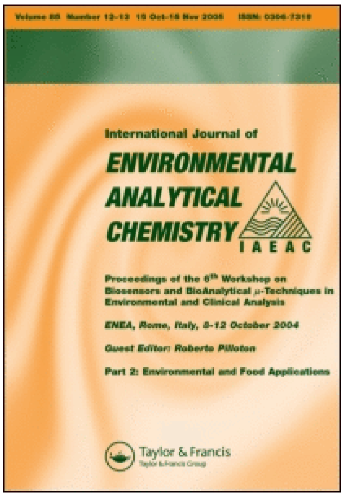

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EVALUATION OF THE SELECTIVITY OF SEQUENTIAL EXTRACTION PROCEDURES APPLIED TO THE SPECIATION OF CADMIUM IN SOILS

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This study aimed at evaluating the selectivity of different extractants – and thus the efficiency of various extraction schemes – used to assess the Cd speciation in the soil of the Swiss Jura. For this purpose, three extractration schemes were selected and all were applied to three different soils. Each extraction scheme consisted of six steps intended to extract Cd bound to: (1) exchangeable, (2) carbonate, (3) Mn-oxides and amorphous compounds, (4) Fe-oxides, (5) organic matter and (6) residual fractions. The results showed that the selectivity of the extraction depended not only on the type of reagents used to extract each phase, but also on the order in which they were applied. In the final analysis, none of the tested schemes were totally satisfactory. The main reason for this is that soil is not a simple addition of pure components but rather the result of complex interactions between its basic constituents. However, one of the schemes would appear to be good enough to characterise adequately the Cd speciation in the soil of the Jura chain.

Keywords: Cadmium; sequential extraction; soil; fractionation; speciation

INTRODUCTION

The mobility, bioavailability and toxicity to plants of trace elements depend on their specific chemical forms and their interaction with the different soil constituents. Consequently, a comprehensive knowledge of the interactions between the traces elements and the soil matrix is required to judge their environmental impact [1–3].

The speciation of a trace element in soils or sediments is usually assessed by the performing of sequential extractions of the solid matrix. The reagents used to

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this end should selectively extract the elements bound to the various characteristic phases of the soil, phases such as clay minerals, organic matter, oxides or carbonates. Although it is widely recognised that selectivity problems affect the results obtained by sequential extractions[4], these methods are still widely used by soil and sediment scientists and numerous recent papers have been published on the subject[5–15]. Most of the authors propose the modification of some of the steps of the two main reference schemes (Tessier et al.[16] and Kersten et al.[17]), so as to adapt the selectivity of the reagents to a specific objective. However, no universal sequential extraction scheme, suitable to all cases, has been proposed yet.

The goal of this work is to optimise the extraction selectivity of some of the reagents used to assess the Cd speciation of the soils of the Swiss Jura. Three sequential extraction schemes were employed to test the influence on the amount of Cd extracted of the reagents' types, concentrations and the order in which they are applied. A mineralogical analysis by X-ray diffractometry was performed at each step to check the complete decomposition of the crystalline soil constituents.

EXPERIMENTAL

Soil samples

Three different soil samples were used for this study. Their main characteristics are presented in Table I. They were chosen according to their carbonate, clay and organic matter contents. "Soil I" was a B horizon of a calcaric Cambisol. "Soil II" was a Bt horizon of a haplic Luvisol, chosen for its large clay content. "Soil III" was an A horizon of rendzic Leptosol, rich in organic matter. The soil names are attributed according to FAO-UNESCO legend [18].

TABLE I Principal characteristics of the samples

Sample	*Clay (%)*	*Silt (%)*	*Sand (%)*	*CEC (cmol kg^{-1})*	*pH_{H2O}*	*$CaCO_3$ (g kg^{-1})*	*C_{org} (g kg^{-1})*
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 on each soil sample (Figure 1). Two schemes (A and B) were modifications of the scheme proposed by Hall et al.[19]. The same reagents were used but in a different order. The C scheme was almost identical to Tessier's reference scheme[16], but the exchangeable fraction was extracted with $CaCl_2$0.05M instead of $MgCl_2$ 1M.

