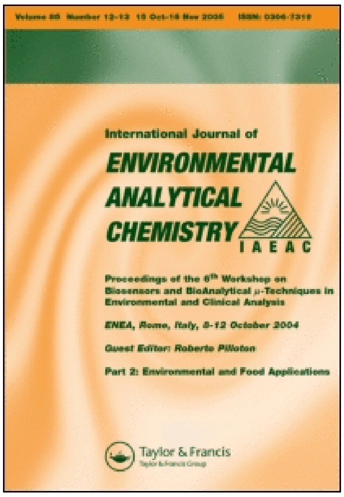

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Trace Element Speciation in Contaminated Soils Studied by Atomic Absorption Spectrometry and Neutron Activation Analysis

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TRACE ELEMENT SPECIATION IN CONTAMINATED SOILS STUDIED BY ATOMIC ABSORPTION SPECTROMETRY AND NEUTRON ACTIVATION ANALYSIS

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Leachable forms of the elements Ag, Cd, Co, Cu, Fe, Li, Mn, Ni, Pb, Sb, and Zn were studied in soils with increased levels of the elements Ag, Cd, Pb, Sb, and Zn due to contamination by sewage sludges from a metallurgical plant as well as in control soil samples. The total element contents, except for Cu, Li, and Pb were determined by INAA. For quality assurance purposes, the reference materials IAEA Soil-5 and IAEA Soil-7 were also analyzed. Partitioning of the elements was studied by AAS and partly by NAA using a multi-step sequential leaching procedure designed to divide elements into five fractions: exchangeable metals, metals bound to carbonates, metals bound to Fe-Mn oxides, metals bound to organic matter, residual metals. Of the metals studied, cadmium appeared to be most readily solubilized from the soil samples. Differences in leachabilities of the elements Co, Fe, and Zn from unirradiated and reactor irradiated samples are discussed.

KEY WORDS: Contaminated soils, element partitioning, sequential leaching procedure, AAS, NAA.

INTRODUCTION

In recent years increased industrialization has led to the environment contamination with many elements including the toxic ones. Contamination of soils may present a long-term risk for ecosystems because of sorption, ion-exchange, and complexing properties of soil components. In the field of environmental control and agricultural chemistry it is becoming apparent that knowledge of chemical forms or association of trace metals in soils is more important than the total element contents. The knowledge of chemical forms of elements is essential for estimating their biological availability, physico-chemical reactivity, and element transport in the environment and into the food-chain.

In response to this increased awareness of the importance of trace element speciation, various leaching procedures have been suggested to study element transfer from soils. Leaching with water is the simplest treatment that matches well the soil-water system and provides information on amounts of water-soluble element forms. Leaching with 6 M HCl or 6 M HNO_3 is considered to inform on

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maximum leachable element amounts that cannot be exceeded in the natural conditions. Exchangeable element fractions were studied by leaching with magnesium chloride, calcium chloride, potassium chloride, ammonium or sodium acetate solutions while complexing agents such as EDTA, DTPA, acetic acid were employed to study element portions bound to organic compounds.[1-4] An increasing concern is now being paid to multi-step sequential leaching procedures that are thought to be useful for estimating the relative importance of various chemical forms in controlling trace metal transport and biological availability.[5-6]

In this work, leachable forms of the elements Ag, Cd, Co, Cu, Fe, Li, Mn, Ni, Pb, Sb, and Zn were studied in soils contaminated by sewage sludges from a metallurgical plant after accidental flooding of agricultural land from a dumping place. The total element contents were determined by instrumental neutron activation analysis (INAA), except for Cu, Li, and Pb, and leachable element forms were studied by atomic absorption spectrometry (AAS) and partly by NAA employing the procedure by Tessier *et al.*[6] for sediment samples. For quality assurance purposes, reference materials IAEA Soil-5[7] and IAEA Soil-7[8] were analyzed by INAA, too.

