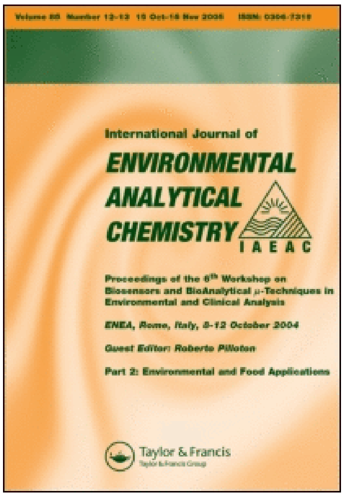

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Some Experiments on Extraction of Heavy Metals Present in Soil

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SOME EXPERIMENTS ON EXTRACTION OF HEAVY METALS PRESENT IN SOIL

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Copper and zinc present in a soil before and after addition of a sewage sludge were extracted using several reagents either with sequential or parallel procedures. The order of extracting reagents had a great influence on the amounts of heavy metals supposed to correspond to different soils fractions (exchangeable, associated with carbonates, oxides, organic matter and silicates). Further, for a given fraction, the nature of the extracting reagent also had an effect on amounts of metals extracted.

Results were discussed on the basis of the possible states of heavy metals in the soil. It was concluded that:

1. no extraction procedure was able to give unequivocally the distribution of heavy metals between several soil fractions.
2. for a given soil fraction, the meaning of results was not straightforward.

KEY WORDS: Zinc, copper, heavy metals, extraction, soils.

1. INTRODUCTION

Agricultural and urban activities can pollute the soils under several circumstances. Sewage sludges, waste waters, some fertilizers, and smoke from factories have been recognized as potential sources of heavy metals. Evaluation of their amounts in the soils, along with their mobility and bioavailability has given rise to numerous works and publications. The main purpose is to get information on the possible behaviour of metals from studies which should be as simple as possible to be used for routine analysis. Thus, chemical procedures have been proposed that allowed the determination of amounts of metal assumed to be in different physico-chemical states. Although these procedures are quite attractive, their meaning is not straightforward considering the effect of the reagents used and the complexity of soils. Under these conditions, it appears necessary to devise experiments which may yield additional information and help interpret soil analyses.

2. NATURE OF THE PROBLEM

It is generally admitted that metallic cations occur in soils in various states as follows:[1-5]

—exchangeable
—associated with carbonates
—associated with metallic oxyhydroxides (adsorbed and occluded)
—associated with organic matter
—trapped in crystalline lattices of silicate minerals (residual fraction).

However, some authors such as Greffard *et al.*,[6] Kuo *et al.*[7] and Miller *et al.*[8] have distinguished a greater number of states for metals associated with oxyhydroxides and organic matter.

Two categories of chemical procedures have been proposed to characterize the pollution status of soils. The first concerns extractive reagents which are considered to be able to extract bioavailable metals. They could, in principle, allow determination of amounts which are likely to be absorbed by plants, but it has not been clearly demonstrated yet. As a matter of fact, several observations have shown that these procedures only lead to valuable predictions for given metal–soil–plant systems.[9] The most frequent procedure is to measure the amounts of metals extracted by reagents such as DTPA and EDTA or the amounts of exchangeable cations. Nevertheless, knowledge of bioavailability requires further research.

The second category of chemical procedures uses sequential extractions to distinguish between the different states or "forms" of metallic cations.[2,3,5,10] They are supposed to be able to extract successively the fractions of metals occurring in different states. It is important to know how such extractions affect the actual state of metals in soil, in order to give a valuable prediction of the behaviour of metallic cations.

Table 1 gives examples of reagents used in sequential extractions. It shows the great variability of the proposed procedures and can explain, at least partly, that comparison between published works is not always a simple matter.

The work reported in this paper presents some results given by a set of various extractive reagents using two ways of extraction:

—sequential extraction according to the procedure of Tessier *et al.*[3] and
—parallel extraction in order to observe the effect of each extractive reagent separately. Parallel extractions have been suggested as alternative procedures because alteration of the soil constituents leads to results which depend on the order used for applying successive reagents.[8,21,22]

The meaning of the described procedures is discussed in Section 4.

3. MATERIALS AND METHODS

3.1 Materials

Soil materials were taken from an experimental field designed to study the effect of sewage sludge applications on soil properties and composition.[23] They were sampled ten years after application of 100 t/ha of sewage sludge (on a dry matter basis). Several chemical characteristics of the sludge are given in Table 2 together with the applied quantities of metals; only copper and zinc were studied.

