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Original Research

Environmental Availability of Trace Metals (Mercury, Chromium and Nickel) in Soils from the Abandoned Mine Area of Merník (Eastern Slovakia)

Edgar Hiller[1]*, Ľubomír Jurkovič[1], Juraj Majzlan[2], Tatsiana Kulikova[1], Tomáš Faragó[1]

[1]Department of Geochemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovak Republic
[2]Institute of Geosciences, Burgweg 11, Friedrich-Schiller University, 07749 Jena, Germany

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Abstract

The former mercury ore deposit of Merník in Eastern Slovakia was selected for the investigation of the environmental availability of mercury (Hg), chromium (Cr) and nickel (Ni) in mine soils. Single-step extractions with four chemical agents (deionised water, ethylenediaminetetraacetic (EDTA), acetic (CH_3COOH) and hydrochloric (HCl) acid solutions) and chemical analysis of the common nettle (*Urtica dioica*) were used to determine the availability of the three metals. Regardless of the type of extraction, the soluble ratios of metals in mine soils increased in the order of Hg≤Cr<Ni, while the extraction efficiency of individual reagents followed generally the order of HCl>CH_3COOH ≈ EDTA>>H_2O. The total or extractable metal concentrations in soil did not correlate with their concentrations in aerial parts of the common nettle, however, its ability to accumulate these trace metals in roots and aerial parts copied the results of extraction tests, i.e. Hg≤Cr<Ni. Only correlations existed between the H_2O extractable metal concentrations and the plant root concentrations. Bioconcentration factor (BCF) and translocation factor (TF) were considerably lower than 1.0, while BCF values for Ni were sensitive to soil pH, with higher values in more acid soils. The plant availability of Hg and Cr was by one order of magnitude lower than that of Ni, indicating that the former mine area poses no serious environmental and health risks, despite high metal concentrations in soil. Higher plant availability of Ni compared to Hg and Cr was likely due to high Ni solubility in CH_3COOH and EDTA solutions (10.3±5.51% and 9.39±4.50% of the total soil concentration, respectively), which release the metals present in exchangeable form, carbonate bound and complexed with soil organic matter. Low Hg availability could

*e-mail: edgar.hiller@uniba.sk

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be explained by its binding to stable cinnabar(metacinnabar) as indicated by extended X-ray absorption fine structure (EXAFS) and μ-X-ray fluorescence (μ-XRF).

Keywords: mercury, mobility, soil, plants, trace metals

Introduction

Mercury, Cr and Ni are trace metals with average concentrations in the upper continental earth's crust of 0.06 mg/kg, 53 mg/kg and 26.3 mg/kg, respectively [1-2]. Increased Hg contents in soils are associated with anthropogenic emissions, mainly from mining, waste management, electrical engineering, the use of Hg in the extraction of precious metals and chlor-alkali plants [3-4]. This metal is characterized by significant toxicity to all living organisms, including humans [5-6]. Similarly, high concentrations of Cr and Ni are commonly detected in mine soils, soils from nickel smelters and non-ferrous metal processing complexes [7-11]. Typical of geochemically anomalous concentrations of Cr and Ni are also the so-called serpentine soils developed on ultrabasic rocks [12-15]. In this case, it is not an anthropogenic soil contamination but geogenic derived from naturally high contents of Cr, Ni and geochemically related elements in the underlying rock substrate [16-18].

Mobility of Hg, Cr and Ni in soils and their transfer from soil to plants is a complex function of several variables, such as geochemical fractionation of metals among soil components, physico-chemical and mineralogical characteristics of soil substrates and plant species [12-13, 19-26]. Total concentrations of trace metals are not of prime importance for assessing the ecological and health risks of contaminated soils. Instead, the readily soluble, exchangeable and weakly bound forms of these metals play the major role because they are available for migration into natural waters and plants [27-28]. Available forms of toxic trace metals are commonly determined by single-step extractions. For example, extraction procedures using water and acetic acid release highly available water-soluble metal fractions from the soil and exchangeable/bound to carbonates and hydroxides [22, 28]. Despite some success of in vitro single-step extractions with a specific reagent to predict plant uptake of trace metals, the most appropriate way to evaluate the actual availability of elements in plants is to measure their concentrations in the sampled plant species [29].

This study focused on the determination of the mobility, potential and actual bioavailability of Hg, Cr and Ni in surface soils from the former cinnabar mine Merník (eastern Slovakia) through single-step extractions with four different chemical reagents and measuring trace metal concentrations in the common nettle (*Urtica dioica*). The reason for the selection of these three metals is the fact that they are the main anthropogenic (Hg) and natural (Cr and Ni) soil contaminants in this mine area [30]. It is a unique example of the differences in the availability of unusual geochemical association of elements due to the rock composition of the mine area: Hg derived from cinnabar mineralization in rhyodacites, and Cr and Ni bound to conglomerates consisting of pebbles of ultrabasic rocks. Therefore, the main objectives of this work were to evaluate (i) the soluble fractions of Hg, Cr and Ni in soils by various reagents that mimic the release of trace metals in natural conditions, (ii) the transfer of metals from soil to the common nettle and (iii) possible influence of physico-chemical characteristics of soils on the mobility, bioavailability and transfer of trace metals into plants.