EXPERIMENTAL

Collection and Preparation of Soil Samples

Two soil samples denoted A, B were taken from the contaminated area, one control sample C1 was taken from the vicinity of the contaminated area and one control sample C2 was taken from a quite geologically different region. The soils A, B, C1 were of the loam type with pH 4.8–5.0 whereas the soil C2 was of the sandy loam type with pH 7.8. About 1.5–2.00 kg soil samples were collected from the 5 cm-surface layer, air dryed, homogenized in an agate mortar and sieved. A fraction with particle size ≤ 2 mm was taken for analysis. Homogeneity of the sieved fraction was tested by determining the studied elements by AAS according to Doerffel and Eckschlager[9] and it was found that inhomogeneity did not significantly exceed the measurement error for sample weight of 1 g.

Leaching

The soil samples were subjected to the sequential extraction procedure according to Tessier *et al.*[6] designed to partition studied metals into the following five fractions:

a) Fraction 1—exchangeable metals: The soil sample was extracted for 10 min with 1 M $MgCl_2$ at pH 7.0 using a shaking device.

b) Fraction 2—metals bound to carbonates: The residue from the step 1 was extracted for 5 hrs with 1 M sodium acetate (NaAc) adjusted to pH 5.0 with acetic acid (HAc) using a shaking device.

c) Fraction 3—metals bound to Fe-Mn oxides: The residue from the step 2 was leached for 6 hrs at 96 °C ± 2 °C with 0.04 M $NH_2OH.HCl$ in 25% (v/v) HAc employing occasional mixing.

d) Fraction 4—metals bound to organic matter: The residue from the step 3 was leached with 0.02 M HNO_3 and 30% H_2O_2 adjusted to pH 2 with HNO_3 at 85 °C ± 2 °C for 4 hrs with intermittent agitation. After cooling, 3.2 M MN_4Ac in 20% (v/v) HAc was added to the sample and agitated continuously at room teperature for 30 min.

e) Fraction 5—residual metals: The residue from the step 4 was dried and mineralized with a mixture of concentrated HF and $HClO_4$ (2:1), evaporated almost to dryness and then $HClO_4$ was added and evaporated until white fumes. The residue was dissolved in 100 ml of 3 M HCl.

After each step, separation was carried out by centrifuging at 3000 rpm for 10 min. The supernatant was withdrawn and aliquots were analyzed for trace metals whereas the residue was washed twice with water. After centrifugation these second and the third supernatants were discarded.

For AAS measurements the 5 g soil samples were treated with 40 ml of solutions in the steps 1 and 2, and with 100 ml of the solution in the step 3. In the step 4, 15 ml of HNO_3 was used, first 25 ml of H_2O_2 was applied for 2 hrs and then another 15 ml portion of the 30% H_2O_2 solution was added. Finally, 25 ml of the 3.2 M NH_4Ac solution were added to prevent back-sorption of extracted metals onto the oxidized sediment. In the step 5, 2 × 50 ml of the HF + $HClO_4$ mixture were used and after evaporation 2 ml of concentrated $HClO_4$ were added.

The leaching experiments studied by NAA were carried out with ten times lower weight of irradiated soil samples (e.g. 0.5 g) and volumes of leaching solutions for fractions 1–4. The results for the fraction 5 were obtained as a difference from the total contents and the contents in the residue of the fractions 1–4.

Atomic Absorption Spectrometry

Analyses were carried out by a flame-AAS technique with a Varian-Techtron AA875 spectrometer equipped with a PSC 55 autosampler. The parameters recommended by the producer for the acetylene—air flame were employed.[10] For the calibration, synthetic standard solutions prepared in corresponding media were used.

