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## EVALUATION OF AMMONIUM OXALATE FOR FRACTIONATING METALLIC TRACE ELEMENTS IN SOILS BY SEQUENTIAL EXTRACTION

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Ammonium oxalate is largely used to extract the trace elements bound to Mn-oxides, amorphous compounds and crystalline Fe-oxides. The objective of this work was to evaluate the selectivity and the efficiency of ammonium oxalate for extracting Cd, Cu, Ni, Pb and Zn by sequential extraction of soils. For this purpose, three schemes were selected and applied to three different soil samples of the Swiss Jura. Each extraction scheme consisted of six steps, where different reagents were used to extract Cd, Cu, Ni, Pb and Zn bound to the Mn and Fe compounds. The results showed that metallic trace elements extraction with ammonium oxalate are very dependant on the metal studied. The reason could be the capability of oxalate to form stable complexes with the metals considered which sometimes are only slightly soluble.

**Keywords:** Heavy metals; trace element; sequential extraction; soil; fractionation; speciation; oxalate solution

### INTRODUCTION

Sequential extraction is a method widely utilised by soil and sediment scientists to study the behaviour of trace elements in soils and sediments. Many criticisms have been outlined by the scientific community because the results obtained by different sequential extraction schemes cannot be compared with each other. For this reason, a group of European experts tried to harmonise the procedures and have proposed a standard sequential extraction scheme<sup>[1,2]</sup>. This procedure considers only three steps for evaluating the exchangeable, reducible and oxidable fractions of heavy metal in soils. However, such a simplified scheme is not sufficient to understand the relationships between trace elements and the soil compo-

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nents. In this case, depending on the aims of the study, different extraction procedures are required. Several reviews have recently pointed out how the sequential extraction procedures could assess the metallic trace <sup>[3,4]</sup> and radionuclide<sup>[5,6]</sup> elements speciation in soils and sediments.

In a recent paper, Benitez and Dubois <sup>[7]</sup> proposed an extraction scheme to assess the Cd speciation in some soils of the Swiss Jura. In that scheme, hydroxylamine hydrochloride, and a mixture of hydroxylamine hydrochloride and acetic acid were recommended to extract selectively the Cd bound to Mn and Fe oxides. However, the X-ray analyses have shown that the hematite was not completely dissolved by these reagents.

Another category of reagents has also been very commonly applied in the sequential extraction schemes to dissolve Mn and Fe-oxides. Instead of hydroxylamine, some authors have recommended ammonium oxalate, buffered to pH 3.0, to extract the trace elements bound to Mn-oxides and amorphous compounds <sup>[8,9]</sup>, while a mixture of ammonium oxalate and a reducing agent like ascorbic acid <sup>[10,11]</sup> or sodium dithionite <sup>[12,13]</sup> has been proposed to extract the trace elements bound to crystalline Fe oxides. The goals of this work were firstly, to evaluate the efficiency of such oxalate solutions to dissolve Mn and Fe-oxides in order to improve the quality of the extraction procedure for amorphous compounds, Mn and Fe oxides. Secondly, to compare the influence of the two types of reagents (hydroxylamine hydrochloride and ammonium oxalate solutions) on the Cd, Cu, Ni, Pb and Zn amount extracted from soil samples taken in the Swiss Jura. After each step of these schemes, the solid remaining was analysed by X-ray diffractometry to check for the complete dissolution of the crystalline soil constituents.

## MATERIALS AND METHODS

### Soil samples

Three different soil samples were used for this study. They were chosen depending on three physico-chemical characteristics: their carbonate, clay and organic matter contents. "Soil I" was sampled in a Sca horizon of a Calcosol or a B horizon of a calcare Cambisol, rich in carbonate. "Soil II" was a Bt horizon of a Neoluvisol Typique or a Bt horizon of a haplic Luvisol, chosen for its large clay content. "Soil III" was an Ah horizon of a calcic Organosol or an A horizon of a rendzic Leptosol, rich in organic matter. The soil names are respectively given according to the "*Referential Pedologique*" <sup>[14]</sup> and the FAO-UNESCO legend <sup>[15]</sup>. The main characteristics of the samples are presented in Table I.

