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Selective leaching of elements associated with Mn – Fe oxides in forest soil, and comparison of two sequential extraction methods

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Abstract For selective dissolution of Mn oxides as components of soil (easily reducible oxides) 0.05 mol L⁻¹ and 0.1 mol L⁻¹ NH₂OH·HCl acidified to pH 2 and for dissolution of Fe oxides (crystalline form of the oxides) 0.25 mol L⁻¹ NH₂OH·HCl in 25% acetic acid, 0.2 mol L⁻¹ oxalate buffer and 0.1 mol L⁻¹ ascorbic acid in oxalate buffer were tested. Dissolved elements were determined by ICP–MS and ICP–OES. The studies indicate that the use of 0.05 mol L⁻¹ NH₂OH·HCl in nitric acid solution (pH 2) and 0.1 mol L⁻¹ ascorbic acid in 0.2 mol L⁻¹ oxalate buffer led to selective leaching of trace metals bound by Mn and Fe oxide phases in soil. Comparison of different extraction schemes indicates that the trace elements investigated are mainly bound to minerals consisting of crystalline Fe oxides and insoluble minerals (under the extraction conditions used). The studies also indicate that Mn oxides and organic matter retain a major mobile fraction of the elements investigated in the soil.

Introduction

A sequential extraction scheme has been used to assess the mobile fraction of different elements, and their proportions in different host phases of soil, sediments, and urban roads [1, 2, 3, 4, 5]. With the aid of chemical extraction the phases of soil are not defined strictly chemically but just operationally by using solutions of different reagents, different pH, or different concentration.

Two different schemes applied to the same set of samples can lead to different estimates of the binding of trace elements to the proposed host phases [6]. It is also emphasized that the results from sequential extraction studies

are strongly influenced by the nature of sample, pretreatment of sample, the concentration of the reagents, the duration of the experiments, and the solid-to-liquid ratio [7].

Several single and sequential extraction schemes have been proposed for determining extractable metal content [1, 2, 3, 8, 9]. A method proposed by Tessier et al. [1] is one of the most frequently used and many speciation studies have been performed on the basis of a modification of the Tessier procedure [10, 11, 12]. The proposed schemes differ not only in the reagents used but also in the leaching procedure.

It is known that manganese oxides, iron oxides, and organic matter are strong scavenging agents for metals ions in soils and sediments [5, 13, 14]. Some authors have stressed that manganese oxides differ from iron oxides in terms of their solubility in the natural environment, and its dependence on the oxidation–reduction conditions and pH [2, 3, 5, 15, 16]. Evaluation of secondary Mn–Fe oxide minerals is also important; the “new” oxides (amorphous forms of Mn–Fe oxides) are easily reducible but “aged” oxides with more crystalline character (crystalline Fe oxides) are more resistant to changes in the oxidation–reduction conditions and the pH in the soil [3].

The different solubilities of Mn and Fe oxides in acidified NH₂OH·HCl solution can be used for separation of the two closely related groups of oxides. The concentration and acidity of the extractants and equilibration time should be kept low enough to restrict the dissolution of iron oxides, but should be sufficient to dissolve manganese oxides effectively [16]. The residue after the dissolution of Mn oxides is used for dissolution of amorphous and crystalline Fe oxides. Suggested fractionation conditions are oxalate solution for amorphous Fe oxides and ascorbic acid in oxalate buffer for crystalline Fe oxides [17].

The aim of this study was to modify the five-step sequential extraction scheme applied to soil samples stored in the German Environmental Specimen Bank [13]. A solution of NH₂OH·HCl in 25% acetic acid used to leach metals bound to Mn–Fe oxides could not be used to dissolve crystalline forms of Fe oxides. For this reason the leaching of elements with a solution of NH₂OH·HCl in

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25% acetic acid (reducing reagent) was split into two steps – for easily and moderately reducible fractions.

Experimental

Sample collection and preparation

The two soil samples were collected in a forest area. A total amount of 2.5 kg of each sample, denoted ESB top soil (SA), layer depth 0–10 cm and ESB bottom soil (SB), layer depth 10–30 cm, were collected and immediately stored at liquid nitrogen temperature.

