Heavy metals and their bioavailability from soils in the long-term polluted Central Spiš region of SR

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ABSTRACT

The heavy metal contents and their bioavailability were monitored in soils of Central Spiš region of SR. This area belongs to long term contaminated and hygienically loaded areas. Soil contamination by heavy metals is caused especially by ore mining, processing and treatment. Soil samples from the Central Spiš contained higher proportions of mobile forms which corresponded to the following sequence Pb > Zn > Cu, while for mobilizable forms the sequence of investigated metals was as follows: Cu > Zn > Pb. Soil pH is one of the parameters that affect significantly the share of bioavailable forms of metals. Higher proportions of mobile fractions of metals were detected in samples taken from soils with acidic pH. Statistical processing confirmed a relationship between the percentage share of lead and zinc in the mobile form and the level of pH/KCl, which was significant for Zn: $r = -0.53$. The relationships for lead and copper were insignificant.

Keywords: heavy metals; soil contamination; heavy metal speciation; bioavailability; mobile and mobilizable form

Soil is considered a critical environment as it accumulates pollutants produced by various anthropogenic activities – industry, agriculture, mining and processing of ores, transportation, etc. In the recent decades, concentration of heavy metals in soil attracted considerable attention because they are non-degradable in comparison with organic pollutants or radionuclides, and in certain concentrations they are essential to plants but in higher concentrations can become toxic. There is always a background level of metals in soil originating from the parent rock; metals can occur in soil in high concentrations in inert, not dangerous forms which, however, may be converted to mobile forms due to changing environmental conditions or changes in soil properties. This situation is considered a "chemical time-bomb" (Stigliani 1993).

Ecotoxicological studies oriented on metal speciation in soil showed that this is one of the key factors affecting uptake of metals by plants. Bioavailability of metals and their potential uptake is determined by the fraction of free metals present in the soil solution in relation to the total content of metals in the solid phase (Hare and Tessier 1996, Moffet and Brand 1996). More detailed analyses showed that chemical properties of metals in soil and their retention in the solid phase of soil is affected by pH, quantity of the metal, cation-exchange capacity, content of organic matter and mineralogy of soil. Changes in chemical properties of soils affect concentration of free metals and result in changes in their availability for plants (Spurgeon and Hopkin 1996). With increasing pH, content of organic matter and clay the solubility of most metals decreases due to their increased adsorption.

The bioavailability of zinc, lead and copper from soil decreases with increasing pH. The decreased availability of metals is affected by higher adsorption and precipitation in alkaline and neutral environments (Moraghan and Mascani 1991, Morel 1997).

The aim of the present study was to determine the bioavailability of heavy metals from soil and

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the influence of pH on the bioavailability in the metal-loaded and hygienically damaged Central Spiš region long-term contaminated by extraction and processing of ores.

MATERIAL AND METHODS

Soil samples from the Central Spiš region of SR were collected to determine the bioavailability of heavy metals contaminating the soil due to anthropogenic load.

Samples were taken in compliance with the relevant methods. Soil samples were air dried, crushed and sieved through a 2 mm mesh prior to analysis.

Soil pH was measured potentiometrically in suspensions. To determine the exchange soil reaction we used 1M KCl and 20 g soil (soil: solution ratio 1:2.5). Samples were agitated on a shaker for 1 h and allowed to stand for 24 h.

Investigation of heavy metals bioavailability from soil focused on releasable, potentially mobilizable and mobile forms. A single-step extraction procedure was used to isolate the individual forms of metals. The releasable forms were determined in a 2M HNO_3 using the present relevant method. The potentially mobilizable forms were extracted with 0.05M EDTA and the mobile forms with 0.1M $CaCl_2$. To prepare the extracts of both forms 10 g of soil was weighed, 100 ml of the reagent was added and the suspension was shaked for 1 h (Ure et al. 1995). The content of selected metals in individual extracts was determined by the AAS method using flame detection and was expressed in mg/kg.