Experimental

Brief Description of the Study Area

The abandoned Hg deposit of Merník is situated approximately 1 km south of the village Merník in Eastern Slovakia, Vranov nad Topľou district, Prešov region (Fig. 1). Mercury ores, mostly cinnabar, were mined in the deposit from 1830 to 1939. In the deposit area, the Hg ores were processed by roasting in two rotary kilns and about 150 t of pure Hg were produced during the whole period. The deposit is hosted by sediments of the Central Carpathian Paleogene, penetrated by stocks and dykes of rhyodacites (Upper Badenian – Lower Sarmatian). The mercury mineralization is dispersed in these rocks and forms veinlets and impregnations [31]. Conglomerates with pebbles of ultrabasic rocks (Lower Miocene), which are typically enriched in Cr and Ni, are abundant in the area. The main ore mineral is cinnabar, accompanied by metacinnabar, pyrite and marcasite. The Quaternary consists of anthropogenic sediments, which are heaps and dumps (Holocene), as well as deluvial sediments, which are loams, sands and clayey gravels (Pleistocene-Holocene).

Soil and Plant Collection

Soil samples were collected at 10 sites and from the same points as the plant samples (Fig. 1). The soil samples were taken from a depth of 0-20 cm from the rhizosphere of each plant in clean polyethylene bags. Soil and plant sampling at each site was performed from an area of 1 m^2, from which 3 soil and 3 plant subsamples were taken, which were then individually analysed for trace metal concentrations. For single-step extraction procedures, the soils were also collected from a depth of 40-60 cm from the same sampling

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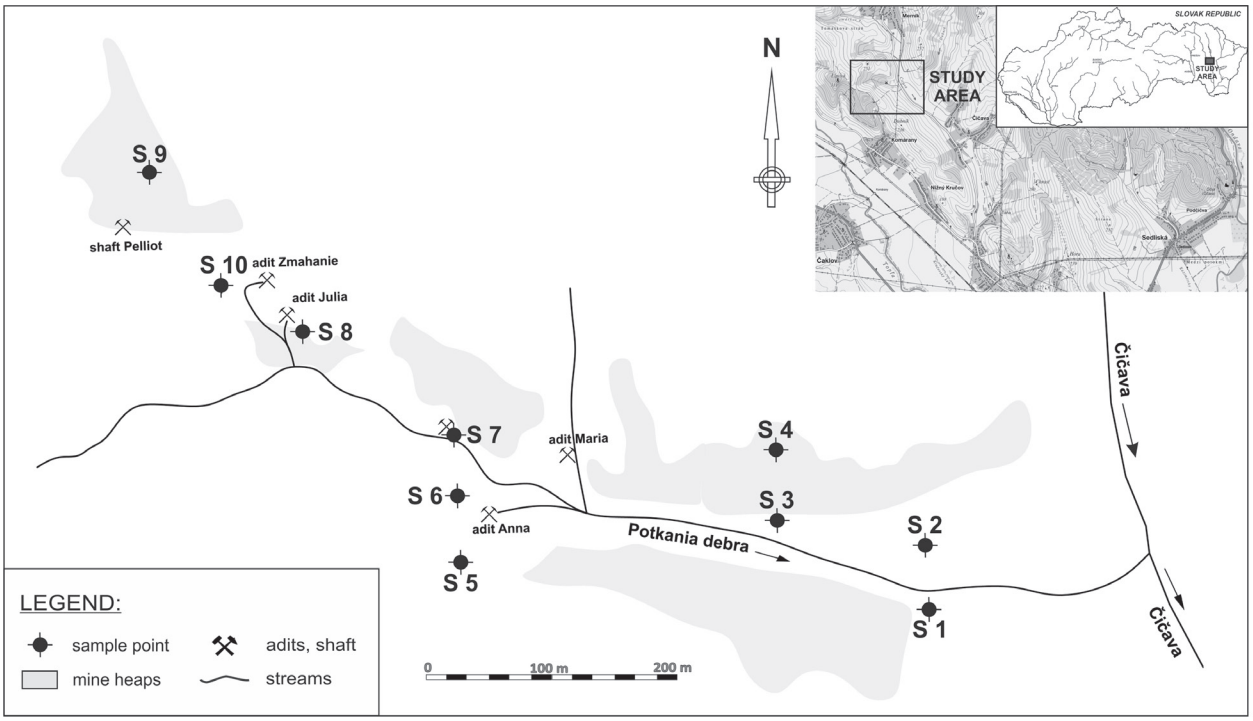

Fig. 1. Location of the study area (former mercury deposit Merník in Eastern Slovakia) and sampling points of soils and common nettle.

points. They were air-dried in the laboratory to constant weight, large aggregates were finely crushed and finally the soil samples were sieved to a size less than 2 mm. During the vegetation period (July 2018), the common nettle (*Urtica dioica*), which is the predominant plant species in the mine area, was harvested. Fresh plants were removed from the soil by spade and divided into the aerial part (stems and leaves) and roots in the laboratory. The plant samples were rinsed thoroughly with tap water and then several times with deionised water to remove any external contamination. Plant parts were dried at room temperature to constant weight, then pulverized and sieved.