Table 1 Some bibliographic data on the extraction of heavy metals present in soils and sediments

Authors	*Exchangeable*	*Fraction associated with carbonates*	*Fraction associated with oxides*	*Fraction associated with organic matter*	*Total amount and residual fraction*
McLaren Crawford[11] (1973)	0.05 N $CaCl_2$	2.5% CH_3COOH	0.1 M $(COOH)_2$ +0.175 M $(COONH_4)_2$ pH = 3.5	1 M $K_4P_2O_7$	HF
Stover *et al.*[12] (1976)	1 M KNO_3 +NaF		0.1 M EDTA pH = 6.5	0.1 M $Na_4P_2O_7$	1 M HNO_3
Gatehouse *et al.*[13] (1977)	1 M CH_3COONH_4 +CH_3COOH pH = 4.5		0.1 M NH_2OH +1 M CH_3COONH_4 pH = 4.5	30% H_2O_2	HF − $HClO_4$
Filipek and Owen[14] (1979)	1 M CH_3COOH		0.25 M NH_2OH, HCl in 25% (v/v) CH_3COOH	Acidified 30% H_2O_2	HNO_3 − HF − $HClO_4$
Tessier *et al.*[3] (1979)	1 M $MgCl_2$ or 1 M CH_3COONa at pH = 8.2	1 M CH_3COONa +1 M CH_3COOH at pH = 5.0	0.04 M NH_2OH, HCl in 25% (v/v) CH_3COOH at 96 ± 3 °C or 0.3 M $Na_2S_2O_4$ +0.175 M Na − citrate +0.025 M citric acid	0.02 M HNO_3 + 30% H_2O_2, pH = 2 at 85 ± 2 °C, 2 h +30% H_2O_2 + HNO_3, pH = 2 at 85 ± 2 °C, 3 h 3.2 M CH_3COONH_4 in 20% HNO_3	HF − $HClO_4$
Förstner *et al.*[2] (1979)	0.2 M $BaCl_2$		0.1 M NH_2OH, HNO_3 + 25% (v/v) CH_3COOH + HCl	30% H_2O_2 + NH_4OH	HF − $HClO_4$
Schalscha *et al.*[4] (1980)	1 M KNO_3	0.5 M NaF pH = 6.5	0.1 M EDTA pH = 6.5 double extraction	0.1 M $Na_4P_2O_5$	1 M HNO_3
Garcia-Miragaya[15] (1981)	1 N $CaCl_2$	2.5% CH_3COOH	0.05 M EDTA pH = 7	0.1 N $Na_4P_2O_5$	HF
Badri and Aston[16] (1981)	1 M CH_3COONH_4 +0.5 M $(CH_3COO)_2Mg$		0.25 M NH_2OH, HCl pH = 2	30% H_2O_2 +1 M CH_3COONH_4	

Table 1 (*Continued*)

Authors	*Exchangeable*	*Fraction associated with carbonates*	*Fraction associated with oxides*	*Fraction associated with organic matter*	*Total amount and residual fraction*
Förstner *et al.*[17] (1981)	1 M CH_3COONH_4 pH = 7		(1) 0.1 M NH_2OH, ClH + 0.01 M HNO_3, pH = 2 (2) 0.2 M $(COONH_4)2$ + 0.2 M (COOH)2, pH = 3	30% H_2O_2, HNO_3 pH = 2 at 85 °C extraction with 1 M CH_3COONH_4	HNO_3 at 180 °C
Greffard *et al.*[6] (1981)		resin − H^+	(1) $(COONa)_2$ (2) $(COONa)_2$ + UV	30% H_2O_2 at 40 °C	
Sposito *et al.*[10]	0.5 M KNO_3		0.5 M Na_2 EDTA	0.5 M NaOH	4 M HNO_3 at 80 °C
Dekeyser *et al.*[18] (1983)		1 M CH_3COONH_4 pH = 4.5	(1) 0.1 M NH_2OH, HCl (2) 0.2 M $(COONH_4)2$ (HCOOH)2, pH = 3.3 obscurité (3) Same as (2) + UV		$HNO_3 - HF - HCl$
Kuo *et al.*[7] (1983)	1 M $MgCl_2$		(1) (COONa)2 (2) Citrate dithionite bicarbonate	6% $NaClO_4$ at 85 °C	$HNO_3 - HClO_4$
Meguelatti *et al.*[5] (1983)	1 M $BaCl_2$	1 M CH_3COOH + 0.6 M CH_3COONa	0.1 M NH_2OH + 25% (v/v) CH_3COOH	30% H_2O_2 + 0.02 M HNO_3 + 3.2 M CH_3COONH_4	HF − HCl
Shuman[19] (1985)	1 M $Mg(NO_3)_2$ pH = 7		(1) 0.1 M NH_2OH, HCl pH = 2 (2) 0.2 M $(COONH_4)2$ + 0.2 M (COOH)2, pH = 3 (3) Same as (2) + ascorbic acid	0.7 M NaOCl pH = 8.5	$HF - HNO_3 - HCl$
Gibson and Farmer[20] (1986)	1 M CH_3COONH_4 pH = 7	1 M CH_3COQNa pH = 5	(1) 0.1 M NH_2OH, ClH + 0.01 M HNO_3 (2) 1 M NH_2OH, ClH in 25% (v/v) CH_3COOH	30% H_2O_2 + 0.02 M HNO_3 at 85 °C	Aqua regia + HF