The results obtained were processed statistically using *F*-test, Spearman's rank correlation with simple regression (parameter pH/KCl) and Pearson's correlation. Results of the *F*-test showed whether the values of pH/KCl and mobile fractions of metals originated, with regard to accuracy, from the same set of data and were, therefore, comparable. Spearman' correlation was used to determine rank correlation of the variables and on the basis of this Pearson correlation was determined (correlation coefficients).

RESULTS AND DISCUSSION

The content of releasable, potentially mobilizable and mobile forms of heavy metals in soil samples from Central Spiš area are summarised in Table 1. The levels of heavy metals were evaluated according to the Decision of the Ministry of Agriculture of SR No. 531/1994-540. The present investigations showed that the concentrations of copper, lead and zinc exceeded the reference levels (A_1) and in some soil samples also the indication levels (B).

The table shows that 7.2–257.6 mg/kg of the releasable copper was present in the potentially mobilizable form which comes to 56.3–79.3%; 0.4–1.4 mg/kg of the releasable copper was in the mobile form which constitutes 0.3–3.8%; 1–84.8 mg/kg (7.2–68.5%) of the releasable lead was in potentially mobilizable form and 4.3–7.1 mg/kg (3.2–48.3%) in the mobile form; 0.2–120 mg/kg (4.3–99.6%) of the releasable zinc was in potentially mobilizable form and 0.6–37 mg/kg (1–28.2%) in the mobile form.

Figure 1 shows the mean shares of potentially mobilizable and mobile forms of metals of the releasable content of these metals in soil. Comparison of individual forms of investigated metals – Cu, Pb and Zn – showed that soil samples contained higher share of mobile forms of lead in comparison with copper and zinc and the respective sequence was Pb > Zn > Cu, while for mobile forms the sequence was just the opposite: Cu > Zn > Pb.

The relationship between mobile shares of copper, lead and zinc in their releasable form is shown in Figure 2. A curve was fitted to the exponential data by means of non-linear regression analysis – the least squares method. Correlation coefficients for copper and lead showed a strong relationship ($r = 0.95$ for Cu; $r = 0.96$ for Pb) while no relationship was confirmed for zinc ($r = 0.18$).

One of the most important soil parameters affecting particularly the content of metals in bioavailable forms is pH. Higher proportion of mobile fraction occurs in acidic soils.

A simple regression method was used to determine the relationship between potentially mobilizable and mobile fractions for Cu, Pb and Zn and pH/KCl. On the basis of Spearman's correlation, using a simple regression and considering only the parameter pH/KCl, the following correlation coefficients were obtained for proportion of metals in the mobile fraction and pH/KCl, together with the F-test value for correlation coefficient:

A suitable *F*-test value for $n = 20$ was $F > 2.12$. Based on Table 2, the percentage content of zinc in the mobile fraction was dependent significantly on pH/KCl. There was no significant relationship between percentage shares of mobile fractions of Pb, Cu and pH/KCl. In the case of Pb and Zn, the values of pH/KCl and their mobile fractions

Table 1. Content of releasable, potentially mobilizable and mobile forms of heavy metals in soil samples from the Central Spiš region

