshold value 852 times. Excess of copper content also exceeded the threshold value 271 times. The highest concentration of mercury in all of the surveyed sites was observed in dry matter of *Betula pendula* in the area of heap in the Poráč Valley, where threshold value was 184 times higher. Statistically significant locations similar in relation to the characteristic species and monitored heavy metals was recorded on the locations of tailing pond and heap as the most important centres of contamination with the following dominant species *Betula pendula*, *Pinus silvestris* and *Agrostis capilaris*.

Key words

Heavy metals, Heaps, Permanent grassland, Bankside vegetation

Introduction

The scientists' interest in the so-called bio-indicators, which are used for the assessment of the environmental load, has greatly increased in the last two decades (Stankovič *et al*., 2013). Numerous research studies have dealt with the assessment of different soil characteristics under the influence of stress factors, such as increased content of heavy metals. Soil contaminated by heavy metals loses its essential biological properties necessary for the functioning of the ecosystem (Kendeler *et al*., 1996; Střelcová *et al*., 2009) and long-term adverse environmental changes negatively affect the viability of plant population. These are mainly global changes associated with global warming and other changes caused by human activities which consequently affect all environmental components (Nicolé *et al*., 2011; Ďurský *et al*., 2006). Most plants are sensitive to the effects of heavy metals (Ernst *et al*., 2004); plants need a small amount of some heavy metals, the so called bioelements, such as copper, zinc, iron, manganese, molybdenum. Higher concentrations of these heavy metals, however, are toxic to plants. Lead, mercury, cadmium, silver and other heavy metals are substantially toxic to plants even in minimal concentrations. Heavy metals are introduced into the environment in the form of emissions from ore processing. Heaps from deep ore mining, as well as tailing ponds and many other toxic waste sites represent substrates with high heavy metal content. They seriously damage vegetation, like reducing its growth, reduce photosynthesis. Soil reaching heavy metals are often unavailable to plants. A portion of these heavy metals can be transformed into the forms that are available for plants through different processes in soil. Soil parameters, such as soil reaction and content of organic matter affect the availability of heavy metals to plants (Xian, Shokohifard, 1989; Otte *et al*., 1993; Mandaokar *et al*., 1994). The entire plant production is contaminated by the absorption of heavy metals (Petříková, 1990; Plieštiková and Škvarenina, 2009). Heavy metals can accumulate in various plant parts according to the plant species, soil conditions, and type of heavy metal (Fazeli *et al*., 1991; Barman *et al*., 2001). Plant ability to cope with excessive amount of heavy metals varies. Some plant species have mechanisms that impose heavy metals in cell walls or bond them chemically in the vacuole, and thus their toxicity is reduced. Others impede penetration of heavy metals from roots to the above-ground parts. Accumulators are such plants species that accumulate a large amount of specific metals in their tissues. Some of the examples are *Silene vulgaris* and *Melandrium rubrum* that accumulate copper in their above-ground parts, and *Acetosella vulgaris* accumulates zinc. *Agrostis capillaris, Calamagrostis epigejos, Deschampsia flexuosa* and *Agrostis stolonifera* are capable of forming tolerant ecotypes. *Elytrigia repens* and *Taraxacum officinale* are also characterized by high ecological valence and are resistance to heavy metals (Banásová, 2004; Boguská *et al.,* 2013). Growth deformation (dwarfism), reduction of leaf growth and lower biomass are typical impacts of high concentration of heavy metals. The present paper aimed at specifying the degree of contamination of biotic components of the environment by heavy metals in different ecosystems in environmentally loaded and hygienically objectionable region of Central Spiš (Slovakia).

Materials and Methods

Site of the present research study : The research was conducted in the Rudňany - Gelnica area, which is included in the environmentally loaded and unhealthy areas of Slovakia. As a result of long and intensive mining and processing of minerals, the area is polluted with heavy metals and the landscape has been altered by extensive anthropogenic forms. Rudňany - Gelnica area covers about 357 km^2. The geological structure of the area is built with Paleozoic (conglomerates, phyllites, schists), Paleogene (central Carpathian flysch in a typical development of sandstone and shale) and Quaternary (Holocene calcareous clays, sands and gravels) materials. Shallow, moderate loam and sandy loam soils have developed on these parent rocks. The location belongs to a mild to moderately warm humid climate with average January temperature of -2 to -5 °C, and average July temperatures of 13-15 °C (Hronec *et al*., 2008; Michaeli *et al*., 2015), respectively.