TABLE I Principal characteristics of the samples

Sample	Clay (%)	Silt (%)	Sand (%)	CEC (cmol kg <sup>-1</sup> )	pH <sub>H2O</sub>	CaCO <sub>3</sub> (g kg <sup>-1</sup> )	C <sub>org</sub> (g kg <sup>-1</sup> )
Soil I	9	63	28	34.3	7.6	147	0
Soil II	58	34	8	38.0	7.3	25	14
Soil III	40	52	8	92.1	6.7	0	166

**Chemical analysis**

Three sequential extraction schemes were applied to each soil sample (Figure 1). Overall, they were similar to those proposed by Benitez and Dubois [7] except for the Mn and Fe oxides extraction steps. In these cases, new reagent combinations were examined. The metallic trace elements bound to amorphous compounds and Mn-oxides were extracted using either NH<sub>2</sub>OH·HCl 0.25M/HCl 0.05M [16,17] or 0.2M ammonium oxalate buffered at pH 3.0 [18–20]. Moreover, two different reagents were also checked to extract those bound to crystalline iron oxide. On the one hand, a mixture of 1M NH<sub>2</sub>OH.HCl and 25% acetic acid at 95°C [21,22] was used and on the other hand, a mixture of 0.2M ammonium oxalate (pH 3.0) and 0.2M ascorbic acid [10,11].

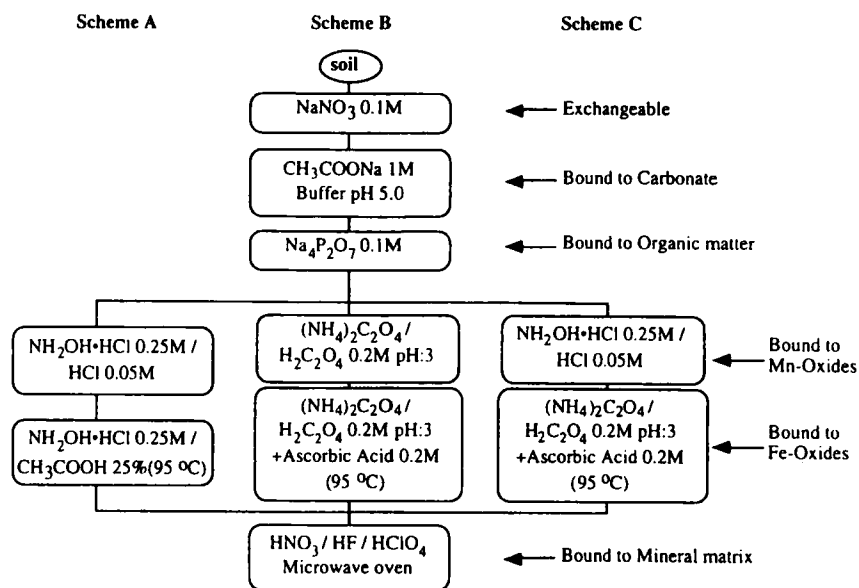


FIGURE 1 Sequential extraction schemes

### Procedure

The procedure applied in scheme A was already described in detail by Benitez and Dubois [7]. The same procedure was also carried out in schemes B and C to extract the exchangeable elements and those bound to carbonate, organic matter, and the final residue.

In scheme B, the Mn-oxides and amorphous compounds were dissolved at room temperature by 0.2M ammonium oxalate buffered to pH 3, according to the Tamm's procedure [23]. In scheme C, this step was identical to that used in scheme A.

In both schemes (B and C), the crystal iron oxides were extracted at 95°C with 20 ml of a mixture of 0.2M ammonium oxalate and 0.2M ascorbic acid. After centrifuging at 23400xG, the supernatant was transferred to a 100 ml volumetric flask. The whole procedure was repeated on the centrifuged residue using 20 ml of fresh reagent and, lastly, using 10 ml deionized water. Finally, the resultant solution was filled up to the gauge level with deionized water.

The soil samples were digested, under pressure, with an acid mixture (HF-HNO<sub>3</sub>-HClO<sub>4</sub>) using a microwave oven. All solutions were stored at 4°C awaiting analysis. To assure the quality of the results, four replications for each sample were carried out with each extraction scheme.

### Instrumentation

The Cd, Cu, Ni, Pb and Zn contents in the solutions was measured by Graphite Furnace Atomic Absorption Spectrometry with Zeeman background correction (Perkin Elmer 5100Z). The other elements were quantified by Inductively Coupled Plasma Atomic Emission Spectrometry (Perkin Elmer Plasma 2000). A X-ray diffractometer Philips PW1710 was used to perform the mineralogical analysis. The acidic digestion was carried out in an MLS 1200 Mega microwave.