The frozen samples were ground in a special vibrating mill using titanium rods under cryogenic conditions. After many cycles of grinding the samples were partitioned into 250 vials, each containing 10 g of the sample. The content of 25 vials, randomly selected from each sample set, were lyophilized for inorganic analysis to ascertain the homogeneity.

The homogeneity (coefficient of variation was less than 0.10) of the soil samples in respect of many trace elements was determined by ICP–MS [18]. The mean content of the elements studied was determined after pressurized nitric acid digestion. The relative standard deviation was 3–5% for the trace elements investigated [18].

Apparatus and equipment

A horizontal rotor-controlled environment shaker (New Brunswick Scientific, Edison, NJ, USA) was used for the extraction. A Centrifon T-324 (Kantron, Italy) ultracentrifuge was used for centrifugation of the extracts. An open wet digestion system with automatic temperature program controller (Gebrüder Liebsch, Bielefeld, Germany) was used for elevated temperature extraction with hydrogen peroxide and concentrated nitric acid. Reinforced centrifuge tubes (16 mL capacity) were used for extraction and centrifugation. Standard filtration equipment and type 589–3 filter papers (equivalent to Whatman 542) were used for filtration. After filtration the extracts were stored in clean polyethylene vials at -20°C ; before analysis they were thawed completely.

Instruments

ICP–MS measurements were performed with a PE–Sciex Elan 5000 (Perkin–Elmer, Germany) using the Total-Quant 2 program which automatically corrects intensities for interferences from isobaric and molecular ions. Because of their negligible concentrations in routine soil samples Re and Rh were used as internal standards [19] to provide suitable corrections in the medium and high mass ranges. Appropriate calibration standards were run periodically, interspersed with the samples, to monitor any loss of efficiency as a result of instrumental drift, etc. ICP–OES measurements were performed with a Perkin–Elmer Plasma 400 Emission spectrometer equipped with an AS 90 autosampler. Scandium was used as internal standard.

Mg, Mn, Fe, Ca, and Zn were determined by ICP–OES. All other elements were determined by ICP–MS.

Reagents

Suprapur nitric acid, hydrogen peroxide, and acetic acid, and analytical-grade hydroxylamine hydrochloride, ascorbic acid, ammonium oxalate, oxalic acid, and ammonium acetate (all from Merck, Germany) were used to prepare the solution for extraction. Three basic reagents were prepared and stored in clean polyethylene bottles. Deionized water from a Milli Q System (18 M Ω) was used throughout.

Extraction procedure

The proposed scheme of the six-step sequential extraction procedure is presented in Table 1. The soil sample (200 mg) was placed in a centrifuge tube, the extractant (10 mL) was added, and the sample was shaken at 200 rev min $^{-1}$ at 20°C , in a horizontal position in the shaker, and then centrifuged for 10 min at 20,000 rev min $^{-1}$; finally, the supernatant liquid was filtered. Extractions in the last two steps were performed in a quartz vial at 90°C .

The filtrate was collected in a polypropylene tube and the pH of the extract was adjusted to 1 with conc. HNO $_3$. Before analysis extracts were stored at -20°C .

The process of leaching in steps 1, 2, 5, and 6 in Table 1 has been described in detail in our previous paper [13]. In the third step 35 mg NH $_2$ OH·HCl, 5 μL conc. HNO $_3$, and 10 mL deionized water were added to the solid residue from step 2. In the fourth step extraction was performed with 0.18 g ascorbic acid dissolved in 10 mL 0.2 mol L $^{-1}$ oxalate buffer.

Results and discussion

This study focused on obtaining a proper sequential extraction scheme applicable to soil samples stored in ESB. The five-step sequential extraction scheme (step 1 – 0.01 mol L $^{-1}$ NH $_4$ Ac; step 2 – 0.1 mol L $^{-1}$ HAc; Step 3 – 0.04 mol L $^{-1}$ NH $_2$ OH·HCl in 25% acetic acid; step 4 – 30% H $_2$ O $_2$; step 5 – conc. HNO $_3$) has been applied in previous work [13]. The reagents were chosen with regard to quantification by ICP–MS and ICP–OES. The solution containing of 0.04 mol L $^{-1}$ NH $_2$ OH·HCl in 25% acetic acid was used to extract trace elements from Mn–Fe oxides. The reagent could be used to leach a significant fraction of major and trace elements. For the top and bottom soils, respectively, 56% and 32% total Mn and 40% and 15% total Ca were found to be extracted, whereas only approximately 5–6% total Fe was leached from the top and bottom soils with this reagent. Iron is leached mainly with hot nitric acid in the five-step scheme. Only approximately 25% total Pb was leached in step 3 (Mn and Fe oxides), but hot nitric acid leached approximately 40% total Pb [13]. It is known that extractable lead is mainly bound to Fe oxides in soils [15]. The results [13] suggest that hydroxylamine in acetic acid