Neutron Activation Analysis

INAA was employed for the determination of total element contents. The soil samples were additionally grinded and homogenized in an agate mill (Pulverizette 5, Fritsch) and about 200 mg subsamples were taken for analysis. They were heat sealed into polyethylene (PE) capsules and irradiated along with synthetic multielemental standards, in the active core of a nuclear reactor VVR-S of the

NRI, Řež in which the thermal neutron flux density amounted to $5.10^{13}\,n.cm^{-2}.s^{-1}$. The standard preparation, irradiation conditions, gamma-ray spectroscopy methods, and data analysis were similar to those described previously for coal fly ash analysis.[11]

For leaching experiments, long-lived radionuclides were used only. After the determination of the total element contents, the PE capsules were opened, three replicate samples of particular soils were combined, mixed and one sample of the 0.5 g weight was prepared for leaching. Aliquots of the solutions resulting from the leaching experiment ($\frac{3}{4}$–$\frac{4}{5}$ of volumes) were adjusted to the same volume of 8 ml in PE flasks and measured by high resolution gamma-ray spectroscopy. Relative amounts of radionuclides in the fractions 1–4 were evaluated from these measurements whereas results for the fraction 5 were obtained as mentioned above.

RESULTS AND DISCUSSION

The total element contents in contaminated soils A, B and control samples C1, C2 determined by INAA from 3 replicates are shown in Table 1 along with average soil composition according to Bowen.[12] Only the contents of the elements Cu, Li, and Pb were calculated as a sum of the element concentrations in the fractions 1–5 determined by AAS. From the comparison of the found and Bowen's values it can be concluded that in the contaminated soils there are considerably increased levels of the elements Ag, Cd, Pb, Sb, and Zn. However, high contents of Mn and Pb appear also in the control sample C1. The high contents of these elements are typical for the area where the soil samples were collected because there are polymetallic ore bodies in the vicinity and increased levels of the elements can also appear in the surface soil layers.

Accuracy and precision of the INAA procedure used can be inferred from the results of control analyses of reference materials IAEA Soil-5 and IAEA Soil-7 that are listed in Table 2. A very good agreement was found between our results and the IAEA certified and/or information value[7,8] because our mean values fall well within the IAEA uncertainty margins. Only somewhat higher value for titanium in Soil-5 compared to the IAEA information value was found. Thus, very good accuracy of the INAA analyses performed seems to be demonstrated.

Results of leaching experiments as determined by AAS (except for Ag and Sb) are summarized in Tables 3–6 in relative per cent of total element contents leached out in particular fractions. The results obtained by AAS are mean values calculated from two independent leaching experiments in which each element concentration was determined from three AAS measurements. The standard deviation due to measurement repeatability did not exceed 3% relative and results of two leaching experiments differed in the range of 2–8% relative. An accuracy check of the AAS determinations was done by calculating a sum of element concentrations found in the fractions 1–5 and comparing it with the total contents determined by INAA. Both values are given at the bottom of Tables 3–5. An acceptable agreement of the AAS and INAA results was found for the elements Fe, Mn, and Zn in most samples studied while positively biased results for the