Table 2 Some characteristics of the sewage sludge used in the reported experiment and amounts applied (kg/ha)

	Water content (39%) *Dry matter (61%)*	
	Content % of dry matter	*Amounts applied*
Dry matter	—	100 000
Organic carbon	17.5	17 500
Nitrogen	2.0	2000
	mg/kg of dry matter	
Zinc	5480	548
Copper	1650	165
Cadmium	95	9.5
Chromium	925	92.5
Lead	970	97
Nickel	106	10.6

Table 3 Some characteristics of the soil used in the reported experiment

	g/kg
Clay	138.0
Fine silt	232.0
Coarse silt	537.0
Fine sand	28.0
Coarse sand	18.0
Organic matter	17.0
Nitrogen	0.98
Carbonates	10.0
pH	7.9
CEC—meq/100g	9.4
	mg/kg
Zinc	16.0
Copper	2.8
Cadmium	0.5
Chromium	7.0
Lead	15.0
Nickel	7.0

Table 3 gives the physico-chemical characteristics of the top layer of soil (0–30 cm). No sample was taken below 30 cm since preliminary observations had shown that the added metals had not been transported deeper.

3.2 Methods

Total amounts of metals were determined by the procedures of Tessier *et al.*[3] (concentrated $HClO_4$ and HF) and Meguelatti *et al.*[5] (concentrated HF and HCl).

Sequential extraction was as described by Tessier *et al.*[3] (Table 4).

Parallel extractions were performed both with reagents used in the sequential extraction and with other reagents (Table 5). These procedures yielded information on the influence of the counter cations and of the accompanying anions. In addition, six successive extractions were made with 1 M $MgCl_2$ in order to evaluate the degree of completeness of the exchange.

Whatever the procedure used, sequential or parallel, extraction of the so-called "carbonate", "oxide" and "organic" fractions was followed by two washings with a 1 M $MgCl_2$ solution in order to avoid or limit possible adsorption of metallic cations on clays.

Liquid phases separated by centrifugation were analyzed for Cu^{2+} and Zn^{2+} by flame absorption spectrometry. All measurements were made in duplicate.

4. RESULTS AND DISCUSSION

4.1 Sequential Extraction

Table 6 shows the results obtained with the sequential extraction.

For the untreated soil, the main features of the distribution of the metallic cations among the different forms were:

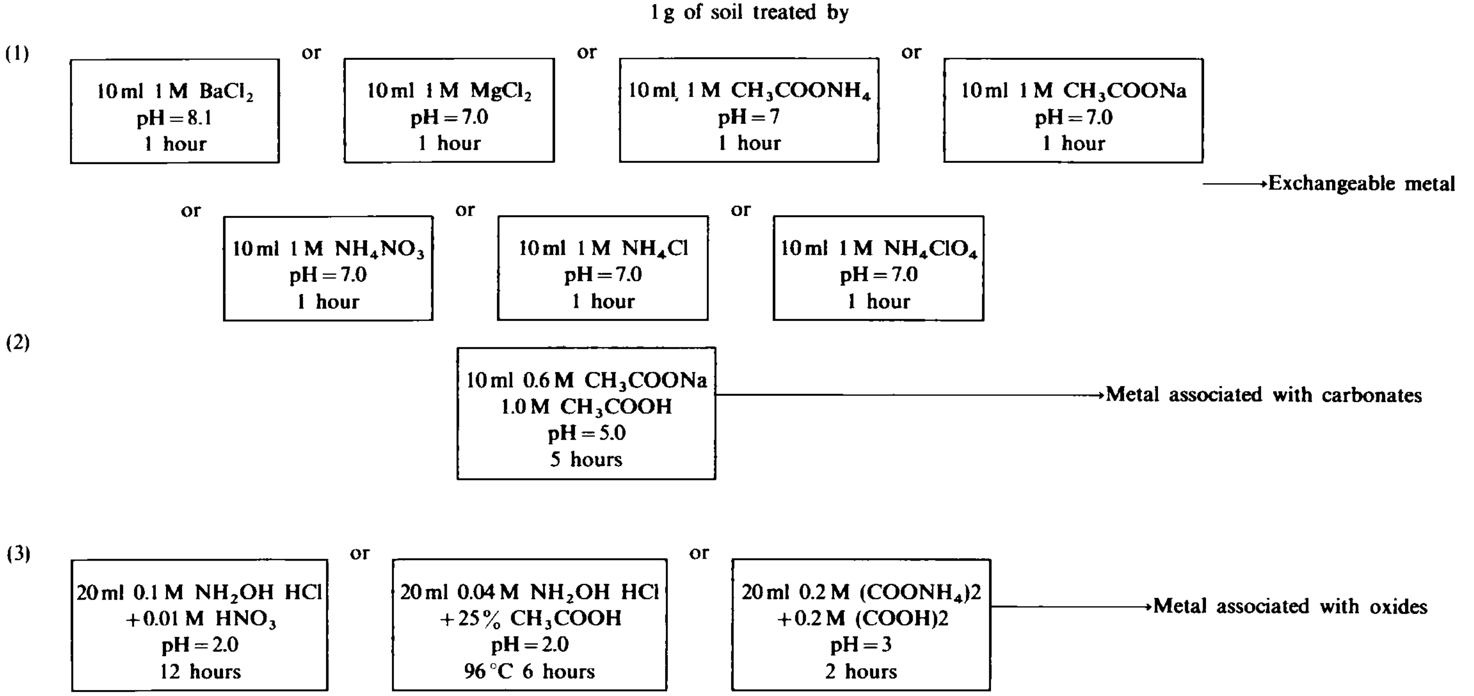
—dominance of the oxide fraction for zinc and to a lesser extent for copper. The opposite result was expected on the basis of the ability of metals to form surface complexes. Further knowledge on the action of extracting reagents is needed to explain this point:
—fractions associated with carbonates were greater for zinc than for copper;
—fractions associated with organic matter were of the same order of magnitude for both metals;
—the exchangeable fraction was small for Zn^{2+} and very small for Cu^{2+};
—the residual fraction was greater for copper than for zinc;
—differences between copper and zinc behaviour chiefly resulted from the residual and exchangeable fractions.

They can be explained for the residual fraction considering that it consists of two parts, one within the crystal lattice of mineral constituents and the other that is specifically adsorbed on the edges of clay lattices and not extracted by the reagents previously used to obtain the fraction associated with oxyhydroxide compounds. Concerning this part, the specific adsorption through surface complexation is more efficient for copper than for zinc. This can explain the observed results because Mg-cations do not interact with the surfaces in a specific way and therefore, are not easily able to desorb copper ions. The strong specific adsorption of copper can also explain the low amount of exchangeable Cu^{2+} from the extraction with $MgCl_2$ solutions.

Table 4 Procedure for sequential extraction according to Tessier *et al.*[3]

1 g of soil +	10 ml 1.0 M $MgCl_2$ pH = 7.0 1 hour	→Exchangeable metal
Residue +	10 ml 0.6 M CH_3COONa 1.0 M CH_3COOH pH = 5.0 5 hours	→Metal associated with carbonates
Residue +	20 ml 0.04 M NH_2OH, HCl + 25% (v/v) CH_3COOH pH = 2.0 96 °C, 6 hours	→Metal associated with oxides
Residue +	(1) 8 ml 30% H_2O_2, 0.02 M HNO_3 pH = 2.0, 85 °C, 2 hours (2) 3 ml 30% H_2O_2, 0.02 M HNO_3 pH = 2.0, 85 °C, 2 hours (3) 20 ml 3.2 M CH_3COONH_4	→Metal associated with organic matter
Residue +	(1) 2 ml $HClO_4$ + 10 ml HF (2) 1 ml $HClO_4$ + 10 ml HF (100–150 °C) (3) 1 ml $HClO_4$ heated to dryness (4) Solubilization in 12 N HCl	→Residual fraction