## RESULTS AND DISCUSSION

The results of Cd, Cu, Ni, Pb, Zn, Mn and Fe extractions are presented in Tables II, III and IV. The roman numerals (I, II or III) label the soil submitted to extraction and the letters (A, B or C) indicate the applied extraction procedure (e.g. the results, obtained for the extraction of soil I according to the scheme A, are presented in column IA). The extraction step with sodium acetate was omitted for soil III, which is a non calcareous sample, to avoid dissolution of organic matter<sup>[1]</sup>. An illustration of the Cd, Cu, Ni, Pb, Zn, Mn and Fe extraction results are given in Figure 2.

TABLE II Results of Cd and Cu extraction: A, B and C correspond to the extraction scheme, I, II and III to soil sample and  $\pm$  to the standard deviation calculated from four replicates (only two replicates for total contents)

<i>Cd (mg kg<sup>-1</sup>)</i>	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC
Exchangeable	0.010 $\pm$ 0.004	0.010 $\pm$ 0.003	0.031 $\pm$ 0.004	0.010 $\pm$ 0.000	0.009 $\pm$ 0.001	0.008 $\pm$ 0.001	0.020 $\pm$ 0.003	0.025 $\pm$ 0.005	0.022 $\pm$ 0.002
Carbonate	2.76 $\pm$ 0.29	2.58 $\pm$ 0.06	2.56 $\pm$ 0.04	1.50 $\pm$ 0.07	1.35 $\pm$ 0.03	1.31 $\pm$ 0.10	ND	ND	ND
Organic matter	1.10 $\pm$ 0.05	0.82 $\pm$ 0.005	0.87 $\pm$ 0.02	0.32 $\pm$ 0.02	0.46 $\pm$ 0.02	0.54 $\pm$ 0.04	0.96 $\pm$ 0.07	0.62 $\pm$ 0.004	0.69 $\pm$ 0.02
Mn-Oxides	1.91 $\pm$ 0.01	1.32 $\pm$ 0.04	1.92 $\pm$ 0.06	0.99 $\pm$ 0.05	1.32 $\pm$ 0.04	1.13 $\pm$ 0.04	0.92 $\pm$ 0.06	0.12 $\pm$ 0.01	1.05 $\pm$ 0.07
Fe-Oxides	2.20 $\pm$ 0.05	0.68 $\pm$ 0.06	0.71 $\pm$ 0.04	1.54 $\pm$ 0.03	0.42 $\pm$ 0.07	0.38 $\pm$ 0.03	0.37 $\pm$ 0.01	0.08 $\pm$ 0.00	0.12 $\pm$ 0.03
Residue	0.52 $\pm$ 0.04	2.41 $\pm$ 0.08	1.86 $\pm$ 0.08	0.32 $\pm$ 0.02	1.38 $\pm$ 0.09	1.19 $\pm$ 0.05	0.050 $\pm$ 0.005	1.49 $\pm$ 0.04	0.57 $\pm$ 0.009
Sum of fractions	8.50 $\pm$ 0.20	7.82 $\pm$ 0.12	7.95 $\pm$ 0.12	4.68 $\pm$ 0.10	4.94 $\pm$ 0.13	4.56 $\pm$ 0.13	2.32 $\pm$ 0.09	2.34 $\pm$ 0.04	2.45 $\pm$ 0.08
Total content	8.10 $\pm$ 0.30	-	-	4.89 $\pm$ 0.22	-	-	2.45 $\pm$ 0.09	-	-
Recovery (%)	105	97	98	96	101	93	95	96	100
<i>Cu (mg kg<sup>-1</sup>)</i>									
Exchangeable	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbonate	ND	ND	ND	ND	ND	ND	ND	ND	ND
Organic matter	1.9 $\pm$ 0.3	1.9 $\pm$ 0.7	1.7 $\pm$ 0.4	2.4 $\pm$ 0.3	1.3 $\pm$ 0.4	1.1 $\pm$ 0.2	3.4 $\pm$ 0.02	3.6 $\pm$ 0.3	3.2 $\pm$ 0.1
Mn-Oxides	ND	0.9 $\pm$ 0.1	ND	ND	1.4 $\pm$ 0.1	ND	ND	4.1 $\pm$ 0.1	ND
Fe-Oxides	4.1 $\pm$ 0.4	4.6 $\pm$ 0.5	4.4 $\pm$ 0.4	7.4 $\pm$ 0.3	8.0 $\pm$ 0.9	7.1 $\pm$ 0.6	6.4 $\pm$ 0.2	2.6 $\pm$ 0.2	6.9 $\pm$ 0.9
Residue	3.7 $\pm$ 0.5	3.2 $\pm$ 0.20	4.0 $\pm$ 0.1	7.4 $\pm$ 0.8	7.8 $\pm$ 0.5	8.6 $\pm$ 0.2	5.1 $\pm$ 0.2	3.7 $\pm$ 0.2	6.4 $\pm$ 0.9
Sum of fractions	9.7 $\pm$ 0.7	10.6 $\pm$ 0.9	10.1 $\pm$ 0.6	17.2 $\pm$ 0.9	18.5 $\pm$ 1.1	16.8 $\pm$ 0.7	14.9 $\pm$ 0.3	14.0 $\pm$ 0.4	16.5 $\pm$ 1.3
Total content	11.2 $\pm$ 0.5	-	-	18.6 $\pm$ 0.9	-	-	15.7 $\pm$ 0.9	-	-
Recovery (%)	87	95	90	92	99	90	95	89	105