Table 1 Elemental characterization of soils

Element ($\mu g\ g^{-1}$)[a]	Soil A	Soil B	Soil C1	Soil C2	Mean composition of soils[12]	
	$\bar{x} \pm s$ ($n=3$)[b]	$\bar{x} \pm s$ ($n=3$)	$\bar{x} \pm s$ ($n=3$)	$\bar{x} \pm s$ ($n=3$)	Median	Range
Ag	25.3±0.4	10.7±0.3	4.4±0.3	<0.3	0.05	(0.01–8)
Al (%)	4.20±0.02	3.93±0.10	4.62±0.06	2.50±0.02	7.1	(1–30)
As	39.8±0.5	118±3	66.6±3.2	6.4±0.3	6	(0.1–40)
Ba	629±23	421±6	583±17	199±19	500	(100–3,000)
Cd	20±5	11±1	<5	<5	0.35	(0.01–2)
Ce	50.3±0.5	56.6±6.4	55.3±1.8	40.7±1.6	50	(3–170)
Co	15.2±0.4	11.1±0.3	14.6±0.3	3.57±0.06	8	(0.05–65)
Cr	59±2	47±1	67±1	35±2	70	(5–1,500)
Cs	3.74±0.10	3.00±0.04	6.03±0.15	1.59±0.03	4	(0.3–20)
Cu[c]	72.2	36.7	37.2	13.6	30	(2–250)
Eu	1.25±0.03	0.98±0.05	1.20±0.04	0.41±0.02	1	(0.1–3.2)
Fe (%)	3.45±0.07	2.28±0.16	3.23±0.06	0.973±0.014	4	(0.2–55)
K (%)	1.01±0.04	0.837±0.034	1.11±0.03	0.767±0.018	1.4	(0.08–3.7)
La	19.3±0.6	21.0±3.8	19.9±0.7	17.0±0.5	40	(2–80)
Li[c]	7.3	6.8	9.1	—	25	(3–350)
Mn	4,256±68	1,768±20	11,570±260	300±3	1,000	(20–10,000)
Na (%)	0.601±0.006	0.577±0.007	0.422±0.008	0.236±0.010	0.5	(0.015–2.5)
Ni	26±6	23±4	18±5	<10	50	(2–750)
Pb[c]	3,035	1,470	1,724	15	35	(2–300)
Rb	41±1	45±1	66±3	54±2	150	(20–1,000)
Sb	167±3	55.7±0.4	44.8±0.6	0.54±0.02	1	(0.2–10)
Sc	9.36±0.12	796±0.39	12.66±0.25	3.30±0.06	7	(0.5–55)
Sm	4.09±0.03	4.29±0.28	5.15±0.13	2.84±0.13	4.5	(0.6–23)
Sr	<450	<330	1,460±88	<150	250	(4–2,000)
Th	5.33±0.25	5.23±0.30	5.03±0.29	6.10±0.17	9	(1–35)
Ti	401±7	329±20	392±150	246±4	5,000	(150–25,000)
U	3.8±0.3	2.8±0.1	5.8±0.1	1.8±0.1	2	(0.7–9)
V	70.9±2.4	55.0±1.1	87.0±2.1	29.2±0.8	90	(3–500)
W	10.1±0.6	3.2±0.1	2.4±1.0	2.32±0.04	1.5	(0.5–83)
Zn	3,022±43	1,619±24	480±12	54±2	90	(1–900)

[a] Unless otherwise stated.

[b] n = number of replicates.

[c] Determined by AAS as a sum in the fractions 1–5 ($n=2$).

elements Cd and Co and negatively biased results for Ni were obtained by AAS. However, considering that the main aim of the study was the determination of relative element amounts leachable in particular fraction and owing to uncertainties involved in the total content determination from the AAS measurements of 5 fractions, the discrepancies observed can be disregarded as far as the present study is concerned.

The NAA results for Ag and Sb were obtained from a single experiment by leaching the irradiated samples and measuring radioactivity of particular long-lived radionuclides (^{110m}Ag and ^{124}Sb, respectively). Besides these two elements, the leaching of the elements Co, Fe, and Zn from the irradiated samples by