Table 5 Procedure used for parallel extraction



1 g of soil treated by

(1)

10 ml 1 M $BaCl_2$
$pH = 8.1$
1 hour

or

10 ml 1 M $MgCl_2$
$pH = 7.0$
1 hour

or

10 ml, 1 M CH_3COONH_4
$pH = 7$
1 hour

or

10 ml 1 M CH_3COONa
$pH = 7.0$
1 hour

or

10 ml 1 M NH_4NO_3
$pH = 7.0$
1 hour

or

10 ml 1 M NH_4Cl
$pH = 7.0$
1 hour

or

10 ml 1 M NH_4ClO_4
$pH = 7.0$
1 hour

→ Exchangeable metal

(2)

10 ml 0.6 M CH_3COONa
1.0 M CH_3COOH
$pH = 5.0$
5 hours

→ Metal associated with carbonates

(3)

20 ml 0.1 M NH_2OH HCl
+0.01 M HNO_3
$pH = 2.0$
12 hours

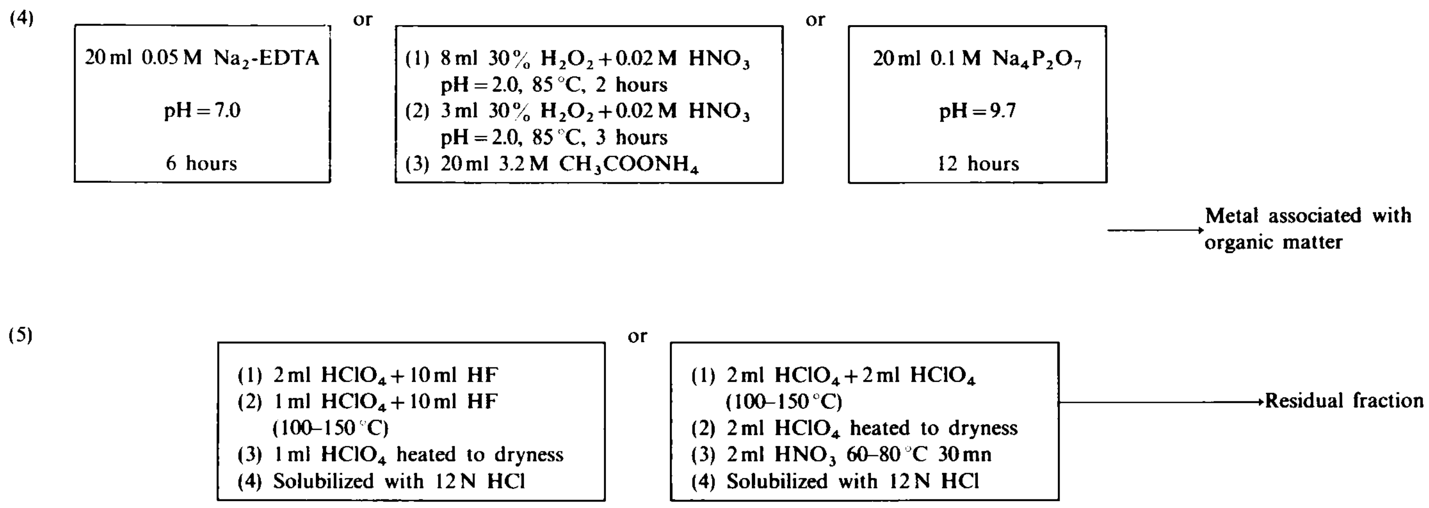
or

20 ml 0.04 M NH_2OH HCl
+25% CH_3COOH
$pH = 2.0$
96 °C 6 hours

or

20 ml 0.2 M $(COONH_4)2$
+0.2 M $(COOH)2$
$pH = 3$
2 hours

→ Metal associated with oxides



(4)

20 ml 0.05 M Na_2-EDTA
pH = 7.0
6 hours

or

(1) 8 ml 30% H_2O_2 + 0.02 M HNO_3
pH = 2.0, 85 °C, 2 hours
(2) 3 ml 30% H_2O_2 + 0.02 M HNO_3
pH = 2.0, 85 °C, 3 hours
(3) 20 ml 3.2 M CH_3COONH_4

or

20 ml 0.1 M $Na_4P_2O_7$
pH = 9.7
12 hours

→ Metal associated with organic matter

(5)