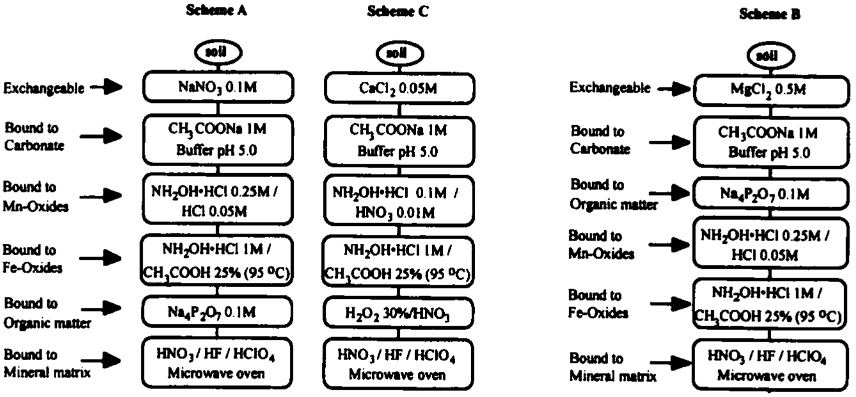

FIGURE 1 Sequential extraction schemes

Following current practise in soil and sediment science, the elements bound to carbonate were extracted using a 1M sodium acetate solution, buffered at pH 5. This procedure was applied in each extraction scheme. The amorphous iron compounds and Mn-oxides, were extracted using two different solutions: $NH_2OH.HCl$ 0.25M/HCl 0.05M[19] and $NH_2OH.HCl$ 0.1M/HNO_3 0.01M[16]. As many authors have proposed[20–23], the crystal iron oxide fractions were extracted using a solution of $NH_2OH.HCl$ 1M and 25% acetic acid at 95°C. Two classic reagents were applied to extract the metal bound to organic matter: $Na_4P_2O_7$ 0.1M[24] and H_2O_2 30%/ HNO_3 0.02M[16]. This extraction was carried out after those for Mn and Fe oxides in the schemes A and C, while in scheme B these steps were reversed in order to examine the capacity of hydroxylamine to dissolve organic matter.

The procedure was carried out as follows: one g of air-dried sample was introduced in a 50 ml screw-cap centrifuge tube. The solid phase was shaken with 10 ml of reagent during 90 minutes, using a rotary shaker at 50 r/min. The solution was separated by centrifugation (20min; 23400 x G) and the supernatant was stored in a polyethylene bottle. The whole procedure was repeated on the centrifugation residue using 10 ml of fresh reagent and, lastly, using 10 ml deionized water. The three supernatants were transferred to a 50 ml volumetric flask and fill up to gauge level with deionized water. This procedure was used to extract the Cd exchangeable, bound to carbonate and to Mn-oxides. The procedure was also used to extract the organic matter with $Na_4P_2O_7$ (schemes A and B). Tessier's procedure[16] was applied to extract the organic matter in the scheme C and to extract the metals bound to crystal iron, in the three schemes. By comparison to the original Tessier's scheme, a washing procedure, as described previously, was included after each extraction step.

The final residue as well as the soil sample were digested, under pressure, with an acid mixture (HF-HNO_3-$HCLO_4$) using a microwave oven. All solutions, were stored at 4°C awaiting analysis. Before use, the vessel was washed for at least two hours with HNO_3 10%.

To insure the quality of the results, four replicates of each samples were carried out with each extraction scheme.

Instrumentation

The Cd content 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 difractometer Philips PW1710 was used to perform the mineralogical analysis. The acidic digestions were performed in a MLS 1200 Mega microwave.

RESULTS AND DISCUSSION

The results of the extractions are presented in Tables II and III, and Figure 2. The roman numerals (I, II or III) label the soil submitted to extraction and the letters (A, B or C), indicate the applied extraction scheme (e.g. the results, obtained for the extraction of soil I according to the scheme A, are labelled IA).

Exchangeable fraction

The results showed that $MgCl_2$ 0.5M extracts more Cd than $CaCl_2$ 0.05M and much more than $NaNO_3$ 0.1M or $MgNO_3$ 0.1M. Although it is widely known that the nature of cation, as well as the concentration of the saline solution used for the ionic exchange, have an influence on the quantity of extractable exchangeable element, this fact cannot account for the broad range of our results.