Table 2 Elemental composition of soil reference materials

Element ($\mu g\ g^{-1}$)[a]	*IAEA Soil-5*		*IAEA Soil-7*		
	This work	*IAEA value*[7]	*This work*	*IAEA value*[8]	
	$\bar{x} \pm s$ $(n=3)$	$\bar{x} = 95\%$ *CI*[b]	$\bar{x} \pm s$ $(n=3)$	$\bar{x}$	(95% *CI*[b])
Ag	1.2±0.2	(1.9)[e]	0.8±0.2	—	—
Al (%)	8.30±0.25	8.19±0.28[c]	4.89±0.03	4.7	(4.4–5.1)[e]
As	93.4±2.7	93.9±7.5[c]	13.0±1.8	13.4	(12.5–14.2)[c]
Ba	533±25	561±53[c]	176±21	(159)	(131–196)[e]
Cd	<5	1.5[e]	<2	(1.3)	(1.1–2.7)[e]
Ce	57.8±2.5	59.7±3.0[c]	59.2±2.6	61	(50–63)[d]
Co	14.8±0.4	14.8±0.76[c]	8.6±0.3	8.9	(8.4–10.1)[c]
Cr	28.1±2.1	28.9±2.8[d]	65.0±2.7	60	(49–74)[d]
Cs	57.4±2.4	56.7±3.3[c]	5.20±0.17	5.4	(4.9–6.4)[d]
Dy	3.8±0.2	4.0±1.0[d]	3.9±0.2	3.9	(3.2–5.3)[d]
Eu	1.11±0.05	1.18±0.08[d]	0.98±0.05	1.0	(0.9–1.3)[d]
Fe (%)	4.36±0.15	4.45±0.19[d]	2.49±0.10	(2.57)	(2.52–2.63)[e]
Hf	6.10±0.44	6.30±0.30[d]	5.15±0.36	5.1	(4.8–5.5)[c]
K (%)	1.83±0.05	1.86±0.15[c]	1.16±0.03	1.21	(1.13–1.27)[e]
La	27.2±0.6	28.1±1.5[c]	27.8±0.9	28	(27–29)[d]
Mn	900±25	852±37[d]	650±10	631	(604–650)[c]
Na (%)	1.95±0.02	1.92±0.11[c]	0.235±0.020	(0.24)	(0.23–0.25)[e]
Ni	<20	13[e]	<30	26	(21–37)[e]
Rb	132±5	138±7.4[c]	53±4	51	(47–56)[c]
Sb	14.8±0.5	14.3±2.2[d]	1.68±0.17	1.7	(1.4–1.8)[d]
Sc	14.81±0.35	14.8±0.66[c]	8.50±0.21	8.3	(6.9–9.0)[d]
Sm	5.18±0.17	5.42±0.39[d]	5.01±0.16	5.1	(4.8–5.5)[d]
Sr	310±51	(330)[e]	105±20	108	(103–114)[d]
Ta	0.75±0.09	0.764±0.056[d]	0.65±0.07	0.8	(0.6–1.0)[d]
Th	10.90±0.15	1.33±0.73[c]	8.13±0.24	8.2	(6.5–8.7)[d]
Ti	5,360±180	(4,700)[e]	3,440±170	(3,000)	(2,600–3,700)[e]
U	3.2±0.3	3.04±0.51[d]	2.4±0.2	2.6	(2.2–3.3)[c]
V	150±4	(151)[e]	71.7±2.1	66	(59–73)[c]
W	4.5±0.9	(5.1)[e]	1.3±0.8	—	—
Zn	379±10	368±8.2[c]	110±7	104	(101–113)[c]

[a] Unless otherwise stated.

[b] Confidence limit of the mean for a significance level $\alpha = 0.05$.

[c] Recommended with a relatively high degree of confidence (Soil-5), certified with a satisfactory degree of confidence (Soil-7).

[d] Recommended with a reasonable degree of confidence (Soil-5), certified with acceptable degree of confidence (Soil-7).

[e] Information (non-certified) values.

measuring activities of ^{60}Co, ^{59}Fe, and ^{65}Zn, respectively, was also followed to compare these results with the AAS ones. Somewhat different yields of the latter elements in particular leachates were observed compared to those determined in unirradiated samples by AAS. For cobalt, 10–20% higher yields in the fractions 1, 2 and lower yields in the fractions 3 and 5 (about 20–30% and 5–10%, respectively) were evaluated from the NAA results. For iron, 15–20% higher yields in the fractions 3 and about 15% lower yields in the fractions 5 were determined by NAA. For zinc, about 10% higher yields were found in the fractions 2 and 5 whereas lower yields were determined by NAA in the fractions 1 and 3 (5–10% and 10–20%, respectively). These differences apply for the samples A, B, C1.

