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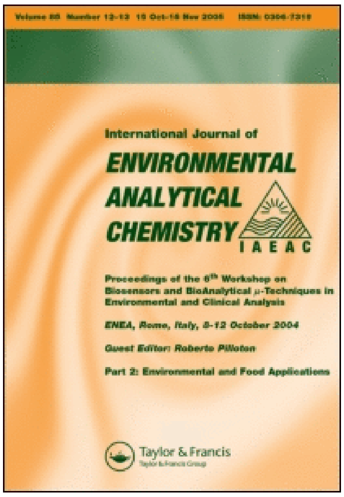

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CHOICE OF EXTRACTION TECHNIQUE FOR SOIL REDUCIBLE TRACE METALS DETERMINES THE SUBSEQUENT OXIDISABLE METAL FRACTION IN SEQUENTIAL EXTRACTION SCHEMES

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Ten agricultural soils were treated with sewage sludge and subjected to two contrasting operationally-defined sequential extraction schemes to extract three trace metal fractions: HOAc-soluble, $NH_2OH.HCl$-reducible and H_2O_2/NH_4OAc-oxidisable. One scheme used 0.10*M* $NH_2OH.HCl$ at pH 2.0 and the other used 0.04*M* $NH_2OH.HCl$ in 25% (v/v) HOAc at 96 ± 3°C to extract the reducible fraction. The latter solution dissolved much more Fe and Mn than did the former, and the higher concentrations of Fe and Mn were accompanied by increased concentrations of Cu and Zn in the reducible fraction. Dissolution of the moderately reducible Fe-Mn oxides also increased the subsequent oxidisable metal fraction. The results demonstrate that reducing reagents with different capacities to extract reducible Fe-Mn oxides produced different distribution patterns of trace metals in sludge-amended and control soils. We conclude that the latter solution is a more useful extractant for dissolution of reducible trace metals in soils.

Keywords: Copper; oxidisable fraction; reducible fraction; sequential extraction; zinc

INTRODUCTION

Trace metals in soils are present in different physicochemical fractions[1]. Sequences of different chemical extractants have become popular for quantification of metals in these different fractions in soils[2,3,4], usually starting with the

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weakest and least aggressive and ending with the strongest and most aggressive[5]. There is a wide range of sequential chemical procedures in use, involving three to nine different fractions in soil and sediment solid matrices[6,7].

Among these procedures the scheme of Ure et al.[8], a three-step sequential extraction method, was recently proposed as the standardised method for The Measurement and Testing Programme of the Commission of the European Communities. Trace metals in the solid phase were fractionated using this scheme into three operationally defined fractions: HOAc-soluble, $NH_2OH.HCl$-reducible and H_2O_2/NH_4OAc-oxidisable. Ure et al.[8] expected that the adoption of the common extraction protocol would give new impetus to the use of the scheme throughout the European Union Member States. It is useful to adopt a common scheme so that results from different scientists and different laboratories can be compared. The three-step chemical extraction procedure has been used for studies on chemical forms of heavy metals in sewage sludge[9], sludge-treated soils[10,11,12] and soils from a mining and smelting area[12,13].

In this scheme a solution of 0.10*M* $NH_2OH.HCl$ at pH 2.0 is used to extract the reducible Fe and Mn fraction of trace metals. This solution is a mild reducing reagent commonly used to mobilise Mn from its oxides or trace metals adsorbed on or occluded in Mn oxides[5,14,15]. The reagent also weakly attacks amorphous Fe oxide[16,17,18], and hence the metal fraction extracted by this extractant may represent the Mn oxide reducible metal fraction rather than the complete Fe-Mn oxide reducible fraction. Reducible Fe oxides may be important because of their great ability to bind and retain trace metals in soils[19,20,21,22], and consequently as important sources of potentially mobile and available trace metals[11,23,24] due to their sensitivity to soil acidification and reduction. Furthermore, the amounts of reducible Fe oxides in soils are usually much higher than those of reducible Mn oxides. Therefore a solution that can effectively extract both the reducible Fe oxides and the reducible Mn oxides should be included in the sequential extraction scheme . Tessier et al.[24] reported that a solution of 0.04*M* $NH_2OH.HCl$ in 25% HOAc at 96 ± 3°C achieved complete dissolution of reducible Fe and Mn oxides in sediment samples without affecting sulfides or organic matter. Using different extracting solutions for dissolution of reducible Fe and Mn fractions might be expected to lead to differential dissolution of the consecutive oxidisable metal fraction and subsequently to different metal distribution patterns in soils. Thus evaluation of metal mobility and bioavailability in relation to metal distribution in polluted and unpolluted soils could be influenced by the extraction procedure and these procedures should be designed carefully.