Vegetation sampling and analysis: Field phytocoenological research in the area of interest of the Spiš region aimed at determining the quantitative and qualitative parameters of vegetation, and was conducted during the growing seasons 2011-2014 in different ecosystems such as permanent grassland, dumping site - heaps of waste material from mines, and stands on the water course banks. The botanical composition of the sites was determined on the basis of phytocoenological relevés within an area of 16 m^2 (Križová, 1995).

The samples of foliage and twigs were collected at selected locations of the polluted area of Central Spiš from the cadastral areas of Poráč, Rudňany, Slovinky and Krompachy: 1PR heap in Poráč Valley (48˚ 52' 45.2"N; 20˚ 43' 36.8"E), 2PR bankside vegetation of Poráč Creek (48˚ 52' 18.7"N; 20˚ 44' 8.2"E), 3PR bankside vegetation of Poráč Creek (48˚ 52' 43.0"N; 20˚ 44' 55.3"E), 4PR bankside vegetation of Poráč Creek (48˚ 52' 42.8"N; 20˚ 45' 22.6"E), 5PR bankside vegetation of Poráč Creek (48˚ 53' 0.2"N; 20˚ 46' 36.4"E), 6PR bankside vegetation of Poráč Creek (48˚ 52' 55.9"N, 20˚ 48' 57.2"E); 7RD permanent grassland in cadastral area of Rudňany, 8SL tailing pond Slovinky (48˚ 53' 15.4"N; 20˚ 52' 08.7"E), 9KR dumping site Halňa in Krompachy (48˚ 55' 24.1"N; 20˚ 53' 59.2"E), 10KR permanent grassland in cadastral area of Krompachy (48° 55' 20.8"N; 20° 53' 58.6"E). The foliage of *Betula pendula*, *Silene vulgaris*, *Geranium sylvaticum*, *Petasites hybridus* and *Mentha longifolia* were collected to determine heavy metal content. The results were statistically analysed using the programme CANOCO for Windows 4.5 and PAST. Vegetation samples were dried at 40 °C, homogenised to the fraction <0.09 mm, burned in a furnace at 550 °C and decomposed with a mixture of HCl and HNO_3 acid. The concentration of heavy metals was (As, Cu, Hg, Pb, Zn) determined, and the measured values of heavy metals were compared with the threshold values of plants determined by law (Law no. 220/2004 Coll). The samples were analyzed atomic absorption spectrometry, and x-ray fluorescence spectrometry following the methodology as devised by Fiala *et al*. (1999).

Results and Discussion

Floristic differentiation of investigated sites : The environment of selected sites of Central Spiš, in which the phytocoenological investigation was conducted, was found to be deteriorated in terms of its quality. The site conditions characterized by a high content of heavy metals in soil pre-determined the existence of resistant species. In all the surveyed locations, species with a wider ecological valence prevailed. During field phytocoenological investigation in the growing seasons 2011-2014, minimal difference in the species composition was found.

Vegetation of tailing pond in Slovinky (8SL) was characterized by low species richness. The soil containing contaminants determines the growing vegetation. The embankment of tailing pond was covered with shrubby vegetation predominant of *Betula pendula* and *Pinus sylvestris*. Tree species *Corylus avellana* and *Larix decidua* with the accompanying species in the undergrowth *Agrostis capillaris*, *Fragaria vesca*, *Tussilago farfara* and *Festuca rubra* were also recorded. In Central Europe, *Betula pendula* was contaminated with heavy metals because it is adapted to a wide range of conditions, such as anthropogenic habitats, similarly as trees like *Salix caprea, Sambucus nigra* or *Pinus sylvestris* (Prach and Pyšek, 2001; Bojarczuk and Kieliszewska-rokicka, 2010; Ots and Mandre, 2012; Zubrovskaya and Gryshko, 2014). The species near to the immission field of tailing pond began to show signs of deterioration; the trees were stunted mostly in the bush form.