Sample	pH (KCl)	Cu 2M HNO_3 (mg/kg)[a]	Cu 0.05M EDTA (mg/kg)[b]	Cu 0.05M EDTA (%)[c]	Cu 0.1M $CaCl_2$ (mg/kg)[d]	Cu 0.1M $CaCl_2$ (%)[e]	Pb 2M HNO_3 (mg/kg)[a]	Pb 0.05M EDTA (mg/kg)[b]	Pb 0.05M EDTA (%)[c]	Pb 0.1M $CaCl_2$ (mg/kg)[d]	Pb 0.1M $CaCl_2$ (%)[e]	Zn 2M HNO_3 (mg/kg)[a]	Zn 0.05M EDTA (mg/kg)[b]	Zn 0.05M EDTA (%)[c]	Zn 0.1M $CaCl_2$ (mg/kg)[d]	Zn 0.1M $CaCl_2$ (%)[e]
1	5.6	17.3	11.9	68.8	0.4	2.3	11.8	2.3	19.5	4.6	39.0	5.1	5.1	99.6	0.6	12.5
2	5.6	14.8	11.0	74.3	0.5	3.4	15.8	3.5	22.2	4.4	27.8	7.2	5.9	82.5	0.7	9.5
3	5.3	21.9	16.3	74.4	0.5	2.3	12.1	2.5	20.7	4.9	40.5	4.7	0.2	4.3	0.8	17.0
4	5.3	10.4	7.2	69.2	0.4	3.8	13.9	1.0	7.2	5.0	36.0	4.4	4.9	111.6	0.7	15.9
5	5.4	26	18.1	69.6	0.4	1.5	12.6	1.9	15.1	5.0	39.7	5.28	5.26	99.6	0.8	15.2
6	4.2	22.9	12.9	56.3	0.6	2.6	14.7	5.0	34.0	7.1	48.3	6.8	3.8	56.1	1.9	28.2
7	5.4	23.4	16.0	68.4	0.5	2.2	16.7	5.8	34.7	6.5	38.9	7.6	4.3	56.9	0.7	9.4
8	5.7	129.2	90.0	69.7	1.0	0.8	60.7	33.5	55.2	6.3	10.4	111.5	65.0	58.3	12.0	10.7
9	7.1	19.4	14.7	75.8	0.5	2.6	21.1	12.1	57.3	6.4	30.3	45.0	21.0	46.7	0.9	1.9
10	5.7	237.4	166.0	69.9	1.4	0.6	101.7	54.7	53.8	6.4	6.3	179.7	105.0	58.4	18.8	10.5
11	6.5	398.6	257.6	64.6	1.1	0.3	190.4	84.8	44.5	6.1	3.2	74.1	29.3	39.5	1.2	1.6
12	6.4	46.1	35.2	76.4	0.5	1.1	40.1	20.0	49.9	6.4	16.0	84.3	44.3	52.6	1.1	1.4
13	3.8	87.7	65.9	75.1	0.6	0.7	75.2	20.8	27.7	6.5	8.6	93.3	41.6	44.6	0.9	1.0
14	5.7	51	33.8	66.3	0.6	1.2	61	12.8	21.0	6.1	10.0	29.9	16.3	54.5	1.3	4.4
15	5.6	32.8	24.9	75.9	0.5	1.5	50.2	10.8	21.5	6.0	12.0	57.8	30.2	52.2	4.1	7.1
16	5.9	30	19.1	63.7	0.6	2.0	23.85	14.9	62.5	5.6	23.3	36.9	19.25	52.2	1.4	3.7
17	5.3	221.0	154.5	69.9	1.1	0.5	95.3	65.2	68.4	4.9	5.1	165.5	120.0	72.5	37.0	22.4
18	5.9	52.0	35.5	68.3	0.6	1.1	38.1	19.7	51.6	4.5	11.8	33.8	18.6	55.0	1.2	3.5
19	6.2	42.16	33.45	79.3	0.5	1.2	30.15	19.4	64.3	4.3	14.1	57.8	34.45	59.6	2.2	3.8
20	6.5	147.0	101.5	69.0	0.7	0.5	67.8	46.4	68.5	4.4	6.4	166.1	97.0	58.4	2.8	1.7

[a]releasable content; [b]potentially mobilizable form; [c]percentage share of potentially mobilizable form of the releasable fraction; [d]mobile form; [e]percentage share of mobile form of the releasable fraction

were comparable with regard to accuracy, which however did not apply to Cu (unsuitable *F*-test value). By revealing the negative correlation between percentage shares of mobile metal fractions and the level of pH/KCl we proved the existence of a non-linear relationship between the respective variables. This relationship means that the share of mobile metal fractions will be higher in acidic soils.