In this paper we report a study in which we compared the ability of these two extraction techniques to mobilise Fe and Mn from their oxides or trace metals

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adsorbed on or occluded in their oxides in sewage sludge-treated and control soils. The concentrations of Fe, Mn, Cu and Zn in the $NH_2OH.HCl/HOAc$ reducible fraction[24] were compared with those in the $NH_2OH.HCl$ (pH 2.0) reducible fraction[8]. The influence of the two reducing solutions on the extraction of the H_2O_2/NH_4OAc-oxidisable metal fraction in the subsequent step of the sequential schemes was also investigated.

MATERIALS AND METHODS

Soils and sewage sludge

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Ten agricultural topsoils (0–20 cm depth) were sampled from various parts of Northern Ireland. They were developed from a range of different parent materials and represented a range of cropping histories (Table I). The fresh soil samples were passed through an 8-mm sieve to remove stones and coarse plant roots or residues and then air-dried prior to experimental use. Subsamples of the air-dried soils were ground to pass a 2-mm sieve prior to the following chemical analysis. Soil pH (soil:water ratio 1:2.5), particle size distribution and cation exchange capacity (CEC) were determined by standard methods[25] and clay mineralogy was analysed semi-quantitatively using a Philips Diffractometer with Co $K\alpha$ radiation. Subsamples of the air-dried soils were further ground using a ball mill (<0.15 mm) prior to the following analysis. Organic carbon and nitrogen were determined by Dumas combustion using a carbon and nitrogen analyser and total contents of Fe, Mn, Cu and Zn were determined by X-ray fluorescence spectrometry (XRF). The physicochemical and mineralogical properties of the ten soils are shown in Table II.

An alkaline stabilised sewage sludge cake made from rural sludge was supplied by the Water Executive of the Department of Environment for Northern Ireland. It was made by dewatering screened and thickened sewage sludge to produce a cake of about 30–35% DM, then mixing the cake with cement kiln dust (CKD) to give 35% CKD by weight. The mixture was then composted for about three weeks. The resulting product had a pH (sludge: water ratio 1:20) of 11.7, an organic C content of 14% and a DM content of 56%. Total concentrations of Fe, Mn, Cu and Zn determined by XRF were 21700, 310, 96 and 315 mg kg^{-1} DM. The material was sieved (<8-mm) and stored in unsealed plastic bags at 4°C before use.

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TABLE I Description of the soils studied

Soil type	*Location*	*Irish Grid Reference*	*Land use (at time of sampling)*	*Parent material*
Silurian shale sandy loam	Corcreeny	J208588	Arable	Silurian Shale/Triassic Sandstone Glacial Till
Basaltic clay loam	Ballyharvey	J170839	Arable	Basaltic Glacial Till
Old Red sandstone clay loam	Castle Archdale	H190592	Grass	Old Red Sandstone
Marine loamy sand	Castleravery	J486711	Vegetable	Marine Coarse Sand and Pebbles
Comber sandy loam	Castleravery	J483712	Arable	Triassic Sandstone
Lough Neagh Clay sandy loam	Clonakate	H939621	Grass	Lough Neagh Clay
Granite sandy loam	Slievenaboley	J261431	Grass	Granite
Limestone sandy clay loam	Loughgall	H918523	Willow coppice	Limestone
Loughry sandy clay loam	Loughry (site 1)	H813753	Grass	Triassic Sandstone
Loughry sandy loam	Loughry (site 2)	H814751	Grass	Triassic Sandstone

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TABLE II Selected properties of the soils