ND: Not detected

TABLE III Results of Ni, Pb and Zn extraction: A, B and C correspond to the extraction scheme, I, II and III to soil sample and  $\pm$  to the standard deviation calculated from four replicates (only two replicates for total contents)

	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC
<b>Ni (mg kg<sup>-1</sup>)</b>									
Exchangeable	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbonate	ND	ND	ND	ND	ND	ND	ND	ND	ND
Organic matter	ND	ND	ND	ND	ND	ND	ND	ND	ND
Mn-Oxides	2.2 $\pm$ 0.3	2.4 $\pm$ 0.3	2.0 $\pm$ 0.1	3.4 $\pm$ 0.3	5.8 $\pm$ 0.2	4.1 $\pm$ 0.2	1.0 $\pm$ 0.3	4.8 $\pm$ 0.1	0.2 $\pm$ 0.0
Fe-Oxides	13.3 $\pm$ 0.4	8.1 $\pm$ 1.4	9.2 $\pm$ 0.7	22 $\pm$ 1	12.2 $\pm$ 2	11.6 $\pm$ 0.2	13.7 $\pm$ 0.5	9.8 $\pm$ 0.6	11.2 $\pm$ 0.7
Residue	28 $\pm$ 1	34 $\pm$ 1	35 $\pm$ 1	46 $\pm$ 1	57 $\pm$ 1	57 $\pm$ 2	18.9 $\pm$ 0.9	19.2 $\pm$ 0.8	23 $\pm$ 1
Sum of fractions	44 $\pm$ 1	45 $\pm$ 2	46 $\pm$ 1	71 $\pm$ 1	75 $\pm$ 2	73 $\pm$ 2	34 $\pm$ 1	34 $\pm$ 1	34 $\pm$ 1
Total content	46 $\pm$ 1	-	-	79 $\pm$ 1	-	-	35 $\pm$ 1	-	-
Recovery (%)	96	98	100	90	95	92	97	97	97
<b>Pb (mg kg<sup>-1</sup>)</b>									
Exchangeable	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbonate	ND	ND	ND	ND	ND	ND	ND	ND	ND
Organic matter	ND	ND	ND	ND	ND	ND	6.3 $\pm$ 0.1	6.4 $\pm$ 0.4	5.3 $\pm$ 0.4
Mn-Oxides	5.7 $\pm$ 0.2	10.0 $\pm$ 0.2	5.6 $\pm$ 0.1	4.0 $\pm$ 0.3	7.9 $\pm$ 0.5	4.9 $\pm$ 0.2	2.2 $\pm$ 0.1	2.5 $\pm$ 0.2	1.8 $\pm$ 0.1
Fe-Oxides	16.3 $\pm$ 0.2	9.3 $\pm$ 1.0	13.0 $\pm$ 1.0	17.3 $\pm$ 0.5	8.8 $\pm$ 0.7	9.3 $\pm$ 0.8	38.1 $\pm$ 0.2	4.0 $\pm$ 0.1	12.5 $\pm$ 1.0
Residue	9.8 $\pm$ 0.4	13.5 $\pm$ 0.6	13.2 $\pm$ 0.4	12.9 $\pm$ 0.1	16.1 $\pm$ 0.7	17.6 $\pm$ 0.9	7.7 $\pm$ 0.4	37.8 $\pm$ 0.4	32.9 $\pm$ 3.0
Sum of fractions	32 $\pm$ 0.5	33 $\pm$ 1	32 $\pm$ 1	34 $\pm$ 0.6	33 $\pm$ 1	32 $\pm$ 1	54 $\pm$ 0.5	51 $\pm$ 0.6	53 $\pm$ 3