Table 1 Proposed scheme for six-step sequential extraction

Step	Fraction	Time	Reagent
1	Exchangeable	1 h	0.01 mol L $^{-1}$ NH $_4$ Ac, pH 7
2	Carbonate	1 h	0.1 mol L $^{-1}$ HAc, pH 3.5
3	Mn oxides	30 min	0.05 mol L $^{-1}$ NH $_2$ OH·HCl, pH 2/HNO $_3$
4	Fe oxides	1 h	0.1 mol L $^{-1}$ ascorbic acid in 0.2 mol L $^{-1}$ oxalate buffer in the dark
5	Organic	3 h	30% H $_2$ O $_2$, pH 2/HNO $_3$ at 90°C
6	Residual	3 h	HNO $_3$ conc. at 90°C

Table 2 Quantities of Mn and Fe leached from top (SA) and bottom (SB) soils in single extractions with 0.1 mol L⁻¹ and 0.05 mol L⁻¹ NH₂OH·HCl, in 30, 60, and 90 min. Results presented are the fraction (%) of the total content

		30 min		60 min		90 min	
		Mn	Fe	Mn	Fe	Mn	Fe
0.05 mol L ⁻¹ NH ₂ OH·HCl	SA	30	1.4	50	2.4	88	5.0
	SB	35	3.4	38	3.7	35	3.5
0.1 mol L ⁻¹ NH ₂ OH·HCl	SA	26	7.1	33	3.9	35	2.0
	SB	34	3.5	-	2.2	40	4.1

reduces completely only the Mn oxides, and partly the amorphous form of Fe oxides, whereas the crystalline forms are dissolved by hot mineral acid. It is probable that the fraction of Fe associated with Mn oxides is rather small in those soil samples.

Data published in literature and results obtained previously enabled us to make a decision to split the third step. The solution of 0.05 mol L⁻¹ and 0.1 mol L⁻¹ NH₂OH·HCl acidified to pH 2 was used to test the selective dissolution of more easily reducible oxides. The solutions 0.25 mol L⁻¹ NH₂OH·HCl in 25% acetic acid (4a), 0.2 mol L⁻¹ oxalate buffer (4b), and 0.1 mol L⁻¹ ascorbic acid in 0.2 mol L⁻¹ oxalate buffer (4c) were tested for dissolution of crystalline Fe oxides.

Soil samples (200 mg) were extracted with each extractant (10 mL). The quantities of Mn and Fe leached with NH₂OH·HCl solutions as function of time are given in Table 2. The extractable amounts of metals were computed relative to the values obtained by pressure digestion (HNO₃/HF) [18].

Increasing the concentration of NH₂OH·HCl had almost no effect on the leaching of Mn. Time had a noticeable effect only on the amount of Mn extracted from top soil by use of 0.05 mol L⁻¹ NH₂OH·HCl. Interestingly, 0.1 mol L⁻¹ NH₂OH·HCl leached less Mn from top soil than 0.05 mol L⁻¹ NH₂OH·HCl, whereas for bottom soil no significant differences were observed. For Fe some influence of time and leaching agent concentration was observed. For top soil iron extraction with 0.05 mol L⁻¹ NH₂OH·HCl was highly dependent on extraction time. Such dependence was not observed for bottom soil. It is worth noting that for longer extraction time the concentration of reagent has almost no effect on the leaching of iron and occasionally less iron was leached. Thus, the optimum conditions for dissolution of the Mn oxide phase were use of 0.05 mol L⁻¹ NH₂OH·HCl acidified with nitric acid to pH 2 as the extractant and an extraction time of 30 min.