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

Cd (*mg kg*$^{-1}$)	*IA*	*IB*	*IC*	*IIA*	*IIB*	*IIC*	*IIIA*	*IIIB*	*IIIC*
Exchangeable	0.010 ± 0.004	0.64 ± 0.18	0.080 ± 0.007	0.010 ± 0.000	0.70 ± 0.01	0.09 ± 0.01	0.020 ± 0.003	0.70 ± 0.04	0.11 ± 0.01
Carbonate	2.76 ± 0.29	2.06 ± 0.05	2.50 ± 0.02	1.50 ± 0.07	0.99 ± 0.05	1.43 ± 0.05	-	-	-
Mn-Oxides	2.51 ± 0.02	1.91 ± 0.01	1.76 ± 0.23	1.32 ± 0.04	0.99 ± 0.05	0.79 ± 0.02	2.08 ± 0.13	0.72 ± 0.06	0.38 ± 0.01
Fe-Oxides	2.62 ± 0.17	2.20 ± 0.05	3.44 ± 0.07	1.80 ± 0.05	1.54 ± 0.03	2.28 ± 0.08	0.52 ± 0.07	0.37 ± 0.01	2.11 ± 0.04
Organic matter	0.030 ± 0.003	1.10 ± 0.05	0.12 ± 0.02	0.020 ± 0.003	0.32 ± 0.02	0.060 ± 0.005	<0.005	0.66 ± 0.07	0.030 ± 0.007
Residue	0.26 ± 0.01	0.52 ± 0.04	0.19 ± 0.03	0.14 ± 0.01	0.32 ± 0.02	0.100 ± 0.004	0.040 ± 0.002	0.050 ± 0.005	0.040 ± 0.004
Sum of fractions	8.18 ± 0.33	8.43 ± 0.20	8.09 ± 0.24	4.79 ± 0.10	4.85 ± 0.08	4.75 ± 0.10	2.66 ± 0.15	2.52 ± 0.10	2.67 ± 0.04
Total content	8.10 ± 0.30			4.89 ± 0.22			2.45 ± 0.09		
Recovery (%)	101	104	100	98	99	97	109	103	109

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

Mn (mg kg^{-1})	*IA*	*IB*	*IC*	*IIA*	*IIB*	*IIC*	*IIIA*	*IIIB*	*IIIC*
Exchangeable		6 ± 0	3 ± 0		13 ± 0	4 ± 0		86 ± 2	49 ± 10
Carbonate	113 ± 2	105 ± 1		58 ± 2	45 ± 1				
Mn-Oxides	783 ± 6	655 ± 4	772 ± 3	653 ± 9	549 ± 22	554 ± 11	1142 ± 14	758 ± 19	669 ± 19
Fe-Oxides	327 ± 4	271 ± 6	440 ± 12	379 ± 7	343 ± 18	536 ± 13	277 ± 10	259 ± 11	830 ± 19
Organic matter	5 ± 0	146 ± 2	12 ± 2	8 ± 1	88 ± 3	14 ± 2	4 ± 0	328 ± 1	10 ± 2
Residue	98 ± 3	114 ± 4	99 ± 1	86 ± 4	117 ± 3	83 ± 3	52 ± 2	63 ± 2	51 ± 3
Sum of fractions	1326 ± 8	1296 ± 9	1326 ± 13	1185 ± 12	1156 ± 29	1192 ± 17	1475 ± 17	1495 ± 22	1609 ± 29
Total content	1291 ± 17			1149 ± 15			1445 ± 10		
Recovery (%)	103	100	103	103	101	104	102	103	111
Fe (mg kg^{-1})									
Exchangeable									
Carbonate	34 ± 2	34 ± 2	37 ± 3	17 ± 2	16 ± 1	18 ± 4			
Mn-Oxides	532 ± 9	108 ± 6	280 ± 4	517 ± 11	108 ± 10	256 ± 7	576 ± 38	123 ± 5	27 ± 6
Fe-Oxides	27595 ± 739	16455 ± 641	27813 ± 878	37121 ±1565	22559 ± 1146	38795 ± 506	23194 ± 948	16740 ± 1004	23158 ± 704
Organic matter	1629 ± 80	2969 ± 118	55 ± 7	2335 ± 433	2889 ± 94	37 ± 24	992 ± 140	1797 ± 14	381 ± 41
Residue	19716 ± 647	27623 ± 1052	22486 ± 851	28499 ± 1652	41025 ± 814	29724 ± 799	14309 ± 961	18945 ± 684	15413 ± 999
Sum of fractions	49506 ± 986	47188 ± 1238	50671 ± 1223	68489 ± 2316	66597 ± 1409	68830 ± 946	39072 ± 1358	37604 ± 1214	38979 ± 1222
Total content	50026 ± 140			69950 ± 12			38752 ± 256		
Recovery (%)	99	94	101	98	95	98	101	97	101