The plant cover on the dumping site of Halňa (9KR) consisted mostly of species growing at ruderal and contaminated areas. It was observed that the plant species such as *Solidago gigantea*, *Geranium pratense* and *Tussilago farfara* were resistant to environmental factors. Significant abundance of *Silene vulgaris* was recorded at this site. Increased occurrence of these species on contaminated soil was also observed by Banásová and Lackovičová (2004).

According to the Catalog of Habitats in Slovakia (Stanová and Valachovič, 2002), the permanent grassland in Krompachy cadastral area (10KR) presents mesophilic pastures and grazed meadows. Its botanical composition, to a certain extent was driven by the position of locality, which was deteriorated by long-term emissions from a nearby copper processing factory. The coverage and species composition of the site did not change significantly during the observed period. Typical meadow and pasture species were *Achilllea millefolium*, *Dactylis glomerata*, *Festuca rubra, Poa trivilialis* and *Plantago major*.

The permanent grassland in the cadastral area of Rudňany was also classified as mesophilic pastures and grazed meadows (Stanová and Valachovič, 2002) with a prevalence of grassland species, namely *Campanula patula*, *Festuca pratensis, Leucanthemum vulgare*, *Poa trivilialis* and *Taraxacum officinale*. The environment of this area was significantly contaminated with mercury, and therefore, resistant species *Silene vulgaris* and *Geranium pratense* had highest coverage at this site.

The heap in Poráč Valley (1PR) has been formed from waste extraction and processing of mercury ore. On the heap there are visible stages of progressive succession. Species, such as *Calamagrostis epigejos*, or, *Betula pendula* belong to the most frequent colonizers of anthropogenic substrates (Prach *et al*., 2008). Shrubbery vegetation on the heap consists of pioneer tree species *Betula pendula*, *Pinus sylvestris* and *Picea abies*. *Calamagrostis epigejos* was the most common species.

The species composition of the localities "bankside vegetation of the Poráč Creek" (2PR, 3PR, 4PR, 5PR, 6PR) are formed by communities of mountain creeks and grasslands along their banks (Stanová and Valachovič, 2002). The negative impact on plant communities of this site is caused by the contaminated mining waste material stored near the Poráč Creek. The individual sites did not significantly differ in their species composition. The most abundant plant species at three sites of the bankside vegetation of the Poráč Creek (2PR, 3PR, 4PR) were *Geranium sylvaticum*, *Mentha longifolia*, *Caltha palustris* and *Petasites hybridus*; at the site 5PR. There were species such as *Maianthemum bifolium, Petasites hybridus* and *Chelidonium majus*; and the most abundant species at site 6PR were *Mentha longifolia* and *Taraxacum officinale*.

The investigated sites were statistically evaluated using an indirect gradient analysis of DCA in CANOCO for Windows 4.5 (Ter Braak and Šmilauer, 1998). The individual sites are shown in the summary chart. The species abundance of the surveyed sites was logarithmized in order to highlight the floristic differentiation of individual sites. Fig. 1 shows that the individual sites differed mainly along the humidity gradient (x-axis, sites of bankside vegetation of the Poráč Creek 2PR, 3PR, 4PR, 5PR, 6PR). The gradient along the vertical axis is successional starting from forests down to grasslands dominated by herbs and grasses (the sites: tailing pond Slovinky, dumping site Halňa, permanent grassland in Krompachy, permanent grassland in Rudňany, heap in the Poráč Valley).

The species were selected on the basis of their significance coefficient at individual sites. Copper, zinc, mercury, lead and arsenic were analyzed in plant species. The highest contamination as compared to the threshold values was found in young plants of *Betula pendula* at the site of tailing pond Slovinky (8SL), in which the zinc content exceeded the threshold values 852 times. The excess of copper was also detected; its content reached the value of 271 mg kg^{-1} (Table 1). The results of the analysis are consistent with the statements of several authors who consider regions with mining activities and production of ferrous metals as the most polluted by copper compounds (Čurlík *et al*., 1998). *Silene vulgaris* was dominant at three sites, where the measured values of heavy metals significantly exceeded their thresholds. *Silene vulgaris* is a resistant species with a wide