Analytical Methods

Mercury concentration in all soils, plants and extracts was determined by an advanced mercury analyser (AMA-254, Altec) in accredited laboratories of EL Ltd., Spišská Nová Ves, Slovakia. To measure the concentration of Cr and Ni in soils, 0.5 g of soil sample was digested in a microwave oven (model MDS 81 D, CEM Corporation) with a mixture of 9 mL HNO_3, 3 mL HCl and 3 mL HF. The cooled, diluted and filtered extracts were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista AX, CCD Simultaneous System). The concentration of Cr and Ni in the nettle was determined after digestion of dry and sieved samples (0.5 g) with 2 mL H_2O, 2 mL H_2O_2 and 4 mL HNO_3 in a microwave. The plant extracts were brought to 25 mL with deionised water and filtered through Whatman filter paper No. 42. Standard reference materials for plant (ERM-CD281 – rye grass) and soil (ERM-CC141 – loam soil) were used to determine the accuracy and precision of the analytical methods. Laboratories declare the following detection limits for solid samples: 0.001 mg/kg for Hg and 0.1 mg/kg for Cr and Ni. The soil pH and electrical conductivity (EC) were measured in soil-deionised water suspensions in a 1:2.5 ratio (w/v) with glass electrode and conductivity meter, respectively. The total organic and inorganic carbon contents (TOC and IC, respectively) were determined by thermal decomposition of soils using a Ströhlein TOC-Analyser C-MAT 5500. The carbonate content was analysed using the pressure calcimeter method with 6 M HCl and expressed as a percentage of $CaCO_3$. The standard pipette method was used for the determination of soil particle-size distribution (sand <2.0 mm, silt <0.05 mm and clay <0.002 mm) [32].

Extraction Protocols

Four single-step extraction schemes using (i) deionised water (H_2O), (ii) dilute ethylenediaminetetraacetic acid solution (0.05 M EDTA), (iii) dilute acetic acid (0.43 M CH_3COOH) and (iv) dilute hydrochloric acid (1.0 M HCl) were adopted in this study. The proportions of elements soluble in H_2O, EDTA, CH_3COOH and HCl are defined as easily mobilisable, potentially phytoavailable, mobilisable and reactive, respectively [27]. Extraction with H_2O was performed with 5 g of soil and 50 mL of liquid phase for 16 h [33]. The potentially phytoavailable pool of trace

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metals was determined by extracting 5 g of soil with 50 mL of 0.05 M EDTA solution (with pH = 7) for 2 h [34]. Extraction of soils with 0.43 M CH_3COOH solution was performed in a soil:solution ratio of 1:40 (w/v) for 16 h [35] and the reactive pool was obtained by extraction of soil with 1.0 M HCl solution in a soil:solution ratio of 1:10 (w/v) for 2 h [27]. All extractions were performed in a mechanical shaker at room temperature. The extracts were separated from the soil by centrifugation (6000 rpm for 10 min) and then filtered through a 0.45 μm filter. The supernatants were kept in a refrigerator at 4ºC prior to the chemical analysis. Concentrations of Hg, Cr and Ni in the soil extracts were analysed by the same analytical methods as used for soils and plants. The detection limits of the analytical methods used for Hg, Cr and Ni in the solutions were 0.0001, 0.002 and 0.01 mg/L, respectively.

Micro X-ray Fluorescence (μ-XRF) and Extended X-ray Absorption Fine Structure (EXAFS) Measurements

Micro-XRF spectroscopy was done on polished sections prepared from selected soil samples. The μ-XRF mapping of selected areas in these sections was carried out with a Bruker M4 TORNADO μ-XRF spectrometer. The X-ray source was a Rh target with an accelerating voltage of 50 kV and anode current of 600 μA. The analyses were performed with a beam of 20 μm diameter, step of 17 μm, in energy-dispersive (EDS) mode, thus allowing simultaneous measurement of all elements between Na and U. Sensitivity of the instrument is limited by spectra overlaps but it is very high for some elements (e.g., 20 ppm for Cu, 40 ppm for Fe, and 20 ppm for Zn).

EXAFS spectra were measured using a SUL-X beam on a synchrotron KARA (Karlsruhe Research Accelerator, Eggenstein-Leopoldshafen, Germany). The spectra of the reference samples were obtained in the transmission mode and of the soil samples in the fluorescence mode at the edges Hg L_1 (14.84 keV) and L_3 (12.28 keV).

Data Analysis

Bioconcentration factor (BCF) was used to evaluate the bioavailability of Hg, Cr and Ni to the common nettle. The values of BCF were calculated as the ratio of the total metal concentration in the root (mg/kg) to its total concentration in the soil (mg/kg). The plant's ability to distribute metal from the roots to the aboveground parts was expressed using a translocation factor (TF), which is defined as the ratio of the total metal concentration in shoots (mg/kg) to its total concentration in roots (mg/kg). Three independent plant samples and respective soil samples at each site were taken into account and arithmetic mean and median were calculated. Nonparametric versions of statistical methods were used to identify the relationships between the two variables (Spearman correlation analysis) and differences in extraction efficiency among extractants for each metal and differences in plant uptake and in vitro single-step extractions among the three studied trace metals (Kruskal-Wallis test with Dunns post hoc test). Non-parametric versions were preferred because most variables did not have a normal distribution.

Results

Soil Physico-Chemical and Mineralogical Properties and Total Metal Concentrations

The pH values of surface soils varied considerably and were between 4.05 and 7.83. The $CaCO_3$ content ranged from 2.75% to 19.5% and was higher in weakly alkaline soils (Table 1). The total organic carbon content in these mine soils was also very variable in the range from 0.95% to 3.77%. The predominant grain categories were sand and silt with a clay content between 4.80–18.6%, so according to the grain triangle, these surface soils fall into the group of silty loam. Subsurface soils had a similar pH, $CaCO_3$ content and grain size distribution as surface soils, only the TOC was significantly lower ($P<0.05$).