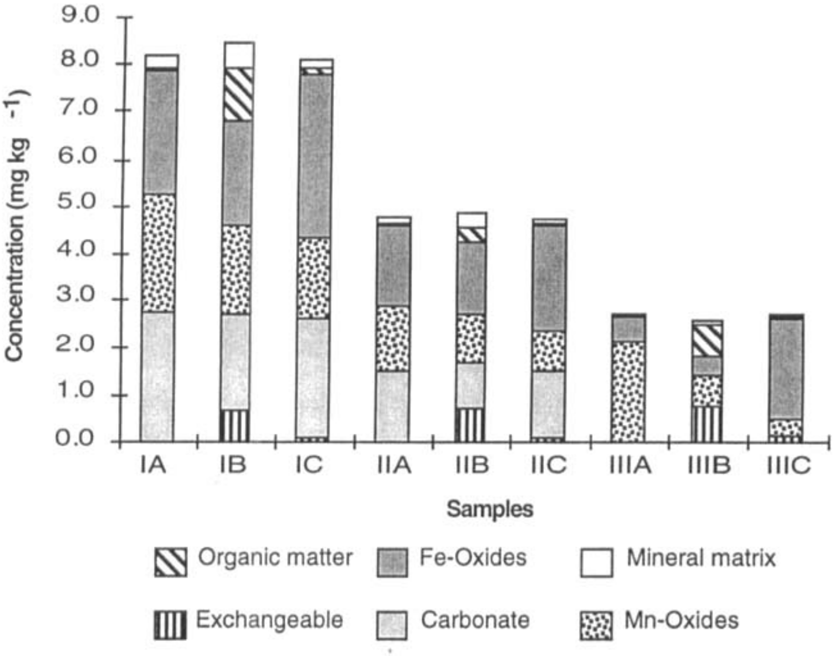

FIGURE 2 Results of Cd speciation

The cation of the extracting solution (Ca, Mg or Na) did not influence the quantity of extracted Cd. The type of anion, on the other hand, exerted a powerful influence. Such a result has already been reported by Calvet et al.[25] for Zn and Cu. The main reason for this is the possible formation of a soluble complex between the Cd and the anion which increases the strength of extraction. This is especially true for chloride since the Cd is able to form chloride complexes like $CdCl^+$, $CdCl_2$ or $CdCl_3^-$. The formation constants cited by Allen et al.[26] are respectively : 95.5, 4.2 and 0.63.

The difference, therefore, between the Cd concentration extracted by $MgCl_2$ 0.5M and that extracted by $CaCl_2$ 0.05M can be explained by an increase in the chloride concentration of the extracting solution and is neither related to the nature of exchange cation nor to its concentration. Another proof was obtained when replacing $NaNO_3$ 0.1M by $MgNO_3$ 0.1M; the same Cd concentrations were found in both extracting solutions. The use of chloride salts during the first step of the extraction scheme may lead to an overestimation of the exchangeable fraction. Indeed, due to the competition between the sorption sites and the formation of complexes, the extracting solution may extract some Cd bound to other soil phases.

Fraction bound to carbonate

The X-ray diagrams (Figure 3) confirmed that 1M NaOAc was the right extractant for the complete dissolution of the carbonate in the most calcareous sample (Soil I).