(1) 2 ml $HClO_4$ + 10 ml HF
(2) 1 ml $HClO_4$ + 10 ml HF
(100–150 °C)
(3) 1 ml $HClO_4$ heated to dryness
(4) Solubilized with 12 N HCl

or

(1) 2 ml $HClO_4$ + 2 ml $HClO_4$
(100–150 °C)
(2) 2 ml $HClO_4$ heated to dryness
(3) 2 ml HNO_3 60–80 °C 30 mn
(4) Solubilized with 12 N HCl

→ Residual fraction

Table 6 Amounts of metals obtained with sequential extraction: q mg/kg; % is the percentage of the total amount

Fraction	*Untreated soil*				*Treated soil*			
	Zn		*Cu*		*Zn*		*Cu*	
	q	%	q	%	q	%	q	%
Exchangeable	1.95	3.3	Traces	0	3.58	1.7	Traces	0
Associated with carbonates	11.00	18.8	0.96	7.5	34.38	16.1	2.57	5.9
Associated with oxides	28.48	48.7	3.85	30.0	118.9	55.8	28.60	65.9
Associated with org. mat.	6.46	11.1	1.11	8.6	6.55	3.1	2.77	6.4
Residual	8.00	13.7	6.43	50.0	41.25	19.4	8.88	20.5
Sum of fractions	55.89	95.6	12.25	96.1	204.66	96.1	42.8	98.7
Total content	58.44		12.86		213.13		43.4	

Table 7 Amount of metal obtained with parallel extraction (mg/kg)

Fraction	*Untreated soil*		*Treated soil*	
	Zn	*Cu*	*Zn*	*Cu*
Exchangeable	1.74	Traces	3.81	Traces
Associated with carbonates	9.45	0.48	33.74	2.40
Associated with coxides	56.34	3.15	171.0	24.85
Associated with org. mat.	12.87	1.15	41.89	6.0
Total content	58.44	12.86	213.13	43.4

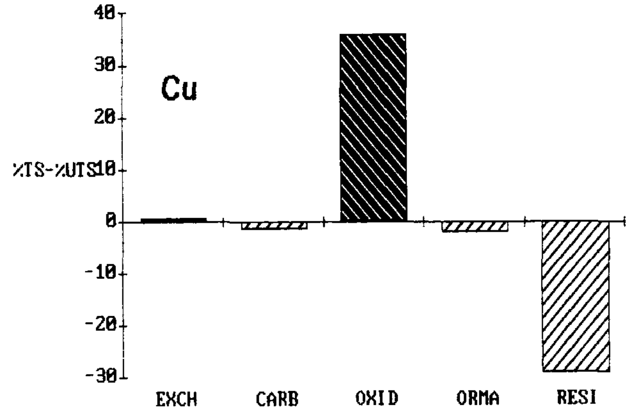


Figure 1 Differences between the amounts of copper extracted from the treated soil (TS) and the amounts of copper extracted from the untreated soil (UTS) for each fraction:

—EXCH: exchangeable

—CARB: metal associated with carbonates

—OXID: metal associated with oxyhydroxides

—ORMA: metal associated with organic matter

—RESI: residual fraction

(amounts are expressed in % of the total metal content).

Examination of the treated soil and comparison with the untreated one indicate that (Table 6, Figures 1 and 2):

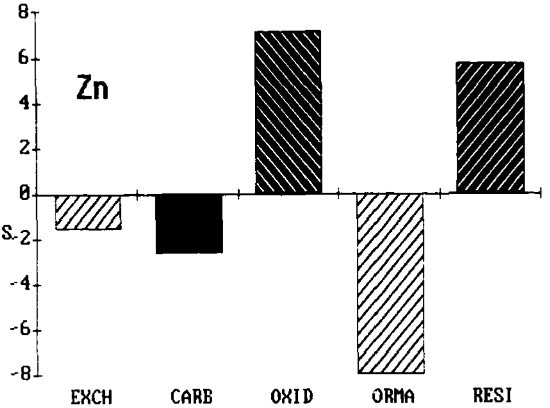


Figure 2 Differences between the amounts of zinc extracted from the treated soil (TS) and the amounts of zinc extracted from the untreated soil (UTS); fractions are the same as for copper. Note that ordinate scales in Figures 1 and 2 are different.

—copper and zinc preferentially accumulated in the oxide fraction. Accumulation was greater for copper because surface complexation is more effective with this metal. This agrees with previous observations on the consequences of sewage sludge applications.[10,24,25]

—the exchangeable fraction slightly varied for zinc and did not vary for copper. However, some other observations showed that the exchangeable fraction is increased after sewage sludge applications.[9]

—the proportion of metal associated with organic matter decreased for both copper and zinc.