The total concentrations of trace metals studied in soils are shown in Fig. 2. Soil concentrations of Hg varied by up to four orders of magnitude (0.46 mg/kg up to 951 mg/kg), highest in soils close to the tunnels and mine waste heaps. The median Hg concentration in these ten soils (14.2 mg/kg) significantly exceeded its global mean value (1.1 mg/kg; [3]) and was up to 170 times higher than the Slovak median Hg concentration in the A soil horizon, which is 0.08 mg/kg [36]. This comparison shows that historical anthropogenic perturbations in the study area (i.e. mining, grinding and smelting of Hg sulfides) are the main cause of soil contamination with Hg. Mercury concentrations in subsurface soils were lower than those in surface soils (Fig. 2) (9.33 mg/kg *vs.* 14.2 mg/kg) but not significantly ($P>0.05$). Concentrations of Cr and Ni in the surface soils ranged between 57-334 mg/kg and 62-654 mg/kg with a median of 146 mg/kg and 206 mg/kg, respectively. Subsurface soils contained 57-286 mg/kg Cr (median of 157 mg/kg) and 84-637 mg/kg Ni with a median of 161 mg/kg and they did not differ significantly from those in surface soils. Chromium and Ni concentrations in soils from each depth interval were significantly correlated ($R = 0.86$, $P<0.001$ for 0-20 cm soil depth and $R = 0.81$, $P<0.01$ for 40-60 cm depth), indicating the same source of the metals. Compared to their mean concentrations in European soils (21.7 mg/kg and 18.4 mg/kg for Cr and Ni, respectively; [37]) and Slovak soils (85 mg/kg and 25 mg/kg for Cr and Ni, respectively; [36]), the soils of Merník are enriched with these two metals. This soil enrichment is related to the occurrence of conglomerates

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Table 1. Determined physico-chemical properties of soil samples. The mean value from the three soil samples at each sampling point is shown.

	pH[a]	$CaCO_3$ (%)[a]	TOC (%)[a]	Sand (%)[a]	Silt (%)[a]	Clay (%)[a]
Surface soils (0–20 cm)						
S1	6.85	4.67	3.37	51.8	43.4	4.80
S2	6.83	2.75	3.37	44.9	40.4	14.7
S3	6.97	4.58	3.77	56.8	34.6	8.60
S4	7.75	9.67	1.71	45.2	47.1	7.70
S5	4.05	3.00	1.20	46.1	40.5	13.4
S6	4.02	4.00	1.87	39.5	47.0	13.5
S7	7.83	12.8	0.95	63.7	26.5	9.80
S8	7.65	4.85	1.84	52.5	36.2	11.3
S9	7.66	19.5	1.94	42.3	39.6	18.1
S10	5.22	3.17	1.21	20.5	60.9	18.6
Mean[b]	6.48	6.90	2.12	46.3	41.6	12.1
Median[b]	6.91	4.63	1.86	45.7	40.5	12.4
Subsurface soils (40–60 cm)						
S1	7.50	1.08	1.73	47.0	47.8	5.20
S2	7.14	4.58	3.68	44.6	42.3	13.1
S3	7.63	9.42	1.89	50.5	39.6	9.90
S4	7.52	12.1	0.83	NA[c]	NA	NA
S5	5.34	1.58	0.58	53.2	38.5	8.30
S6	6.47	1.58	0.72	34.6	52.5	12.9
S7	7.57	14.2	1.33	NA	NA	NA
S8	7.37	3.85	0.12	50.9	35.7	13.4
S9	7.71	8.08	0.83	38.4	45.4	16.2
S10	5.88	1.07	0.44	21.5	61.0	17.5
Mean[b]	7.01	5.75	1.22	42.6	45.4	12.0
Median[b]	7.44	4.22	0.83	45.8	43.9	13.0

a: Arithmetic mean of three plant samples from each site. b: Arithmetic mean and median for all sampling sites. c: Not available.

with pebbles of ultrabasic rocks, enriched in Cr and Ni. Hence, the soil contamination with Cr and Ni is geogenic, which was also confirmed in distant areas from this deposit [18].

The μ-XRF measurements indicated that mercury was present in isolated hotspots whose major elements are Hg and S (Fig. 3). They could represent cinnabar or metacinnabar; the method is unable to distinguish the two polymorphs. The Hg-S grains are smaller than 100 μm. We note that in the beam diameter of 20 μm, very small grains could remain unnoticed. Spurious signals of elevated Hg concentrations were associated with some quartz grains. Spot analyses in these grains showed broad peaks centered at 10.3 keV, misinterpreted as Hg emission lines. They did not appear in every quartz grain and their intensity was variable even within a single quartz grain. This variability suggests that it could be a diffraction peak from quartz; the exact nature of this spectral feature was not further investigated. It is, however, unlikely that detrital quartz would harbour mercury. EXAFS spectra (L_3) for soil and reference samples are shown in Fig. 4. However, the spectral signal of many soil samples was weak due to the low Hg concentration in the soil. Significant results were obtained only for some soils, where the local coordination of Hg could be compared to its bonding environment in cinnabar/metacinnabar. The best match is the spectrum of metacinnabar, that is, however, not too much different from that of cinnabar. Because of low Hg concentrations, the EXAFS spectra are noisy at