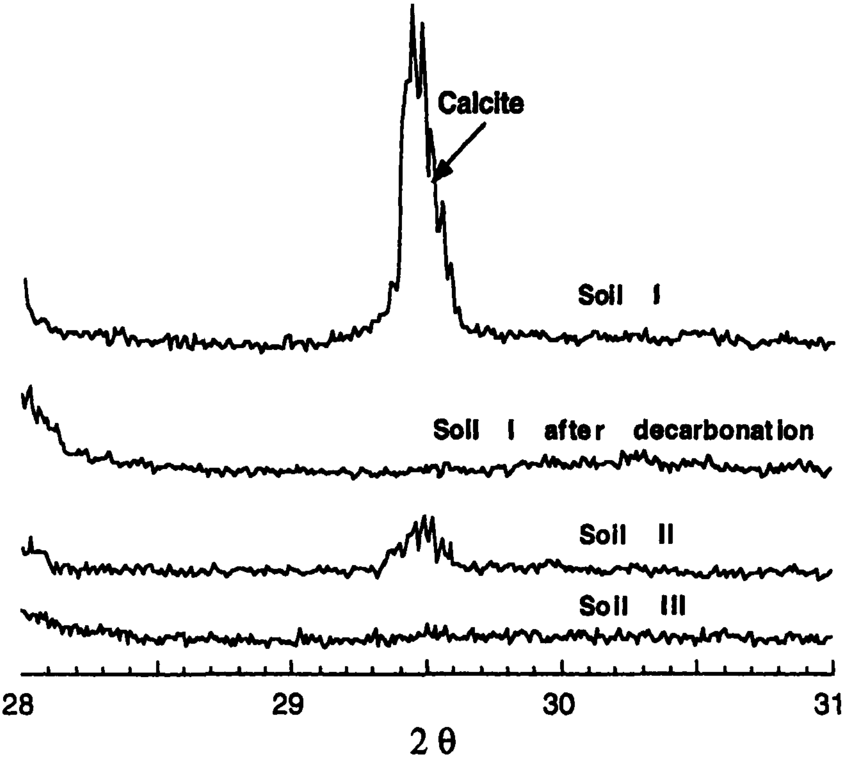

FIGURE 3 X-Ray diffractograms of soil I, soil II, soil III and soil I after treatment with CH_3COONa, pH 5.0

To ensure that NaOAc dissolved only the carbonate phase, we applied the extraction scheme with and without the "carbonate step" to the non carbonated sample (soil III). The results of this experiment demonstrated that the use of NaOAc strongly affected the most concentration of Cd bound to Mn and Fe oxides (Figure 4). By contrast Cd bound to organic matter was little affected in both situations.

In conclusion, the action of NaOAc was not limited to a simple acidification effect, but extracted some Cd bound to phases other than the carbonate. The ace-