The influence of the extraction time, using different reagents that dissolve Fe oxides from top and bottom soils, is presented in Table 3. All the reagents tested (4a, 4b, 4c) leached similar amounts of Mn (approximately 70–80% of total content), irrespective of extraction time. Mn oxides, in contrast to the moderately reducible Fe oxides, were dissolved by 0.25 mol L⁻¹ NH₂OH·HCl in 25% acetic acid. The reagent leached only 6–9% total iron. Ascorbic acid in oxalate buffer, and oxalate buffer, dissolved approximately 30–40% total Fe, but by use of the first solution it is possible to leach Fe in a shorter time.

Table 3 Comparison of single extraction with different reagents and extraction times. 4a – 0.25 mol L⁻¹ NH₂OH·HCl in 25% HAC, 4b – 0.2 mol L⁻¹ oxalate buffer, 4c – 0.1 mol L⁻¹ ascorbic acid in 0.2 mol L⁻¹ oxalate buffer. Results presented are the fraction (%) of the total content

		60 min		120 min		180 min	
		Mn	Fe	Mn	Fe	Mn	Fe
4a	SA	81	6.2	72	5.9	99	9.0
	SB	51	-	56	8.7	66	14
4b	SA	80	29	78	31	70	30
	SB	66	34	55	30	74	34
		30 min		60 min		90 min	
		Mn	Fe	Mn	Fe	Mn	Fe
4c	SA	71	28	71	32	77	40
	SB	72	40	69	41	70	42

Apart from reagent study, sequential extraction (semi-extraction) was also performed with only three extractants (for 3rd, 4th and 5th step). The results of the semi-extraction enable assessment of the effect of changing the reagents in steps 3 and 4 for extraction from organic matter. Results from comparison of two semi-extraction steps with different reagents for Fe oxides phase (4c – 0.1 mol L⁻¹ ascorbic acid in 0.2 mol L⁻¹ oxalate buffer and 4d – 0.04 mol L⁻¹ NH₂OH·HCl in 25% acetic acid) are shown in Figs. 1 and 2. A solution of 0.05 mol L⁻¹ NH₂OH·HCl (pH 2) was used to dissolve Mn oxides (step 3) whereas 30% H₂O₂ was used to treat organic matter (step 5) in both semi-extractions. Figure 1 shows that the solution of NH₂OH·HCl in nitric acid can be used to leach the largest amount of Mn, irrespective of the reagent used in step 4. It should be emphasized that 0.05 mol L⁻¹ NH₂OH·HCl (proposed reagent) and 0.04 mol L⁻¹ NH₂OH·HCl in acetic acid (reagent from the five-step scheme) dissolve approximately 40% of total Mn but in shorter time. Figure 2 illustrates that the amount of Fe leached in step 5, from organic matter, does not depend on the reagent used in the preliminary step. Ascorbic acid (4c – proposed reagent) leached significantly larger amounts of Fe than NH₂OH·HCl in acetic acid (4d – reagent from the five-step scheme) in the same time and at the same temperature. A solution of 0.1 mol L⁻¹ ascorbic acid in 0.2 mol L⁻¹ oxalate buffer dissolves approximately 30–40% total Fe; the reagent attacks easily and moderately reducible Fe oxide phases.

Fig. 1 Comparison of Mn leaching in two semi-extractions with different reagents in step 4. *SA* – top soil, *SB* – bottom soil, *4d* – 0.04 mol L⁻¹ NH₂OH·HCl in 25% HAc, *4c* – 0.1 mol L⁻¹ ascorbic acid in 0.2 mol L⁻¹ oxalate buffer. Data are presented as a percentage of total Mn content