—the main difference between the two metals arose from the residual fraction. It increases for zinc and decreases for copper. This quite surprising behaviour is not yet clearly explained and raises questions about the meaning of the residual fraction.

4.2 Parallel Extraction with the Reagents used in Tessier's Procedure

Comparison between Tables 6 and 7 shows that: amounts corresponding to the exchangeable and carbonate fractions were nearly similar although some modifications would have been expected. Applying the mixture ($CH_3COONa + CH_3COOH$) would have increased the amount of the exchangeable fraction removed together with the carbonate fraction, owing to the complexing power of acetate ions (see next paragraph). However, no such observation was made, probably because the quantity of exchangeable cations was low compared with that corresponding to the carbonate fraction.

On the contrary, the amounts associated with oxides and organic matter markedly increased for zinc. Because acid reagents were used to extract these fractions (Table 4), they also caused a part of the exchangeable and almost all of the carbonate fractions to pass in solution. For copper, a marked difference

Table 8 Amounts (mg/kg) of exchangeable zinc obtained from the treated soil by successive extractions with $MgCl_2$; x = mean values; Sd = standard deviation; CV% = variation coefficient

	Extr. 1	*Extr. 2*	*Extr. 3*	*Extr. 4*	*Extr. 5*	*Total*
1	3.48	3.21	3.85	2.99	2.83	16.36
2	3.48	3.21	4.06	3.10	2.73	16.58
3	3.39	3.26	3.58	2.89	2.73	15.85
4	3.48	3.26	3.80	2.99	2.78	16.31
5	3.42	3.15	3.96	3.05	2.78	16.36
6	3.42	3.32	3.69	2.99	2.67	16.09
x	3.45	3.24	3.82	3.00	2.75	16.26
Sd	0.036	0.053	0.160	0.064	0.051	0.232
CV%	1.1	1.6	4.2	2.1	1.8	1.4

Table 9 Effect of the counter cation on the amount of exchangeable metal (mg/kg)

Reagent	*Untreated soil*		*Treated soil*	
	Zn	*Cu*	*Zn*	*Cu*
$BaCl_2$	1.26	0.45	3.85	0.60
$MgCl_2$	1.95	Traces	3.81	Traces
CH_3COONH_4	1.74	0.80	4.86	1.06
CH_3COONa	9.45	0.48	33.74	2.40

between the two procedures was only observed for the fraction associated with organic matter in the treated soil. These observations show the unspecificity of extracting reagents and agree with previously published results.[26]

4.3 Comparing the Action of Several Reagents

Exchangeable fraction: the exchangeable fraction is especially interesting because it is frequently considered to be the bioavailable fraction. Table 8 shows that one extraction with 1 M $MgCl_2$ could not yield the right amount of exchangeable cations. It must be related to observations on adsorption selectivity showing that the adsorbing surfaces of the soil constituents have a greater affinity for zinc and copper than for Mg-cations (Msaky).[27] One can note the good reproducibility estimated from six measurements.

From Table 9 it appears that for a given anion, the nature of the cation influenced the amount of desorbed metal. The amount of desorbed copper was greater with Ba^{2+} than with Mg^{2+}, whereas, the amount of desorbed zinc was not greatly modified. Na^+ was more efficient than NH_4^+ in desorbing zinc for the two soils, and copper for the treated soil. Its dispersive action on clay minerals may be the cause of this behavior. However, further results are required to propose an explanation since different exchange sites with several selectivities are implied.

As shown in Table 10, the nature of the anion must also be taken into account. The effect of acetate anions can be clearly observed and may be attributed to its great complexing power compared with that of NO_3^-, Cl^- and ClO_4^- anions.

Nevertheless, definitive interpretation is not yet possible. Adsorption/desorption

Table 10 Effect of the anion on the amount of exchangeable metal extracted from the untreated soil (mg/kg)

Reagent	*Zn*	*Cu*
CH_3COONH_4	1.74	0.80
NH_4NO_3	0.10	Traces
NH_4Cl	0.26	Traces
NH_4ClO_4	0.29	Traces

Table 11 Amounts of metal associated with oxyhydroxides extracted with different reagents (mg/kg)

Reagent	*Untreated soil*		*Treated soil*	
	Zn	*Cu*	*Zn*	*Cu*
$0.04\,NH_2OH + CH_3COOH$	56.34	3.15	171.04	24.85
$0.1\,M\,NH_2OH + HNO_3$	12.45	0.95	117.25	4.59
$(COONH_4)2 + (COOH)2$	48.22	6.38	115.70	36.71