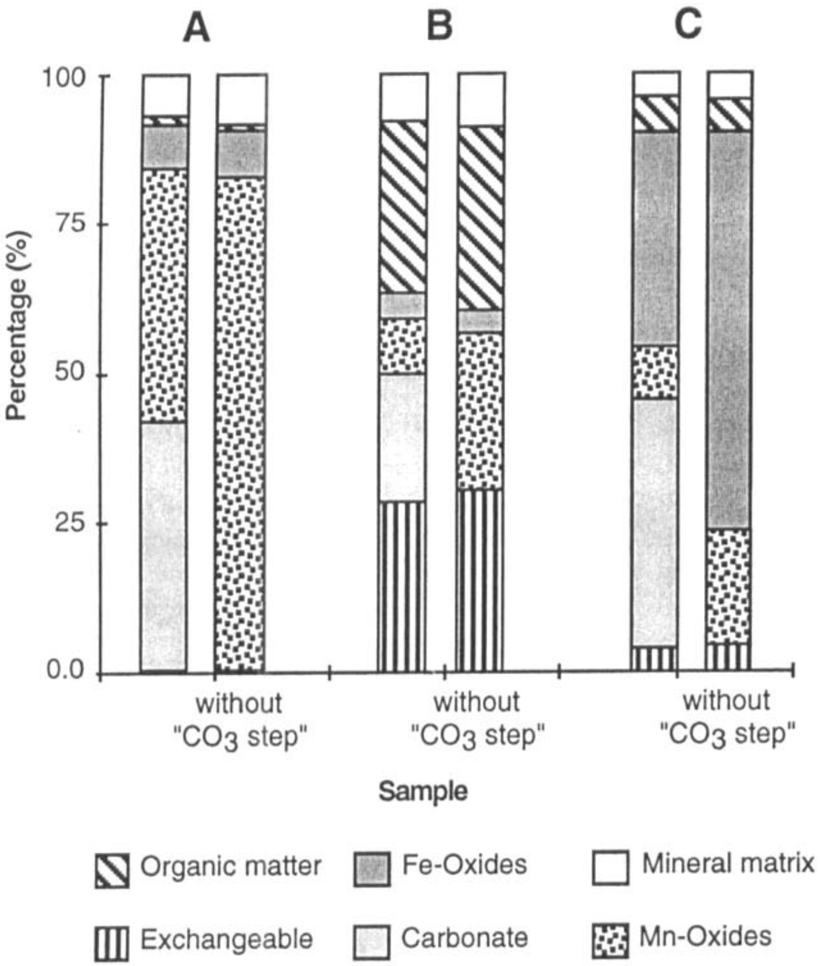

FIGURE 4 Comparison with and without the "carbonate" step of the three schemes for a non calcareous soil

tate, like the chloride, is able to form complexes such as $CdOAc^+$ or $Cd(OAc)_2$. Their formation constants (respectively: 85.11 and 16.60[27]) are on the same order of magnitude as those of chloride and could be sufficient to favour the formation of soluble acetate complexes with Cd at the expense of the sorption on Mn oxides. Such complexes were already mentioned for Cu and Pb by Qiang et al.[28] and, for Cd, by Naidu et al.[29] More generally, the results, presented in figure 2, showed that a large proportion of Cd was extracted by NaOAc in the two calcareous samples. This concords with the hypothesis of a geogenic Cd enrichment of the soil by calcareous rocks in the Swiss Jura[30].

Fraction bound to amorphous Fe and Mn oxides

Comparing the results obtained with schemes A and B and presented in Figure 2, we observed that more Cd was extracted during this step when the reagent was applied before the extraction of organic matter than when it was applied after. This result indicated clearly that hydroxylamine extracts some Cd bound to the organic matter. On the other hand, as the organic matter was extracted with $Na_4P_2O_7$ 0.1M, the pH remained alkaline, and therefore, neither the manganese oxides nor the amorphous compounds were dissolved. As has been previously shown by Hall et al.[19], the concentration of $NH_2OH.HCl$ did not have an influence on extraction efficiency while the acid concentration did. Comparing the results obtained for schemes A and C, Cd was better extracted in presence of HCl 0.05M than HNO_3 0.01 M. In this case, two of the acid's parameters may have played a cumulative role. In one hand, an augmentation of the acid concentration increases the metal extraction[19] and in the other, the associated anion might extract more or less metal depending on its complexing effect[26,31].

Moreover, it seems that the mixture $NH_2OH.HCl$ 0.1M/HNO_3 0.01M did not dissolve the Mn oxides completely. Indeed, the lowest concentration of Mn was measured in this reagent (see table III) and, by the same token, much more Cd was extracted in the next step of the scheme, by $NH_2OH.HCl$ 1M/HOAc 25%.

Fraction bound to crystal Fe-oxides

For the three soils, a large amount of Cd was extracted with this reagent but these amounts depend strongly on the Cd quantity extracted in the precedent step (amorphous compounds and Mn oxide). Although the total amount of Cd bound to Mn and Fe oxide was almost the same in scheme A and C, a larger Cd proportion was extracted in the crystalline iron step when a smaller Cd amount was obtained in the Mn-oxides step and vice-versa.

However, the X-ray diffractogram of the residue showed that all of the crystal iron was not dissolved (Figures 5 and 6). After extraction, hematite was still observed in each soil but goethite was only seen in soil II, the sample richest in iron. In conclusion, in this case, the reagent is not sufficiently strong to dissolved the crystal Fe-oxides completely. However, this fact has not been mentioned by most authors.