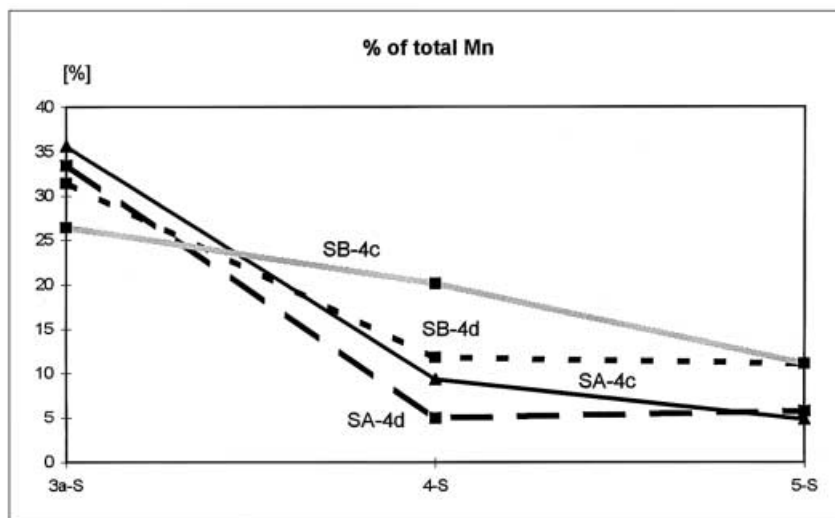
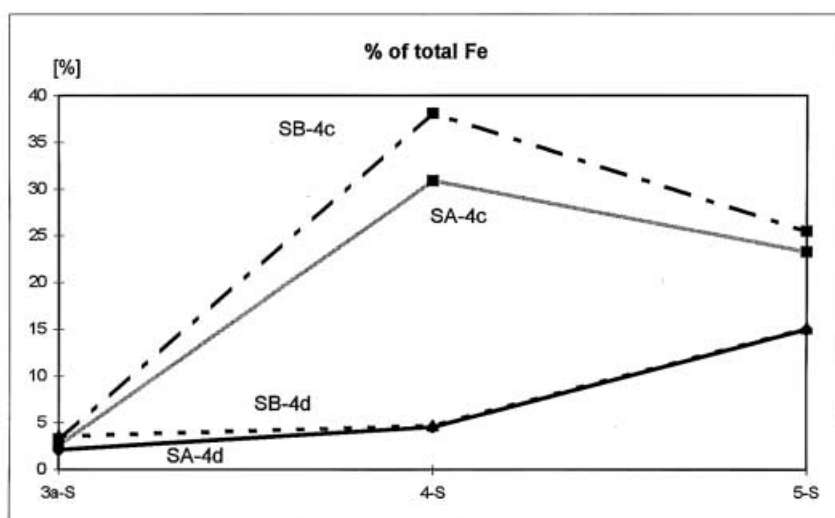


Fig. 2 Comparison of Fe leaching in two semi-extractions with different reagents in step 4. *SA* – top soil, *SB* – bottom soil, *4d* – 0.04 mol L⁻¹ NH₂OH·HCl in 25% HAc, *4c* – 0.1 mol L⁻¹ ascorbic acid in 0.2 mol L⁻¹ oxalate buffer. Data are presented as a percentage of total Fe content



The six-step scheme (Table 1) and the five-step scheme were used to define the distribution of some elements between phases of the top and bottom forest soils (*SA* and *SB*). The results, based on two sets for top soil and four sets for bottom soil are presented and further discussed. The data obtained are presented in Table 4. The results of leaching from Mn–Fe oxides with reagent 4d (step 3 of the five-step scheme) are compared with the results from leaching of Mn oxides with reagent 3a (step 3 of the six-step scheme). Step 4 of the six-step scheme, related to metals leached from Fe oxides, is presented in a separate column. Steps 4 and 5 of the five-step scheme were compared with steps 5 and 6, respectively, of the six-step scheme.

The sum of the amounts of Mg and Ca extracted in the five-step scheme differs from the corresponding sum in the six-step scheme by less than 10%. No significant difference was expected; the modification should not significantly influence the extraction of these elements. In the presence of HAc in step 3 the extraction recovery of Mg and Ca with NH₂OH·HCl was as high as without acetic

acid. This confirms nearly total dissolution of carbonate minerals in the second step in both schemes.