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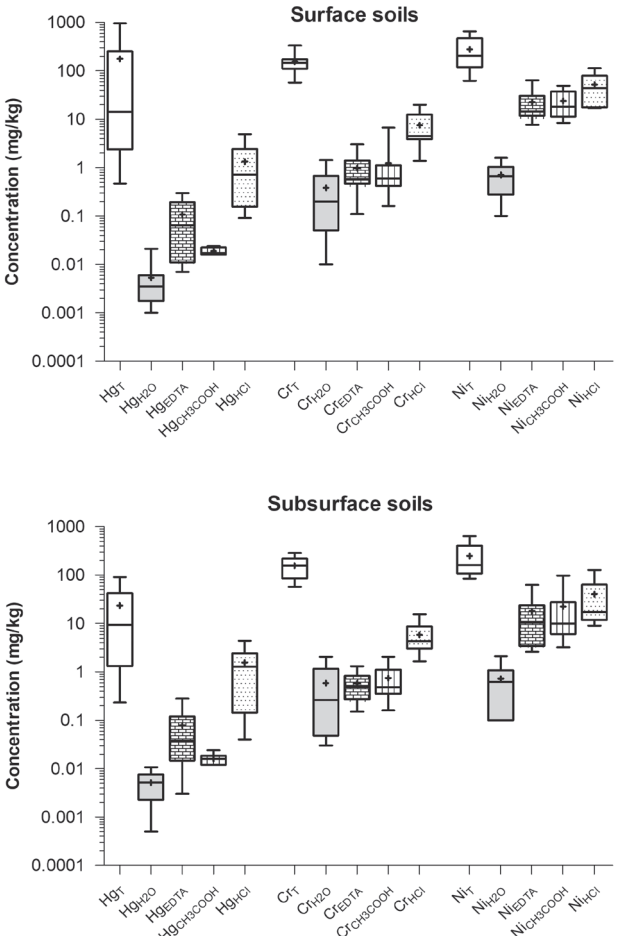

Fig. 2. Total (T) and extractable concentrations of Hg, Cr and Ni using deionised water (H_2O), ethylenediaminetetraacetic (EDTA), acetic (CH_3COOH) and hydrochloric (HCl) acids in mine soils from the abandoned cinnabar deposit of Merník (Eastern Slovakia). Interpretation of the boxplots is the following: the length of the box indicates the interquartile range, the horizontal line within box represents the median, the bars denote the minimum and maximum values and the crosslet is the arithmetic mean.

higher *k* values. This noise precludes a more detailed determination if other spectral components are present, such as Hg adsorbed on Fe oxides or metallic Hg. Nevertheless, if they should be present, they would constitute only minor Hg reservoir in our samples. Most of the Hg is stored in metacinnabar or cinnabar.

Single-Step Extractions and Metal Concentrations in the Common Nettle

The statistics of extractable concentrations of the three trace metals along with the respective total metal concentrations in soils is presented in Fig. 2 and the extractable ratio, expressed as the percentage of the total concentrations in soil that is extracted by each extraction agent, is shown in the form of boxplots (Fig. 5). Statistical comparisons among the extractable ratios of each trace metal showed that the extractability of Ni was significantly higher than that of Hg and Cr

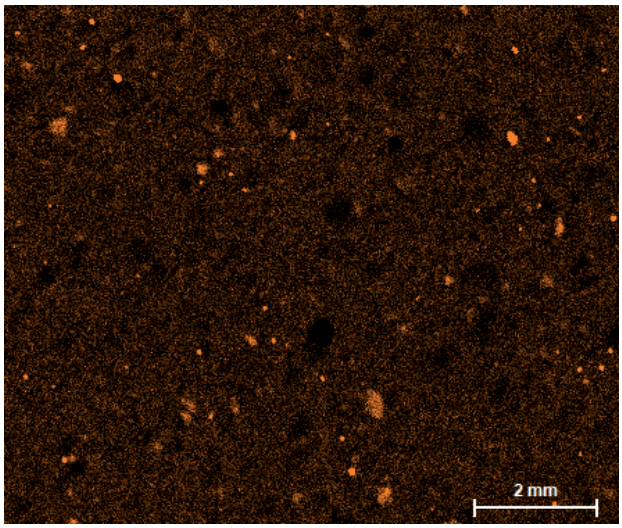

Fig. 3. Distribution of Hg in a thin section made of soil from Merník. Note the individual discrete spots that correlate with spots rich in sulfur. The diffuse, low-concentration anomalies are located in quartz grains and show false elevated concentrations of Hg. For details, see text.

for all reagents, with the exception of extraction with H_2O (no difference between Ni and Cr) (Fig. 5). It can be concluded that Ni is a more mobile and bioavailable metal than the other two metals evaluated. When comparing the efficiencies of the individual extractants for Hg in soils from both sampling depths, HCl was found to be statistically the most effective (with a median of 5.67%), followed by EDTA (0.46%), with no difference in extraction efficiency between H_2O and CH_3COOH solution. The following order in the extraction efficiency of the individual reagents was observed for Ni: HCl ≥ CH_3COOH ≈ EDTA>>H_2O, and finally for Cr, this order: HCl>CH_3COOH ≈ EDTA ≈ H_2O. Extractable metal concentrations were positively

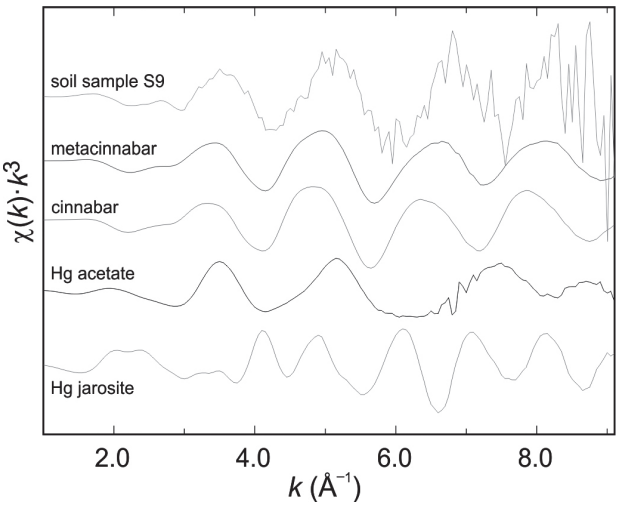

Fig. 4. EXAFS spectra of the soil sample S9 and standards, all collected at the Hg L_3 edge. The spectra are vertically offset for clarity.