Table 3 Partitioning of elements in the contaminated soil A

Fraction	*Relative contents, %*										
	Ag[b]	*Cd*[a]	*Co*[a]	*Cu*[a]	*Fe*[a]	*Li*[a]	*Mn*[a]	*Ni*[a]	*Pb*[a]	*Sb*[b]	*Zn*[a]
1	2.1	59.6	0.4	0.1	0.02	<0.1	2.4	3.7	7.0	1.9	22.6
2	<0.9	10.6	2.7	2.3	0.08	<0.1	1.2	2.5	4.0	9.8	5.0
3	22.5	24.4	61.6	33.9	33.9	16.4	69.3	21.2	70.3	12.4	59.1
4	31.4	0.8	3.1	41.1	3.4	4.4	16.3	8.8	9.8	5.2	3.3
5	43.1	4.6	32.2	22.6	62.5	79.0	10.8	63.8	8.9	70.7	10.0
Method	*Absolute content,* $\mu g\, g^{-1}$[c]										
AAS	—	28.3	20.8	72.2	3.53	7.27	4,198	16.0	3,035	—	2,935
INAA	25.3±0.4	20±5	15.2±0.4	—	3.45±0.07 (%)	—	4,256±68	26±6	—	167±3	3,022±43

[a] Determined by AAS.
[b] Determined by INAA.
[c] Unless otherwise stated.

Table 4 Partitioning of elements in the contaminated soil B

Fraction	*Relative contents, %*										
	Ag[b]	*Cd*[a]	*Co*[a]	*Cu*[a]	*Fe*[a]	*Li*[a]	*Mn*[a]	*Ni*[a]	*Pb*[a]	*Sb*[b]	*Zn*[a]
1	2.6	64.6	<0.1	<0.1	0.1	<0.1	2.6	4.1	8.5	<0.5	26.3
2	<1.1	8.0	1.3	2.2	0.1	<0.1	1.4	1.4	5.0	7.4	4.4
3	48.6	23.3	56.7	24.7	32.1	25.0	77.8	22.4	68.9	8.4	56.7
4	9.1	<0.1	1.9	37.6	2.5	7.4	8.0	10.9	9.0	5.2	3.8
5	38.6	4.0	40.0	35.4	65.2	67.4	10.2	61.2	8.6	78.5	8.8
Method	*Absolute content,* $\mu g\, g^{-1}$[c]										
AAS	—	15.0	15.5	36.7	2.43	6.80	1,767	14.7	1,474	—	1,722
INAA	10.7±0.3	11±1	11.1±0.3	—	2.28±0.16 (%)	—	1,768±20	23±4	—	55±4	1,619±24

[a] Determined by AAS.
[b] Determined by INAA.
[c] Unless otherwise stated.

Another pattern of differences was found for the sample C2. This indicates that both procedures used to study leachable amounts of elements do not provide quite comparable results. Two explanations can be assumed for the differences observed. First, the samples analyzed by INAA and consequently used for leaching experiments were additionally grinded and homogenized prior to irradiation to assure sufficient homogeneity for smaller sample weights used in contrast to the AAS procedure. Although the same solid-to-liquid phase ratio was kept, enlarged surface of the solid phase might influence the leaching of elements. The second reason can be a consequence of the irradiation in the reactor by high fluences of neutrons and gamma-rays. Under these circumstances, physico-chemical properties of soils, especially of organic constituents, are changed owing to breakage of