Manganese is mainly leached from carbonate minerals (Mn substitutes Ca and Mg in calcite or dolomite) and from Mn oxide phases. The use of the weaker reagent, i.e. a solution of NH₂OH·HCl instead of NH₂OH·HCl in 25% HAc in step 3, did not change the sum of Mn extracted in the three first steps. The total amounts of Mn leached in both extraction schemes differed by less than 4%. This result supports the choice of the reagent used in step 3 of the six-step scheme. These results from Mn leaching suggested that the presence of HAc is for pretreatment of the soil before extraction of metals from organic matter by 30% H₂O₂. Similar trends were found for Co and Ni, and this might suggest a similar mechanism of binding of Co, Ni, and Mn to organic matter in soil. It is worth noting that NH₂OH·HCl leached less Fe than the NH₂OH·HCl in 25% HAc. In the modified scheme, iron is mainly leached in step 4. The efficiency of extraction of the metal with hot nitric acid in the six-step scheme is much less than in the five-step scheme. The sums of the amounts of Fe ex-

Table 4 Quantities of elements extracted during sequential extraction from top and bottom soil. The data are presented as means ($n \geq 2$) or as a mean \pm UNC ($n \geq 4$) in mg kg^{-1} (5s – five-step scheme; 6s – six-step scheme)

	Top soil (SA)						Bottom soil (SB)					
	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6
Zn 5 s	8.2 \pm 2.4	25.1 \pm 2.8	23	23	24	41	6.3 \pm 2.3	15.0 \pm 0.1	7.5	10 \pm 2	22	25
6 s			26	23	12	39		9.4 \pm 0.8			14.9 \pm 0.1	32
Mn 5 s	35.8 \pm 0.4	366 \pm 16	347	66	58	79	5.02 \pm 0.5	77.6 \pm 2.8	100	60 \pm 20	43	55
6 s			364	66	15	63		109 \pm 5			29 \pm 6	45 \pm 6
Fe 5 s	28.8 \pm 1.9	40.0 \pm 5.2	699	3.55 $\times 10^3$	1.68 $\times 10^3$	7.64 $\times 10^3$	23.4 \pm 2.6	80 \pm 5	862	3.89 \pm 0.50 $\times 10^3$	2.44 $\times 10^3$	6.04 $\times 10^3$
6 s			422	3.55 $\times 10^3$	1.99 $\times 10^3$	5.19 $\times 10^3$		472 \pm 86			2.48 \pm 0.14 $\times 10^3$	3.40 \pm 0.86 $\times 10^3$
Mg 5 s	47.1 \pm 2.2	163 \pm 6	38	33	135	502	11.3 \pm 2.3	37.7 \pm 2.8	5.0	37 \pm 6	128	471
6 s			35	33	178	417		5.0			207 \pm 19	410 \pm 14
Ca 5 s	156 \pm 8	1.06 \pm 0.7 $\times 10^3$	606	108	308	268	58.8 \pm 6.7	211 \pm 4	55	37 \pm 14	85	157
6 s			672	108	91	393		70 \pm 7			71 \pm 7	196 \pm 28
Cu 5 s	0.75 \pm 0.16	0.45 \pm 0.08	0.56	7.2	2.1	10	0.51 \pm 0.05	0.40 \pm 0.04	1.1	2.93 \pm 0.01	1.5	7.5
6 s			0.47	7.2	0.77	7.3		0.48 \pm 0.02			0.98 \pm 0.01	4.2
Cr 5 s	<0.05	<0.05	13.5	2.2	5.0	19	<0.05	<0.05	14	2.93 \pm 0.01	5.5	2.0
6 s			0.23	2.2	25	22		0.211 \pm 0.002			10.5 \pm 0.4	18
Co 5 s	0.057 \pm 0.0	0.058 \pm 0.0	1.3	0.56	1.1	1.9	0.06 \pm 0.01	0.44 \pm 0.07	0.85	0.69 \pm 0.01	1.05	1.7
6 s	10	11	1.3	0.56	0.26	2.6		0.74 \pm 0.05			0.39 \pm 0.01	1.7
Ni 5 s	<0.01	<0.01	1.1	1.3	6.5	11	0.01	0.87 \pm 0.04	0.93	1.3 \pm 0.2	8.0	11
6 s			1.4	1.3	2.3	24		0.22 \pm 0.08			2.3 \pm 0.1	13
As 5 s	0.32 \pm 0.06	0.30 \pm 0.06	2.9	5.0	5.0	4.5	0.18 \pm 0.02	0.16 \pm 0.01	2.8	6.2 \pm 0.2	4.5	4.4
6 s			1.3	5.0	1.8	2.1		0.19 \pm 0.01			0.70 \pm 0.06	1.7
Pb 5 s	0.67 \pm 0.06	1.3 \pm 0.2	28	33	37	45	0.43 \pm 0.08	2.83 \pm 0.30	37	43 \pm 1	23.5	21
6 s			7.1	33	6.9	18		12.4 \pm 1.7			4.4 \pm 0.1	14