A number of authors (Facchinelli et al. 2001, Chun-Shu Lee and Ming-Muh Kao 2004) considered Cu, Pb and Zn as metals originating from anthropogenic load and Cr, Co and Ni as metals indicating the geogenic load as they are released from the parent rocks. Total concentration of anthropogenic metal (Cu, Zn, Pb) originating from metallurgical dusts, were much higher in top – surface soil than in sub – surface soil. Metal speciation was found to depend strongly on soil properties and metal origin.

Table 2. Relationship between percentage share of the mobile fraction of respective metal and pH/KCl

Element	Coefficient of correlation *r* at P = 95%	*F*-test value for correlation coefficient
Cu	–0.15	1.84
Pb	–0.28	389.07
Zn	–0.53	96.91

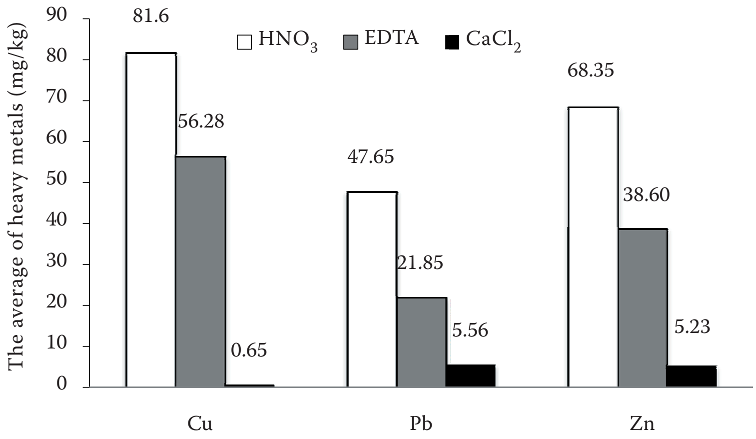

Figure 1. Share of mobilizable and mobile forms of the releasable fraction in soil from the Central Spiš region

A sequential extraction method was used to determine bioavailability of heavy metals from long-term contaminated soils of the Silesian region Tarnowskie Gory. The investigations showed a relatively low bioavailability of metals in this region. Zinc and lead were observed in low bioavailable forms, bound to Fe–Mn oxide or residual fractions. Cadmium was mainly present in exchangeable fraction but some of it also in immobile one. Extractable metals and their contents in wheat were mostly depended on soil pH and were not correlated to their total soil concentration.