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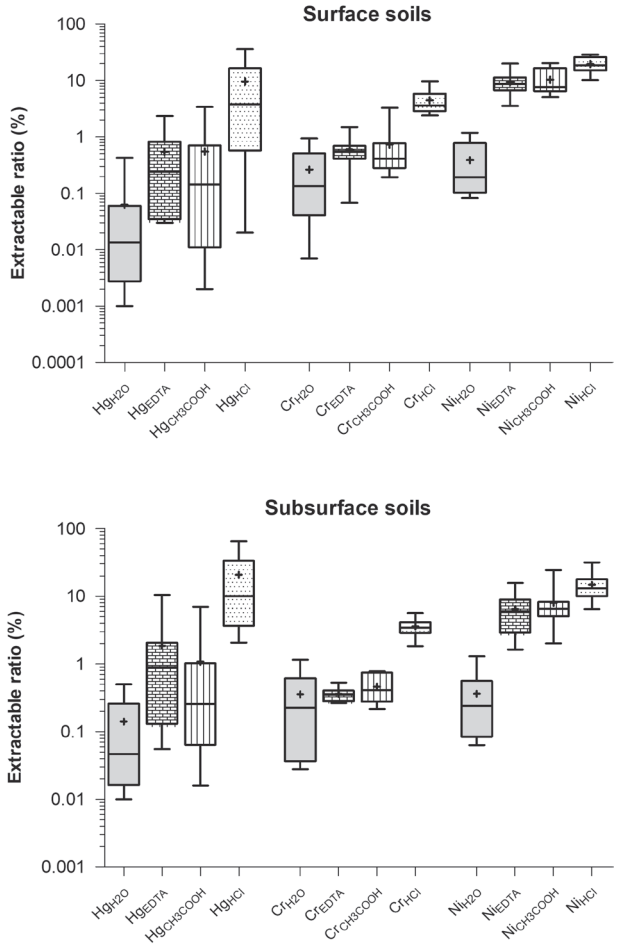

Fig. 5. Extractable ratios of Hg, Cr and Ni using deionised water (H_2O), ethylenediaminetetraacetic (EDTA), acetic (CH_3COOH) and hydrochloric (HCl) acids in mine soils from the abandoned cinnabar deposit of Merník (Eastern Slovakia). Interpretation of the boxplots is the following: the length of the box indicates the interquartile range, the horizontal line within box represents the median, the bars denote the minimum and maximum values and the crosslet is the arithmetic mean.

correlated with the respective total concentrations. The soil pH had a significant (negative) effect on the water-soluble ratios of Cr and Ni (R = –0.61 and –0.64 at P<0.01, respectively), being much higher in soils with acidic pH. Other soil properties did not correlate significantly with extractable ratios. Higher extractable Hg ratios in subsurface soils compared to those in surface soils were noted, while extractable percentage ratios of Cr and Ni did not differ significantly between surface and subsurface soils.

The concentrations of Hg, Cr and Ni in the root and aboveground part of the common nettle (*Urtica dioica*) and the calculated values of BCF and TF are given in Table 2. There were significantly higher concentrations of Hg, Cr and Ni in roots than in aboveground parts in almost all sampling stations, while TF values were below 1.0, with two exceptions. This means that nettle roots served as a biogeochemical barrier for all three elements, which is consistent with previous studies [21, 23, 25]. Mercury concentrations in the aboveground parts were always below 0.05 mg/kg and BCF values were quite low. The roots and aboveground parts of the common nettle had significantly higher concentrations of Cr and Ni than Hg (Ni concentrations were also higher than Cr contents), while BCF for Ni was significantly higher than BCF for Hg and also higher than BCF for Cr, but not significantly. The order of BCF indicates that Ni is most available to the common nettle, followed by Cr and finally Hg, copying the results of *in vitro* extraction assays (Fig. 5). It was documented that total concentration of trace metals in soil or some soil properties could be related to plant metal concentrations [25, 29] but other studies found no relationships [18-19, 21]. Correlation analysis did not confirm positive relationships between Hg, Cr and Ni concentrations in the roots/aboveground parts of nettle and their total concentrations in soil. More importantly, significant positive correlations between water-soluble Cr/Ni concentrations and their concentrations in roots were observed (R = 0.699, P = 0.024 for Cr and R = 0.638, P = 0.047 for Ni). A positive correlation slightly below the significance threshold was also found between water-soluble Hg concentration and its concentration in roots (R = 0.599, P = 0.067). Also, Ni concentration in the aboveground part of the common nettle and BCF values were negatively related to soil pH (R = –0.636 and –0.675, P = 0.048 and 0.032, respectively). No further correlations of trace metal concentrations in plant parts with soil properties or metal concentrations leached by different reagents were documented.

Discussion

The results show that the soils are contaminated with Hg, Cr and Ni due to the mining of cinnabar and the occurrence of ultrabasic-rock fragments in the conglomerates. Mercury concentrations in these mine soils do not deviate from those in soils from other mine areas with cinnabar mineralization [20, 38-42]. Although the soils were shown to have increased concentrations of the three metals studied, they may not yet represent a risk to the environment because environmental hazards are mainly governed by metal mobility and availability. Therefore, the potential availability of Hg, Cr and Ni in these soils as well as their actual transfer to the most widespread plant species at the site were further investigated. In general, low mobilisable Hg ratios were found (Fig. 5), in agreement with the spectroscopic (EXAFS) analysis that indicated that Hg is mostly stored in cinnabar (Fig. 4). Cinnabar possesses high resistance to chemical weathering and releases Hg only very slowly [43-44]. Low mobilisation of Hg corresponds also to the findings of other studies [22, 45]. The transfer of Hg to the common nettle was considerably limited, with BCF values well below 1.0 and Hg concentrations in the aboveground parts below its reference concentration

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Table 2. Arithmetic mean of the concentrations of Hg, Cr and Ni in the common nettle (in mg/kg) and the corresponding values of bioconcentration factor (BCF) and translocation factor (TF) (three independent determinations for each sampling site).