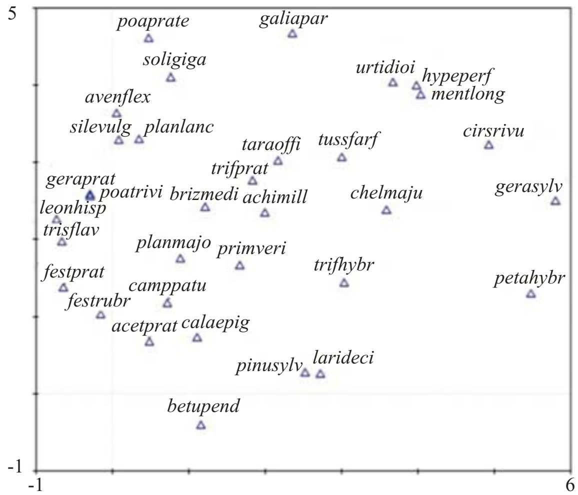

Fig. 1 : Ordination diagram with floristic differentiation of investigated sites in Central Spiš (Slovakia) Characteristic values: 1st axis 9.9%, 2nd axis 5.4%, length gradient is 5.814. The parameters are detrended by segments with logarithmic transformation. Legend: acetprat - *Acetosa pratenis*, achimill - *Achillea millefolium*, avenflex - *Avenella flexuosa*, betupend - *Betula pendula*, brizmedi - *Briza media*, calaepig - *Calamagrostis epigejos*, camppatu - *Campanula patula*, cirsrivu - *Cirsium rivulare,* festprat - *Festuca pratensis*, festrubr - *Festuca rubra*, geraprat - *Geranium pratense*, galiapar - *Galium aparine*, gerasylv - *Geranium sylvaticum*, hypeperf - *Hypericum perforatum*, mentlong - *Mentha longifolia*, petahybr - *Petasites hybridus*, primveri - *Primula veris*, planlanc - *Plantago lanceolata*, planmajo – *Plantago major*, pinusylv - *Pinus sylvestris*, soligiga - *Solidago gigantea*, silevulg - *Silene vulgaris*, trifhybri - *Trifolium hybridum*, trifprat - *Trifolium pratense*, taraoffi - *Taraxacum officinale*, tussfarf - *Tussilago farfara*, trisflav - *Trisetum flavescens*, urtidioi - *Urtica dioica*

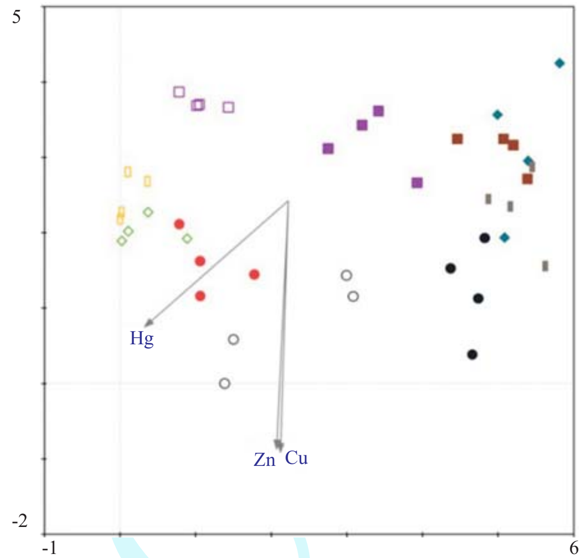

Fig. 2 : DCA ordination diagram of surveyed sites with the highest concentration of heavy metals in the area of Central Spiš (Slovakia) Characteristic values: 1st axis 9.9%, 2nd axis 5.4%, the gradient length is 3.258 SD. The parameters are detrended by segments with logarithmic transformation. Legend: filled red circles–1PR heap in Poráč valley, filled brown squares –2PR bankside vegetation of the Poráč Creek, filled blue diamonds–3PR bankside vegetation of the Poráč Creek, filled grey rectangles–4PR bankside vegetation of the Poráč Creek, filled black circles–5PR bankside vegetation of the Poráč Creek, filled purple squares – 6PR bankside vegetation of the Poráč Creek, empty yellow rectangles – 7RD permanent grassland in Rudňany, empty black circles – 8SL tailing pond Slovinky, empty purple squares – 9KR dumping site Halňa, empty green diamonds – 10KR permanent grassland in Krompachy.