tracted in both schemes differ much less than when leaching with a strongly reducing reagent is applied in step 4. An additional extraction step with a strongly reducing reagent, after leaching with a solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in dilute nitric acid, enables crystalline Mn and Fe oxides phase to be dissolved separately.

The application of the weaker reagent in step 3 has no effect on the leaching of zinc from easily reducible oxides. The additional step of extraction with a strongly reducing reagent after leaching with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in dilute nitric acid resulted in a decrease in the amount of zinc leached with hydrogen peroxide. This observation might suggest that after extraction with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in acetic acid, readsorption of Zn by the organic matter might have occurred in the five-step scheme. The sums of the amounts of Zn extracted were similar for both schemes.

The $\text{NH}_2\text{OH}\cdot\text{HCl}$ extracts contain less lead than the $\text{NH}_2\text{OH}\cdot\text{HCl}$ in HAc extracts. For both soils the ascorbic acid in oxalate buffer leaches the largest amount of Pb. The decrease of Pb leaching with hydrogen peroxide in the six-step scheme compared with the five-step scheme suggests that Pb is mainly bound to the crystalline Fe oxides phase in the forest soils.

Leaching of Co with $\text{NH}_2\text{OH}\cdot\text{HCl}$ is nearly the same as leaching with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in acetic acid. Additional extraction with ascorbic acid in oxalate buffer caused a decrease in Co leaching with hydrogen peroxide. The results suggest that Co is bound to the easily reducible oxide phase – Mn and Fe oxides.

Determinations of other trace elements showed that the sums of their leaching recoveries in all steps in five- and six-step extraction are similar. Modification of the five-step scheme changed only the proportion of the elements recovered in each step. Interestingly, leaching from moderately reducible phases in the six-step scheme is either comparable with or even higher than (particularly for As) extraction from the residue (extraction with hot nitric acid). The amounts of the trace elements leached from the residue in five-step scheme are the dominant fractions.

Conclusion

Modification of the sequential extraction scheme leads to selective leaching of trace metals bound to Mn and Fe oxides and other phases in the type of soil studied. The reagents proposed in the six-step scheme are suitable for quantification using ICP–MS and ICP–OES. The content of total dissolved salts should be less than 0.1% for reliable quantification with ICP–MS; this would require very large dilution of extracts. A very dilute solution of NH_4Ac was therefore chosen for the first step, a dilute solution of HAc for the second step, and a dilute solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$ for the third step.

By use of a “weaker” reagent and a shorter extraction time in step 3 (extraction of easily reducible fraction) it is possible to leach a large amount of Mn and to reduce

leaching of Fe. The use of a solution that dissolves the crystalline forms of oxides enables extraction of metals bound to Fe oxides in step 4. Modification of the extraction procedure does not have any noticeable effect on extraction of elements from organic matter. In addition, when the reducible fraction is split the sum of the amounts of metals leached remains almost unchanged.

Comparison of results obtained for the same soil under the different extraction conditions provides information about the binding of elements in soil. The data obtained enable several conclusions: the carbonate fraction and the easily reducible fraction are important for the extraction of Zn, Co, and Ni from soils; cobalt is mainly bound to Mn oxide minerals, and arsenic and lead to Fe oxide phases in the soil, whereas chromium distribution in soil is dominated by organic matter.

In environmental studies, the leaching and/or re-adsorption of elements are important in establishing their real mobile fraction. The mobile fraction of trace elements is mainly formed by the elements bind to easily reducible minerals and organic matter.

The trace elements studied are mainly bound to Fe oxide minerals and insoluble minerals. The fractions bound to these phases will be not leached by natural processes in a relatively short time.

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