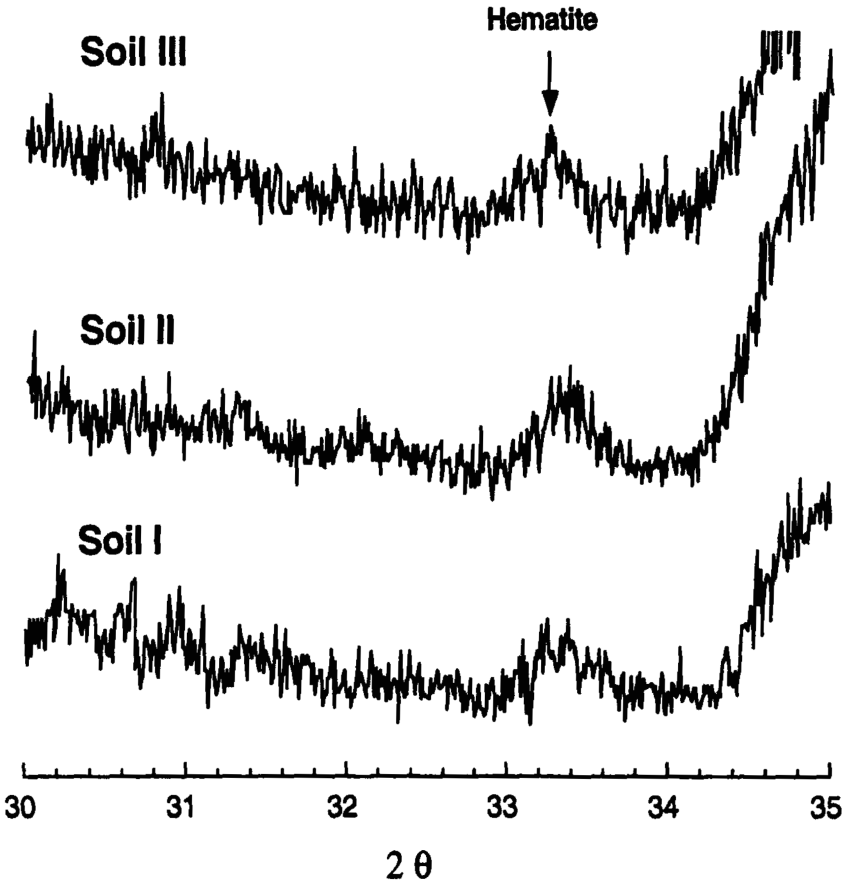

FIGURE 5 X-Ray diffractogram of the samples after theoretical destruction of crystalline iron oxides

Fraction bound to organic matter

The results presented in Figure 2 showed that a larger amount of Cd bound to organic matter was obtained if this step is carried out before the extraction of amorphous compounds and Mn oxides. As a consequence, a part of the Cd supposed to be bound to these compounds in schemes A and C is, in fact, derived from Cd bound to some organic matter. Although alkaline 0.1M $Na_4P_2O_7$ is suspected to disperse microcrystalline Fe oxides[32], this reagent could have been used as the suspension was centrifuged at more than 20000 x G[33].

The Cd amount extracted with the acidic H_2O_2 solution (scheme C) is larger than those extracted with $Na_4P_2O_7$ (scheme A). It is possible that hydrogen per-