## SEQUENTIAL EXTRACTION

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Total content	34.6 ± 0.6	-	-	-	34.7 ± 0.7	-	-	47 ± 1	-	-	-
Recovery (%)	92	95	92	98	95	92	92	115	108	113	113
<i>Zn (mg kg<sup>-1</sup>)</i>											
Exchangeable	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbonate	2.7 ± 0.2	2.1 ± 0.1	1.5 ± 0.2	ND	ND	ND	ND	ND	ND	ND	ND
Organic matter	11.4 ± 0.7	12.7 ± 0.2	11.6 ± 0.7	4.9 ± 0.5	6.6 ± 1.2	20 ± 2	19 ± 0.1	20.0 ± 0.6	19.3 ± 0.3	19.3 ± 0.3	19.3 ± 0.3
Mn-Oxides	6.4 ± 0.1	11.2 ± 0.5	6.7 ± 0.2	2.5 ± 0.2	2.8 ± 0.4	2.8 ± 0.3	9.8 ± 0.3	15.0 ± 0.3	4.4 ± 0.6	4.4 ± 0.6	4.4 ± 0.6
Fe-Oxides	132 ± 5	145 ± 13	133 ± 10	84 ± 4	74 ± 13	63 ± 5	77 ± 3	46 ± 2	42 ± 3	42 ± 3	42 ± 3
Residue	492 ± 16	506 ± 13	514 ± 13	278 ± 4	306 ± 10	303 ± 18	78 ± 3	103 ± 2	120 ± 8	120 ± 8	120 ± 8
Sum of fractions	645 ± 17	677 ± 18	667 ± 16	369 ± 6	389 ± 16	389 ± 19	184 ± 4	184 ± 3	186 ± 9	186 ± 9	186 ± 9
Total content	733 ± 2	-	-	394 ± 1	-	-	190 ± 2	-	-	-	-
Recovery (%)	88	92	91	94	99	99	97	97	97	98	98
ND: Not detected											



### Extraction of metals bound to amorphous compounds and Mn oxides

The proportion of metals extracted respectively with hydroxylamine (schemes A and C) and oxalate (scheme B) are illustrated in Figure 2. These two reagents were well adapted for their goals as they dissolved 42 to 60% of the total Mn content. However, the ammonium oxalate/oxalic acid reagent was more efficient than the mixture of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  0.25M/HCl 0.05M, since it extracted a larger amount of Mn and some Fe. Except for Cd, this better extraction efficiency was also observed for the other trace metals (see Figure 2). This could be due to the formation of soluble oxalate complexes, which might favour the extraction of the metal at the expense of the sorption to other soil phases. Complexing reactions have often been mentioned for chloride and acetate<sup>[24–26]</sup>, but we did not observe it with oxalate. However, we know that oxalate is theoretically a good complexing agent whose stability constants for Cd, Cu, Ni, Pb and Zn have already been reported<sup>[28–30]</sup>. According to these values, the order of complex stability is:  $\text{Cu} > \text{Ni} > \text{Zn} > \text{Pb} > \text{Cd}$ , but from a different point of view the solubility products of Zn, Pb and Cd complexes are very low. Therefore, the poor efficiency of oxalate reagent to extract Cd could be attributed to the low solubility of Cd-oxalate ( $9 \times 10^{-8}$ ). Furthermore, Cd forms oxalate complexes with the lowest stability in comparison with Cu, Ni, Pb and Zn. As a result, Cd precipitation could occur in oxalic extracts and the residual fraction is, therefore, overestimated. Our statement is also supported by the Cu results. These indicated that this metal was better extracted by ammonium oxalate than by hydroxylamine hydrochloride solutions. According to the large stability constant of Cu (6.23 and 4.04), Cu-complexes were preferentially formed to the prejudice of adsorption on to the mineral surfaces. Therefore, it could be overestimated in that fraction.