	Hg				Cr				Ni			
Sampling site	Root[a]	Stem+leaves[a]	BCF×1000	TF	Root[a]	Stem+leaves[a]	BCF×1000	TF	Root[a]	Stem+leaves[a]	BCF×1000	TF
S1	0.053	0.008	7.10	0.15	1.20	0.30	3.59	0.21	2.61	1.77	3.99	0.68
S2	0.074	0.037	3.76	0.50	0.88	0.25	9.89	0.28	2.58	1.84	23.9	0.71
S3	0.024	0.012	0.05	0.50	0.67	0.25	5.73	0.37	2.49	2.54	17.7	1.02
S4	0.046	0.018	17.9	0.39	1.15	0.74	7.14	0.64	4.78	2.43	10.7	0.51
S5	0.031	0.008	66.0	0.26	1.42	0.64	9.40	0.45	17.9	8.98	107	0.50
S6	0.052	0.023	0.38	0.44	2.10	1.06	16.2	0.51	12.8	6.09	105	0.48
S7	0.019	0.011	11.2	0.58	1.11	0.57	7.55	0.51	2.94	1.62	12.0	0.55
S8	0.040	0.019	4.63	0.48	1.04	1.13	7.17	1.02	3.00	1.88	10.5	0.63
S9	0.114	0.037	0.61	0.33	2.46	2.37	12.1	0.96	5.01	2.60	9.35	0.52
S10	0.084	0.016	0.09	0.19	3.77	1.26	66.1	0.33	9.81	3.81	158	0.39
Mean[b]	0.054	0.019	11.2	0.38	1.58	0.85	14.5	0.54	6.39	3.36	45.9	0.60
Median[b]	0.049	0.017	4.20	0.42	1.18	0.69	8.48	0.48	3.89	2.49	14.8	0.54
Reference concentration[c]	0.10				1.50				1.50			

a: Arithmetic mean of three plant samples from each site. b: Arithmetic mean and median for all sampling sites. c: Reference concentration in plants (mg/kg) according to Markert [41].

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in plants [46] (Table 2). Relatively low concentrations of Hg in the common nettle and other vegetation species have also been reported in previous studies [23, 25, 47-49] but there are studies, suggesting significant Hg contamination of plants, although with low BCF values [38, 50-53]. No correlations of Hg concentration in roots and aboveground parts of the common nettle with its total soil content, pH, TOC, grain-size distribution and Hg extractable concentrations in single-step procedures (except H_2O extraction) indicate the complexity of metal interaction with soils developed in heterogeneous mine environments. Significant positive relationships between Hg concentration in plants and its total concentration in soils or TOC were established [e.g. 47, 53-55] but in agreement with results obtained in this study, other authors also indicated no such correlations [20, 38, 56]. The results of all *in vitro* extractions showed higher availability of Hg in subsurface soils than in surface soils (Fig. 5). This fact suggests that the mobility and availability of Hg could be influenced by soil properties varying with depth, e.g. organic carbon content. Subsurface soils had lower TOC (Table 1) but the expected negative correlations of Hg extractable ratios with TOC were insignificant, however, not excluding the role of soil organic matter in the retention of Hg in the soils [22]. In general, the low availability of Hg can also be attributed to its binding to cinnabar/metacinnabar found by EXAFS and μ-XRF in surface soils with higher Hg concentrations. It is speculated that the presence of these two stable Hg sulfides in soils could control the transfer of Hg into the common nettle as the lowest BCF values were found for soils with the highest Hg concentration (samples S3, S6, S9 and S10) and probable occurrence of cinnabar/metacinnabar as indicated by EXAFS and μ-XRF mapping. Robson [57] showed that the addition of cinnabar to the soil led to higher Hg concentrations in wheat and rice compared to the control soil but the BCF values were tens of times lower in the cinnabar-amended soil.

Regarding Cr, its plant uptake and potential mobility and availability were higher compared to Hg but still very low. Moreover, the common nettle was not able to translocate Cr from roots to aboveground parts (TF values <0.1). Despite its low availability, Cr was present in the aboveground parts of the plant in concentrations that exceeded the respective reference concentration in plants according to [46] (Table 2). Several studies evaluated the transfer of soil Cr to plants and also recorded its minimal migration with BCF values below 0.1 [13, 21, 23]. From the point of view of geochemical fractionation, Cr in soils occurs mainly in residual pools that are generally stable and not available [11]. Although no attention has been paid here to the mineralogy of chromium in soils, Soták et al. [58] confirmed that Cr occurs in conglomerates in the form of Cr-bearing spinels, i.e. in minerals that are resistant to weathering [59-60]. This also explains the lack of correlations between Cr concentration in the common nettle and the soil physico-chemical properties/total Cr concentration in soil. Only a significant correlation of total Cr concentration in roots with water-extractable Cr concentration was found, which may suggest that the most readily available Cr is preferentially accumulated from the soil.