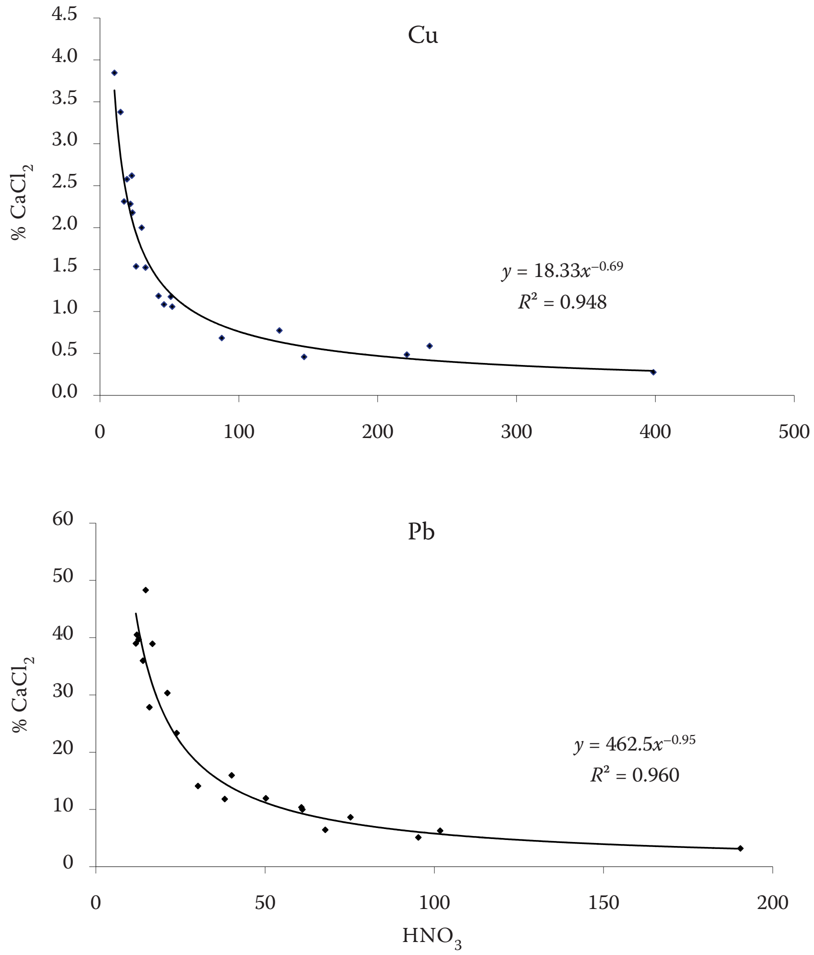

Figure 2. The relationship between the mobile share of the releasable fraction and the content of the releasable fraction in soil from the Central Spiš region

Percentage of bioavailable Pb was the lowest in the most contaminated soils. Generally, Zn, Pb, Cd availabilities decrease as soil pH increases in the range of pH typical for soils (Siebielec et al. 2006).

The study of chemical forms of heavy metals in soil and plants in the copper-mining region showed 30–60 fold higher levels of Cu, Cd, Pb and Zn in comparison with the control. The levels of heavy metals in clover showed a significant positive correlation with their exchangeable and organic forms in soil and significant, even highly significant negative correlation with Fe-Mn oxide and carbonate forms and absence of correlation with residual forms (Wang et al. 2005).

Contamination of soil and plants with heavy metals in industrial regions of China, resulting from ironworks, ore mining and application of sewage sludge was described by Quing-Ren Wang et al. (2003). Concentrations of heavy metals, particularly Cd and Zn in soil was increased significantly in comparison with relevant standards so were increased their extractable forms. The bioavailability of metals from the investigated soils was affected by soil pH. The results of measurements indicated an increased dynamics of contamination of plants grown on such soils and therefore also contamination of the entire food chain. As much as 22–24% of the total concentration of Cd, Cr and Zn in soil accumulated in rice grains which posed a threat to human health.

A number of authors (Vácha et al. 2002, Borůvka et al. 1997) recommended to determine the share of potentially mobilizable and mobile forms of heavy metals of the releasable fraction (2M HNO_3). This content represents maximum potentially mobilizable amount of metals in soil. The authors stated that the content of metals determined with 2M HNO_3 is a more effectual in risk assessment of metals in the environment than total content.

Bioavailability of metals plays a key role in risk assessment for metal contaminated sites such as highly industrialized areas under former and present pressure of metal – ore mining and smelting industry. We can assume that metal availability depends on metal source and the form of the metal that enters the soil as well as time of this presence in soil (Siebielec et al. 2006).

In relation to assessment of the potential risk it is important to know the content of bioavailable forms as well as the properties of soil as this can help significantly to select the measures for reduction of such forms and thus also for reduction of contamination of the food chain.

CONCLUSION

The results obtained during determination of the influence of anthropogenic load on bioavailability of metals from soil allowed us to draw the following conclusions:

1. Soils in Central Spiš are long – term contaminated with anthropogenic metals: Cu, Zn, Pb from metallurgical dusts. Soil samples contained increased contents of mobile forms which corresponded to the following sequence Pb > Zn > Cu, while for potentially mobilizable forms the sequence of investigated metals was as follows: Cu > Zn > Pb.
2. Of the soil parameters, soil pH is one of the parameters that affect significantly the share of bioavailable forms of metals. Increased proportions of mobile fractions of metals in the Central Spiš region were detected in samples taken from soils with acidic pH.
3. Statistical processing confirmed a relationship between the percentage share of lead and zinc in the mobile form and the level of pH/KCl, which was significant for Zn: $r = -0.53$. The relationships for lead and copper were insignificant.

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