### Extraction of metals bound to Fe oxides

The results (Tables II-IV, Figure 2) showed that the mixture of 1M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and 25% acetic acid (scheme A) extracted a larger amount of trace metals than the reagent composed of 0.2M ammonium oxalate/oxalic acid and 0.2M ascorbic acid (scheme C). The difference was particularly important for Cd, Pb and Zn and in a lesser degree for Ni. No trend was observed for Cu. Therefore, it seems that the combination of oxalate buffer and ascorbic acid was a less effective agent to extract trace elements bound to Fe oxides. In contrast, the X-Ray diffractograms (Figure 3) demonstrated that the iron oxides were better dissolved by a mixture of 0.2M ammonium oxalate (pH 3.0) and 0.2M ascorbic acid than with 1M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and 25% acetic acid. Indeed, after extraction with this last reagent, the crystalline iron oxide (hematite) was not completely dissolved in all samples, while it was the case when the ammonium oxalate was applied. This apparent contradiction can be explained by considering the amount of trace ele-

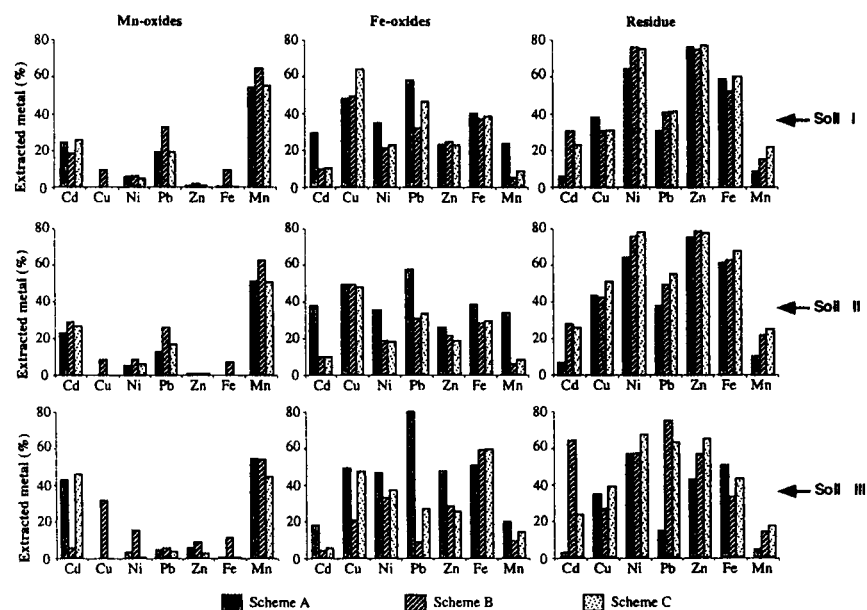


FIGURE 2 Extracted metal in the three last steps of soil for each scheme

ments measured in the last step of each scheme. A significant increase of elements bound to mineral matrix was observed each time oxalate was used in the two previous steps (Mn-oxide and Fe-oxide). This result confirmed the assumption of a precipitation of trace metals as oxalate just after their extraction from Mn oxides, Fe oxides or both. The precipitation process particularly affected Cd and Pb which have low stability product constants ( $9 \times 10^{-8}$ ,  $8.5 \times 10^{-9}$ ). Therefore, the Cd and Pb amount measured in the last extraction step were the largest when oxalate reagents were applied in both extraction steps of Mn and Fe oxides (scheme B). The behaviour of Zn was not identical to that of Cd and Pb, even if their stability constants and solubility products with oxalate were similar. The large Zn proportions found in the last extraction step indicated that, in our case, this metal was principally bound to a soil silicate matrix and not the result of a precipitation in previous steps. Nevertheless, a slight Zn increase was observed in the residual fraction when the oxalate solutions were used in the previous steps. The residual Zn fraction could also be overestimated if a large part of this metal was not originally bound to silicate matrix (e.g. anthropogenic sources). In that case, it might be differently distributed and could precipitate with oxalate reagents. Although the stability constants of oxalate Cu-complexes are high, the extraction of Cu bound to Fe oxides seemed to be independent of the choice of reagents.