Nickel was the most mobile and available among the studied metals. The median BCF value for Ni was 2-3 times higher than the BCF values of Hg and Cr (Table 2) and the concentration of Ni in the common nettle exceeded the respective background concentration in plants (1.5 mg/kg) at all sampling sites. The obtained results agree with the study of Čurlík et al. [18] who examined the concentrations of Cr and Ni in plants (common dandelion – *Taraxacum officinale* and common agrimony – *Agrimonia eupatoria*) and confirmed the geogenic contamination of plants growing on soils derived from rocks of the Central Carpathian Paleogene, i.e. in the area geologically similar to that investigated in this study. These authors and others [13, 18, 21, 61-62] also pointed to the higher plant availability of Ni than Cr regardless of different geological and soil conditions. The highest availability of Ni to the common nettle among the studied metals agreed with its highest ratios extractable by EDTA and CH_3COOH solutions, which release Ni from exchangeable positions, bound in carbonates and organic matter [27-28]. Detailed mineralogical studies of mineralization in the ultrabasic rock pebbles in conglomerates showed that Ni occurs here as awaruite and millerite accompanied by supergene Ni-rich vermiculite [31]. Nickel in vermiculite was shown to be located in the interlayer space and the octahedral layer of intercalated vermiculite [63], meaning that Ni could be easily released at least from the interlayer space of vermiculite where it is in exchangeable form. Nickel was also not translocated to the aboveground parts of the common nettle (TF<1.0, Table 2) but it accumulated predominantly in the roots. Nickel sequestration proceeds in the cation exchange sites of the walls of xylem parenchyma cells and immobilization in the vacuoles of the roots [64], the latter mechanisms responsible also for Cr accumulation in plant roots [65]. Bioconcentration factor and water-soluble ratios of Ni were sensitive to soil pH, with higher values in more acid soils, which indicated higher Ni availability from acid soils. An identical finding was described by [18] for Ni uptake by the common dandelion and agrimony. pH-dependent Ni availability is due to the fact that its adsorption and leaching behaviour in soils depend strongly on the soil pH with a significant increase of Ni solubility at pH less than 6.5 [60, 66].

This study reveals that the soils in the abandoned mine area of Merník are contaminated with Hg due to historical cinnabar mining. The specific geology of the mine area also led to geogenic contamination of soils with other trace metals, mostly Cr and Ni (details can be found in an accompanying study of Kulikova et al. [30]). This hints that there would be a risk to the environment resulting from soil contamination.

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However, the results of *in vitro* single-step extractions of the soils and bioavailability study with the common nettle showed that mobile and available ratios of the three trace metals were low. This finally agreed well with previous studies in the mine area, which showed that Hg concentrations in tree leaves were negligible [67] as well as Hg and Cr concentrations in surface and groundwater were low, not exceeding their respective limit values [67-68]. Only the concentrations of Ni in some water samples were increased, which is probably related to its higher leachability found in single-step extractions. Bottom sediments were shown to be enriched in Hg and Ni, suggesting that they serve as a significant sink for these trace metals [67-68], possibly *via* sulfidation. Other works from Slovak mine areas with similar Hg mineralization also showed considerable contamination of soils and sediments with Hg but no significant impact on biota and surface water quality in terms of concentrations of this toxic metal [20, 41, 69-71]. In addition, soil contamination is present only within the former mine area, while Hg concentrations in soils outside the mine area do not exceed the background concentration of 0.08 mg/kg [36]. Therefore, the mine area does not pose any contamination risk to the environment outside it. One of the explanations is that in the mine area of Merník, Hg in soils occurs mostly as cinnabar/metacinnabar. These sulfide minerals have considerable stability towards the chemical weathering in supergene conditions [43-44]. As a result, mobile and plant available ratios of Hg are low and the greatest part of the metal is accumulated in soils and aquatic sediments. From that reason, natural waters typically contain low Hg concentrations [43, 45].

Conclusions

This study aimed to evaluate the potential mobility and environmental availability of three trace metals – Hg, Cr and Ni – in highly disturbed mine soils of the abandoned cinnabar deposit of Merník (Eastern Slovakia). The surface soils of the former mine area are enriched in all three metals (median of 14.2 mg/kg, 146 mg/kg and 206 mg/kg for Hg, Cr and Ni, respectively), with soil contamination related to the Cr- and Ni-enriched bedrock and mining and roasting of Hg ores (mainly cinnabar) in the case of Hg. However, the high total concentrations of trace metals in soils do not mean that the area is hazardous in relation to other components of the environment, such as water, plants and humans. According to *in vitro* single-step extractions with four chemical agents of different reactivity and selectivity (deionised H_2O, CH_3COOH, EDTA and HCl) and the plant uptake study with the common nettle (*Urtica dioica*), Hg and Cr are immobile in soils and their uptake by the common nettle is low, with plant root:soil ratios not exceeding 0.20 and even lower plant aerial part:soil ratios. Complementary experimental work with selected soil samples using μ-XRF and EXAFS techniques, and existing data on the mineralogy of underlying sedimentary formations show that host Hg phases in soils are stable Hg sulfides (cinnabar/metacinnabar) under supergene conditions and Cr is bound to insoluble spinels. This explains the negligible mobility and plant uptake of the two metals in the mine soils of the Merník deposit. Nickel released from soils only in low concentrations and its uptake by *Urtica dioica* was not very significant but compared to Hg and Cr, it had significantly higher availability, which correlated with soil pH. The explanation can be found in the fact that Ni is present in more unstable pools, i.e. exchangeable form and carbonates as indicated by its higher ratios in 0.43 M CH_3COOH and 0.05 M EDTA solutions and sulfides (millerite), alloys (awaruite) and Ni-vermiculite in the pebbles of ultrabasic rocks, which are part of the country rocks of the deposit.

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Conflict of Interest

The authors declare no conflict of interest.

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