Table 5 Partitioning of elements in the contaminated soil C1

Fraction	*Relative contents, %*										
	Ag[b]	*Cd*[a]	*Co*[a]	*Cu*[a]	*Fe*[a]	*Li*[a]	*Mn*[a]	*Ni*[a]	*Pb*[a]	*Sb*[b]	*Zn*[a]
1	<1.0	45.8	<0.1	<0.1	0.08	<0.1	1.2	3.0	5.5	<0.3	12.8
2	<1.6	6.2	<0.1	0.5	0.02	<0.1	0.5	1.5	2.2	2.4	3.1
3	14.8	35.4	56.5	18.0	26.7	23.1	0.3	13.0	64.0	2.5	38.2
4	11.0	<0.1	2.8	33.6	1.7	6.6	0.9	18.2	7.0	2.6	9.4
5	71.6	12.5	40.5	47.8	71.5	70.1	97.1	64.1	20.3	92.2	36.4
Method	*Absolute content,* $\mu g\,g^{-1}$[c]										
AAS	—	4.8	17.8	37.2	2.79	9.1	10,269	13.1	1,724	—	319
INAA	4.4±0.3	<5	14.6±0.3	—	3.23±0.06	—	11,750±260	18±5	—	44.8±0.6	380±12
					(%)						

[a] Determined by AAS.
[b] Determined by INAA.
[c] Unless otherwise stated.

Table 6 Partitioning of elements in the control soil C2

Fraction	*Relative contents, %*										
	Ag[b]	*Cd*[a]	*Co*[a]	*Cu*[a]	*Fe*[a]	*Li*[a]	*Mn*[a]	*Ni*[a]	*Pb*[a]	*Sb*[b]	*Zn*[a]
1	ND	47.5	31.4	5.9	0.9	—	9.0	6.5	29.4	<3.1	4.9
2	ND	23.8	20.6	12.5	0.3	—	5.6	8.6	4.1	<3.0	9.9
3	ND	<0.1	18.4	8.8	32.3	—	67.4	45.6	<0.1	<3.7	34.6
4	ND	4.8	4.9	19.9	4.7	—	1.6	30.4	<0.1	<3.2	22.2
5	ND	23.8	24.6	52.9	61.8	—	16.4	10.9	66.3	87.7	29.6
Method	*Absolute content,* $\mu g\,g^{-1}$										
AAS	—	2.1	8.1	13.6	10,184	—	377	4.6	14.6	—	81
INAA	<0.3	<5	3.57±0.06	—	9,730±140	—	300±3	<10	—	0.54±0.02	54±2
					(%)						

[a] Determined by AAS.
[b] Determined by INAA.
ND Not detected.

chemical bounds, changes in association of elements in soil components or element valency by radiolytic decomposition or recoil effects. The detailed discussion of the gamma and other radiation damage and specific recoil effects on leachability of neutron irradiated coal fly ash has been given by James *et al.*[13] These authors concluded on minor radiation damage and observed changes of leachability of elements with deionized water in a similar extent as in our work except for antimony where 715% difference was found compared to unirradiated ash. In the case of soils where a part of elements is bound to organic substances, the differences of element leachabilities from irradiated and unirradiated samples may differ not only in comparison with fly ash but they may also depend on a soil type as observed in our work. This remains to be evaluated in a further study. Thus, interpreting leachability of Ag and Sb from irradiated soils and comparing that with results determined from unirradiated samples should be done with caution.

Results of partitioning of elements studied in the samples A, B, C1 can be summarized as follows. The fraction of exchangeable metals (fraction 1) includes those held by electrostatic adsorption as well as those specifically adsorbed. The highest percentage of total cadmium, about 25% and 10% of zinc and lead, respectively and only a small percentage of other metals were found in this fraction. The absolute concentrations of exchangeable metals decrease in the order Mn > Pb > Zn > Fe > Cd > Ni > Co > Cu > in the control sample C1 and the order is changed as Zn > Pb > Mn > Fe > Cd > Sb > Ag > Co > Cu in the contaminated soils A, B.

In the carbonate-bound metals fraction (fraction 2), the lowest percentage of total metal contents were found except for cadmium. The absolute concentrations decrease in the order Pb > Mn > Zn > Fe > Sb > Cd > Cu > Ni for the C1 sample whereas the order is Zn > Pb > Mn > Fe > Sb > Cd > Cu > Co > Ni for the samples A, B. The high percentage of Cd and high concentrations of Pb and Zn found in the exchangeable and carbonate-bound metals fraction suggest that these portions of the elements can easily be solubilized and become readily available from contaminated soils by an increase in salinity and/or by lowering pH as a consequence of acid rains, for instance. This may be especially harmful for ecosystems and for transfer into the food chain in the case of contamination with Cd and Pb.