TABLE IV Results of Mn and Fe extraction: A, B and C correspond to the extraction scheme, I, II and III to soil sample and  $\pm$  to the standard deviation calculated from four replicates (only two replicates for total contents)

<i>Fe (mg kg<sup>-1</sup>)</i>	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC
Exchangeable	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbonate	34 $\pm$ 2	32 $\pm$ 1	33 $\pm$ 2	16 $\pm$ 1	16 $\pm$ 1	16 $\pm$ 2	ND	ND	ND
Organic matter	2969 $\pm$ 118	3084 $\pm$ 89	2813 $\pm$ 67	2889 $\pm$ 94	3999 $\pm$ 306	3940 $\pm$ 562	1797 $\pm$ 14	1800 $\pm$ 114	1628 $\pm$ 46
Mn-Oxides	108 $\pm$ 6	4392 $\pm$ 118	106 $\pm$ 3	108 $\pm$ 10	4564 $\pm$ 109	98 $\pm$ 5	123 $\pm$ 5	3973 $\pm$ 112	235 $\pm$ 3
Fe-Oxides	16455 $\pm$ 641	16323 $\pm$ 1407	16358 $\pm$ 845	22559 $\pm$ 1146	17659 $\pm$ 559	16664 $\pm$ 1308	16740 $\pm$ 1004	19821 $\pm$ 556	19911 $\pm$ 586
Residue	27623 $\pm$ 1052	25952 $\pm$ 1119	29196 $\pm$ 1000	41025 $\pm$ 814	44227 $\pm$ 3667	43781 $\pm$ 1801	18945 $\pm$ 684	12669 $\pm$ 489	16426 $\pm$ 1126
Sum of fractions	47189 $\pm$ 1238	49783 $\pm$ 1804	48506 $\pm$ 1310	66595 $\pm$ 1409	70465 $\pm$ 3724	64500 $\pm$ 2296	37605 $\pm$ 1214	38263 $\pm$ 757	38200 $\pm$ 1270
Total content	50026 $\pm$ 140	-	-	69950 $\pm$ 12	-	-	38752 $\pm$ 256	-	-
Recovery (%)	94	100	97	95	101	92	97	99	99
<i>Mn (mg kg<sup>-1</sup>)</i>									
Exchangeable	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbonate	113 $\pm$ 1	109 $\pm$ 6	105 $\pm$ 1	58 $\pm$ 1	46 $\pm$ 1	47 $\pm$ 2	ND	ND	ND
Organic matter	146 $\pm$ 2	161 $\pm$ 4	145 $\pm$ 5	88 $\pm$ 3	116 $\pm$ 6	192 $\pm$ 26	414 $\pm$ 1	404 $\pm$ 7	423 $\pm$ 9
Mn-Oxides	655 $\pm$ 4	789 $\pm$ 12	663 $\pm$ 13	549 $\pm$ 22	674 $\pm$ 11	541 $\pm$ 16	758 $\pm$ 19	739 $\pm$ 14	619 $\pm$ 19
Fe-Oxides	271 $\pm$ 6	57 $\pm$ 8	101 $\pm$ 9	343 $\pm$ 18	62 $\pm$ 10	83 $\pm$ 3	259 $\pm$ 11	122 $\pm$ 10	186 $\pm$ 5
Residue	114 $\pm$ 4	202 $\pm$ 7	280 $\pm$ 16	117 $\pm$ 3	253 $\pm$ 13	288 $\pm$ 10	63 $\pm$ 2	205 $\pm$ 9	257 $\pm$ 6
Sum of fractions	1299 $\pm$ 9	1318 $\pm$ 17	1294 $\pm$ 23	1155 $\pm$ 29	1151 $\pm$ 24	1163 $\pm$ 22	1494 $\pm$ 22	1470 $\pm$ 20	1485 $\pm$ 22
Total content	1291 $\pm$ 17	-	-	1149 $\pm$ 15	-	-	1445 $\pm$ 10	-	-
Recovery (%)	101	102	100	101	100	101	103	102	103

ND: Not detected

**Analytical quality of the results**

The results showed in Tables II, III and IV, indicate the average value  $\pm$  standard deviation of four independent extractions. The reproducibility of the extraction results had a maximum variation coefficient of 10%.