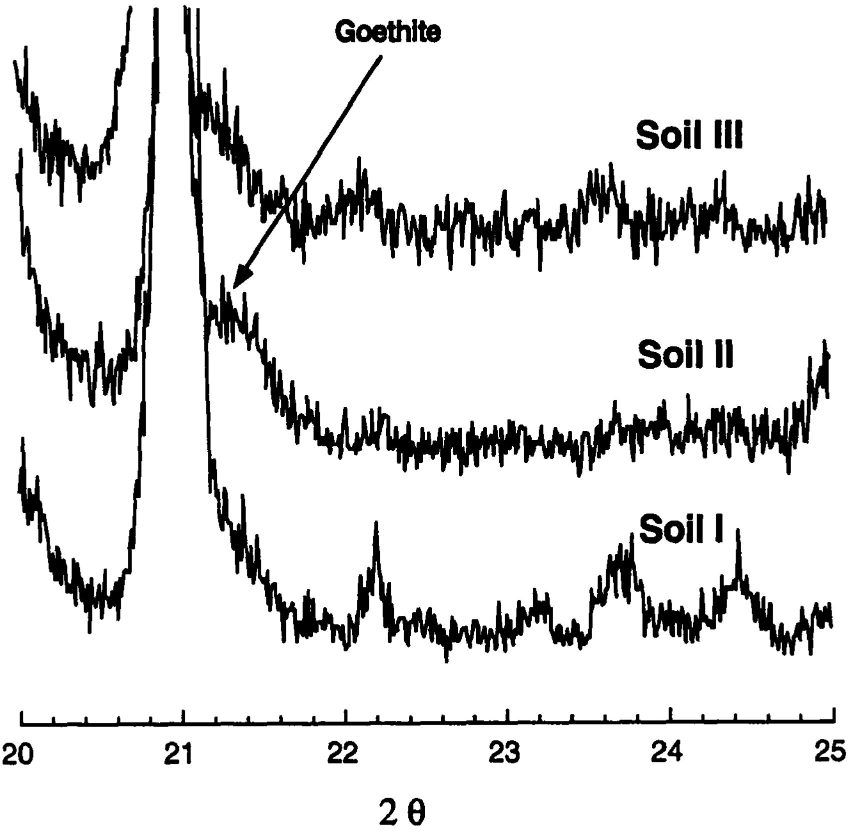

FIGURE 6 X-Ray diffractogram of the samples after theoretical destruction of crystalline iron oxides

oxide dissolved other mineral phases, such as sulphide compounds[34] for example, while, theoretically, $Na_4P_2O_7$ extracted only the Cd bound to organic molecules[35,36]. Consequently, the residual fraction might be underestimated when H_2O_2 is used. However, in both schemes A and C, the Cd amount were very low in comparison with those extracted in the scheme B where the organic matter was extracted before the Mn and Fe oxides. Therefore, to avoid an overestimation of the Cd amount bound to Mn and Fe oxides, the organic matter should be extracted before these two fractions.

Analytical quality of the results

The results shown in Tables II and III, indicate the average value ± standard deviation of four independent extractions. The reproducibility of the extraction results had a variation coefficient lower than 7%, even for the lowest concentrations.

The mass balance of Cd, 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 Cd, Fe and Mn content in the samples, were measured in the resultant solutions obtained after the total dissolution of the soil samples. These results can thus be considered as good when the cumulative risks of analytical errors are taken into account.

CONCLUSION

The results obtained with the three schemes demonstrated that the selectivity of extraction depended not only on the type of reagents used to extract each phase but also on the order in which they were applied.

Due to their relative abilities in forming complexes, a better yield of extraction was obtained when using a chloride salt instead of a nitrate salt to assess the exchangeable fraction of Cd. In our opinion, this increase in efficacy is unfortunately compensated by a decrease in selectivity and, therefore, the content of "exchangeable Cd" is overestimated in chloride extracts.

The Cd bound to the carbonate fraction is well extracted by the sodium acetate buffer. However, the selectivity of this reagent is not very good as it was demonstrated that, for the non calcareous soil, this reagent was also able to extract some Cd bound to the amorphous compounds and Mn oxides. This extracting step, therefore, must be skipped if the samples are not carbonated; but, even in the case of calcareous soils, the content of Cd bound to the carbonate fraction might be overestimated.

The organic matter should be extracted before the extraction of Mn-oxides and amorphous compounds since the hydroxilamine also extracts a part of the Cd bound to the organic matter. This implies the use of an alkaline reagent such as $Na_4P_2O_7$ which is able to extract organic matter without affecting the amorphous phases. However, the main disadvantage of $Na_4P_2O_7$ is its weakness in dissolving some raw organic compounds like wood or roots. From this point of view, the mixture H_2O_2 30% /HNO_3 0.01M is better but, because of its acidity, it cannot be used before the "Mn oxide step".

The solution of $NH_2OH.HCl$ 1M/HOAc 25% is not aggressive enough to extract the totality of crystalline iron oxides. Some complementary studies are in progress to test other better reagents.

In conclusion, none of the tested schemes are entirely satisfactory. Whatever the choice of reagents and of the order in which they are applied, the extraction of Cd bound to a specific soil phase is not selective enough. The main reason for this is that soil results from complex interactions between its basic constituents; it is much more complicated than a simple addition of the pure components such as organic compounds, oxides and carbonates which represent the phases widely used to test the selectivity of extractants. In our case, the B scheme is the compromise that produces the most realistic results - exchangeable fraction excepted. This scheme is, therefore, to be recommended for the sequential extraction of the soils of the Jura chain provided that the exchangeable step is extracted with $NaNO_3$ 0.1M instead of $MgCl_2$ 0.5M.

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