Metal concentrations and their percentage bound to the Fe-Mn oxides (fraction 3) are relatively high and constitute a large portion of the nonresidual metals except for Cd. The highest percentage of the elements Co, Mn, Pb, and Zn was found here. Trace metal concentrations in this fraction should depend on such factors as the affinity of various metals for the Fe-Mn oxides and the concentration of the former available. The absolute concentrations in this fraction decrease in the order Fe > Pb > Zn > Mn > Co > Cu > Li > Cd > Ni > Sb > Ag in the control sample C1 while in the order Fe > Mn > Pb > Zn > Cu > Co > Sb > (Ag) > Cd > Ni > (Ag) > Li in the contaminated samples.

Treatment of soils with nitric acid and acidized hydrogen peroxide in the fraction 4 oxidizes a large portion of the organic matter and sulfide minerals present and thus organically complexed and/or sulfide-bound metals can be preferably solubilized. A high percentage of Cu and in some cases not negligible percentage of Mn, Ni, and Pb was found in this fraction. This can be explained by the highest stability constants of Cu with many organic ligands of the metals considered.[14,15] The absolute metal concentrations follow the order Fe > Pb > Mn > Zn > Cu > Ni > Sb > Li > Co > Ag > Cd for the control sample and a rather similar order Fe > Mn > Pb > Zn > Cu > Sb > Ag > Ni > Co > Li > Cd can be observed for the contaminated samples.

The residual trace metals in the fraction 5 are those associated with detrital silicate minerals, resistant sulfides, and refractory organic materials. Metals found in this fraction are expected to be chemically stable and biologically inactive. The highest percentages of Fe, Li, Ni and considerable portions of Co, Cu, Mn, and Pb in some cases were found in this fraction. The absolute metal concentrations in the fraction 5 decrease in the order Fe > Mn > Pb > Zn > Sb > Cu > Ni > Co > Li > Ag > Cd in the control soil C1 and similarly in the order Fe > Mn > Zn > Pb > Sb > Cu > Ni > (Ag) > Co > Li > (Ag) > Cd in the contaminated soils.

By comparing the results in Table 6 with those in Tables 3–5 it can be seen that somewhat different pattern of metal leachabilities were found for the control sample C2 because of a different soil type. Obviously, the multi-step sequential leaching procedure may be used for a certain type of soil geochemical characterization.

CONCLUSIONS

The multi-step sequential leaching procedure used in this work was found profitable to study geochemical behaviour of elements in soils and to estimate bioavailability of elements contained in soils in anomalously high concentrations as a consequence of contamination by industrial sewage sludges. Application of the procedure to three soils of the same type (two of them contaminated) yielded reasonably constant speciation patterns for the metals studied while another pattern for the majority of metals was observed for a soil of another type. Of the elements studied, cadmium appeared to be most readily solubilized what makes the element potentially bioavailable. This may present a real threat for cadmium transfer into the food chain from agricultural land contaminated by cadmium rich sewage sludges or fertilizers, especially in the connection with acid rains.

Reference materials of soils and independent analytical techniques AAS and NAA were employed to check accuracy of analyses performed. In most cases, an acceptable agreement was found between the results of the INAA and AAS determination of total element contents in the soils studied (the AAS values were calculated from element portions found in particular fractions). In this way, the results of the AAS determination of element leachabilities were validated. However, differences up to 30% relative were observed for partitioning of the elements Co, Fe, and Zn that was studied both by AAS on unirradiated samples and by NAA on samples irradiated in the nuclear reactor. Two explanations for the differences found were suggested. Nevertheless, a more detailed study for more elements is needed to elucidate the effect of reactor irradiation on element leachabilities.

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