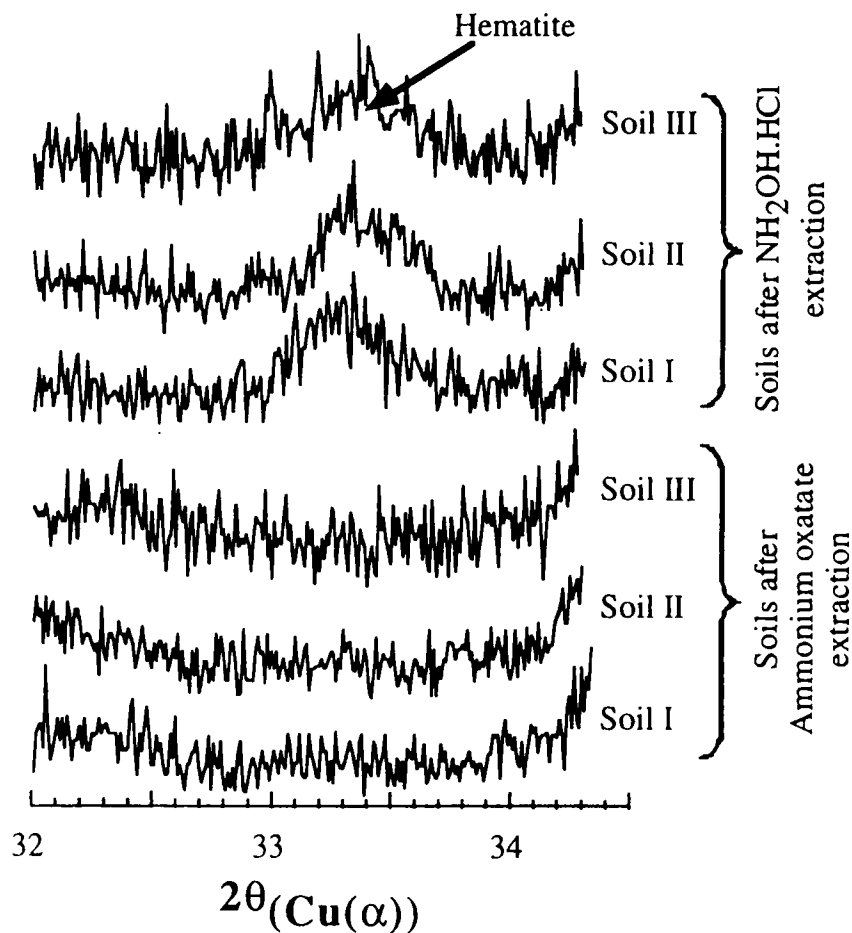


FIGURE 3 X-Ray diffractogram, using Cu-K $\alpha$  radiation, of the soil samples after theoretical destruction of crystalline iron oxides

The mass balance of heavy metals, Fe and Mn, showed that the sum of all the fractions recovered in the sequential extractions amounted to almost 100% of total content in the samples. The total metal content in the samples, were measured in the resultant solutions obtained after the total dissolution of the soil sam-

ples. These results can thus be considered satisfactory when the cumulative risks of analytical errors are taken into account.

## CONCLUSION

In a sequential extraction scheme ammonium oxalate is more efficient than hydroxylamine hydrochloride to dissolve amorphous compounds and Mn-oxides. The increase of efficiency is attributed to the faculty of the metals to form stable oxalate complexes. The addition of ascorbic acid to ammonium oxalate allows complete dissolution of Fe oxides like hematite. This is not the case for the mixture  $\text{NH}_2\text{OH}\cdot\text{HCl}$  1M/HOAc 25%, which has not been sufficiently aggressive against such oxides. Nevertheless, the final results of the trace metal speciation have indicated that ammonium oxalate solutions are less effective for extracting Cd, Pb and Zn. Indeed, these elements are able to form oxalate-complexes which have a low solubility product. A precipitation occurs simultaneously with the dissolution of Mn or Fe oxides and, therefore, the residual fractions are overestimated. The overestimation of the residual fraction concerns mainly Cd and Pb fractionation. The Zn behaviour is different because the largest proportion of this element was bound to silicated materials in our soil samples.

In conclusion, we recommend avoiding the use of oxalate reagents in sequential extraction schemes to study Cd and Pb speciation. Depending on the sources of zinc, its speciation can also be affected by the use of oxalate reagents. Nickel will not be influenced because this element is normally bound to the silicate matrix. Due to the high stability constants, Cu-complexes are easily formed, and therefore some fractions can be overestimated. Consequently, the scheme A is still the best compromise to study the Cd speciation in the soil of the Swiss Jura.

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