Table 12 Amounts of metal associated with the organic matter extracted with different reagents (mg/kg)

Reagent	*Untreated soil*		*Treated soil*	
	Zn	*Cu*	*Zn*	*Cu*
H_2O_2	12.87	1.15	41.89	6.01
$Na_4P_2O_7$	44.71	3.27	78.88	24.09
Na_2-EDTA	46.75	5.52	82.34	32.04

of metallic cations depends on several factors which must be controlled and, as a consequence, any comparison between soils is only meaningful for a given set of experimental conditions.

Oxide fraction (Table 11): It is well known that cations such as Zn^{2+} and Cu^{2+} are retained on oxyhydroxides by surface complexation. They can thus, pass into a solution phase through either transformations of the minerals under the action of a reagent (such as NH_2OH) or complexation by dissolved ligands such as acetate and oxalate anions. Examination of the results in Table 11 reveals that complexation is probably more effective (greater amounts extracted in presence of acetate anions). On the other hand, it is more pronounced for Cu^{2+} than for Zn^{2+} as expected from their ability to be complexed.

Organic fraction (Table 12): To explain the observed differences, it is worth noting that in addition to the preceding considerations, extraction of metallic cations can be due to destruction of the organic matter and to complexation of the metals in solution. It might therefore be concluded from the results presented in Table 12 that, at least in the systems studied, destruction of the organic matter is not the main factor.

Total amount: As shown in Table 13, total amounts obtained with acid treatments also varied slightly. It can probably be attributed to the final dissolution step with concentrated HCl.

Table 13 Amounts of total metal given by two procedures (mg/kg)

Reagent	*Untreated soil*		*Treated soil*	
	Zn	*Cu*	*Zn*	*Cu*
$HClO_4$ + HF (Tessier *et al.*[3])	58.44	8.51	213.1	42.86
HF + HCl (Meguellati *et al.*[5])	58.44	12.86	191.9	43.93

5. CONCLUSION AND GENERAL COMMENTS

Characterization of heavy metal pollution of soils requires determination of both the total amount of metals and the amount that can be transported and/or absorbed by plants and soil organisms.

Determination of total amounts is not particularly difficult, but it does not lead to useful information on metal mobility and bioavailability. These characteristics have been estimated so far by determining the quantities of metal assumed to correspond to definite states, although this assumption is probably not correct as we have just shown.

The procedures described in the literature led to estimations of the "exchangeable", "carbonate", "oxides", "organic" fractions. They are useful tools, but are not suitable from a physico-chemical point of view for the following reasons.

1. Since the surfaces of soil minerals and organic constituents are heterogeneous, metallic cations are retained with varying retention energies. It is thus possible to define a distribution function for the retention energies for a metal-substrate couple. This function is a basic physico-chemical characteristic. In a complex system such as soil, which contains mixtures of several minerals and organic compounds, an overall distribution function for retention energies could also be defined as for adsorption.[28–31] As a consequence, an univocal relationship never exists between soil fractions defined on the basis of an extraction procedure and retention energy values, because sites can have the same retention energy but be associated with different constituents. Such considerations can explain different results obtained with several reagents supposed to extract the same fraction. It is also often difficult to compare published data. It is therefore better to relate a quantity of extracted metal to the nature of the extracting reagents than to a given soil constituent. In other words, for example, it is better to speak about the fraction extracted with an hydoxylamine/nitric acid mixture than to speak about an oxyhydroxide fraction. However, the use of distribution functions for retention energies should improve prediction of metal mobility and bioavailability.

2. Defining metal fractions on the basis of extraction procedures can also be misleading owing to possible secondary phenomena. A typical example is given by recent data on extractions by H_2O_2 treatments which showed that the concentration of metallic cations in the extraction solution is time-dependent.[32] As a result, the amount of metal assumed to be associated with the organic matter depends on the contact time between the soil and the extractive solution.

3. In addition, the reagents used were apparently not able to allow complete extraction of the different fractions of metal as shown for exchangeable fraction (this study) and by Kheoboian and Bauer[33] with model aquatic sediments.

The exchangeable fraction is also frequently closely related to mobility and bio-availability. It is also quite easy to determine. The main point concerning the exchangeable fraction is however that experimental conditions must be accurately defined, namely: nature of the counter cation, nature of the anion, ionic force, pH, and soil/solution ratio values.

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