Table 1: Content of heavy metals [mg kg^{-1}] in the plant species in the area of Central Spiš (Slovakia)

Location name	Plant species	Cu	Zn	Hg	Pb	As
1PR Heap in Poráč Valley	*Betula pendula*	44	283	1.84	-	-
2PR Bankside vegetation of the Poráč Creek	*Geranium sylvaticum*	7	32	0.02	< 5	< 1
3PR Bankside vegetation of the Poráč Creek	*Geranium sylvaticum*	7	28	0.02	< 5	< 1
4PR Bankside vegetation of the Poráč Creek	*Geranium sylvaticum*	6	25	< 0.01	< 5	< 1
5PR Bankside vegetation of the Poráč Creek	*Petasites hybridus*	16	27	0.03	< 5	< 1
6PR Bankside vegetation of the Poráč Creek	*Mentha longifolia*	11	27	0.05	< 5	< 1
7RD Permanent grassland in Rudňany	*Silene vulgaris*	22	48	0.49	-	-
8SL Tailing pond Slovinky	*Betula pendula*	271	1649	0.07	-	-
9KR Dumping site Halňa in Krompachy	*Silene vulgaris*	21	88	0.12	-	-
10KR Permanent grassland in Krompachy	*Silene vulgaris*	23	159	0.37	-	-
Threshold value*		1.0	2.0	0.01	0.1	0.4

* Threshold values according to Act No. 220/2004 Coll.

ecological valence. It is also referred to as a metallic-tolerant ecotype, binding high contents of heavy metals in its tissues (Banásová, 2004; Khan *et al*., 2000). At the grassland sites of cadastral areas of Krompachy (10KR) and Rudňany (7RD) and the dumping site Halňa (9KR), mercury content in the dry matter of *Silene vulgaris* ranged from 0.12 to 0.49 mg kg^{-1}, and hence significantly exceeded the threshold. The highest concentration of mercury in all the surveyed sites was observed in the dry matter of *Betula pendula* in the area of the heap in Poráč Valley (1PR), where the threshold value of 1.84

mg kg^{-1} was exceeded 184 times. High concentrations of mercury in soils and vegetation in the area of Central Spiš were reported by Čurlík and Šefčík (1999), and Kimáková and Bernasovská (2005).

At the sites of bankside vegetation of Poráč Creek (2PR, 3PR, 4PR), the content of heavy metals was analyzed in *Geranium sylvaticum*. The copper content in the species at three sites (2PR, 3PR, 4PR) was 6-7 mg kg^{-1}, which was sevenfold excess over the threshold value. The values of lead and arsenic in the dry matter of *Geranium sylvaticum* reached excessive values in the range from <1 to <5 mg kg^{-1}. For the site of bankside vegetation of the Poráč Creek (5PR), the samples of *Petasites hybridus* were analysed. In its dry matter zinc (27 mg kg^{-1}) and copper (16 mg kg^{-1}) were found in high level. The content of mercury, lead and arsenic in *Petasites hybridus* was similar to those at other locations. From the site of bankside vegetation of the Poráč Creek (6PR) the samples of *Mentha longifolia* were analysed, in which the highest value of zinc was 27 mg kg^{-1} and copper 11 mg kg^{-1}. Mercury, lead and arsenic contents were approximately at the same level as at other sites of the Poráč Creek bankside vegetation.

DCA ordination diagram (Fig. 2) shows the position of all the surveyed sites with highest concentration of heavy metals in plants. The most significant sites in the diagram from the point of contamination of plant species were tailing pond of Slovinky and heap in Poráč valley.

It was discovered that in the Central Spiš (Slovakia), old dumps and heaps of waste material, such as mining residues and processing operations are sources of contamination of vegetation by heavy metals. The present study produce valuable information that can be used in implementing the remediation process in the territories contaminated by heavy metals.

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