Soil type	*Clay* %	*pH* (H_2O)	*Total C* %	*CEC* cmol kg^{-1}	*Total N* %	Fe_2O_3 %	*MnO* %	*Cu* mg kg^{-1}	*Zn* mg kg^{-1}	*Clay minerals*[†] (<0.002 mm fraction)
Silurian shale sandy loam	13.2	6.5	2.4	15.2	0.2	3.67	0.07	31.3	57.0	Sm>Illite>Chl=Kaol
Basaltic clay loam	29.2	6.4	4.7	49.2	0.4	15.04	0.26	132.6	194.3	Sm
Old Red sandstone clay loam	24.3	7.3	5.1	24.8	0.4	4.72	0.07	33.6	78.6	Illite>Vm>Chl
Marine loamy sand	9.2	6.0	3.7	14.1	0.3	2.99	0.06	20.8	52.5	Sm>Chl=Illite
Comber sandy loam	16.6	6.4	4.0	23.4	0.4	5.80	0.13	39.3	104.6	Sm>Illite>Chl>Kaol
Lough Neagh Clay sandy loam	16.1	5.8	5.1	22.9	0.4	3.73	0.06	50.4	77.0	Kaol>Sm>Vm>Illite
Granite sandy loam	11.5	4.6	6.4	27.6	0.5	5.76	0.10	48.6	64.3	Vm>Illite>Chl
Limestone sandy clay loam	24.5	7.1	5.0	33.6	0.5	5.52	0.16	56.8	115.3	Sm>Illite>Kaol
Loughry sandy clay loam	18.3	6.1	5.8	27.7	0.5	4.87	0.09	62.6	116.1	Kaol>Vm=Illite
Loughry sandy loam	15.3	5.9	4.2	19.3	0.4	4.48	0.10	59.7	93.8	Kaol>Vm=Illite
Mean	17.8	6.2	4.7	25.8	0.4	5.66	0.10	51.2	94.3	

[†] Sm, Smectite; Vm, Vermiculite; Chl, Chlorite; Kaol, Kaolinite.

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Glasshouse experiment

One kilogram (oven dry basis) of each soil (<8 mm air dried) was mixed with the sieved (<8 mm) moist sewage sludge product (22.3 g oven dry basis) to give a mixture equivalent to an application rate of the sludge product of 33.5 t DM ha^{-1}. Unamended controls were also prepared. No inorganic fertiliser was applied. After thorough mixing the mixtures of soil and sludge were placed in plastic pots (15 cm diameter), watered with deionised water to 75% of water holding capacity (WHC) and equilibrated in the glasshouse for two days.

Six spring barley seedlings (*Hordeum vulgare* L. cv. Forrester) with one complete leaf were transplanted into each pot. There were four replicates of each treatment in a randomised block, giving a total of 80 pots. The soil moisture content in each pot was maintained regularly by mass balance at 75% WHC during growth of the plants. After the shoots were harvested (after 15 weeks' growth) the soil was air-dried and ground to pass a 2-mm sieve for sequential chemical extraction.

Sequential extraction scheme

Soil samples were subjected to two three-step sequential chemical extraction schemes. The two schemes differed in the second extraction step, the extraction method for the operationally defined reducible Fe and Mn oxides.

The first scheme was modified from that of Ure et al.[8]. Two modifications were made to Ure's procedure. Firstly, the first two steps of the original extraction scheme were modified slightly by using a soil:solution ratio of 1:20 instead of 1:40 to avoid high dilution of the metals for reliable determination. Use of a high solution:solid ratio makes analysis more difficult because of the very low concentrations of the metals in the extracts, especially when the original samples contain low concentrations of heavy metals[8]. Secondly, in each extraction step the wet residue remaining after removal of the supernatant was also weighed instead of washing with distilled water before the next extraction step to avoid loss of solid material.

One gram (±0.01 g) of each sieved soil sample was placed in a 50-cm^3 polypropylene centrifuge tube to minimise loss of solid material and extracted using the following operationally defined fractionation procedures.

1. Samples were shaken with 20 cm^3 of 0.11*M* HOAc for 16 hours (overnight) in 50-cm^3 polyethylene centrifuge tubes and centrifuged at 3000 × g for 10 minutes. The supernatants were filtered through Whatman No. 40 paper. Then the weight of the tubes and their contents was recorded. This extracted primarily the water-soluble and exchangeable, weakly bound with organic matter and carbonates fraction of the metals (HOAc-soluble).
2. The residue from 1) was shaken with 20 cm^3 of 0.10*M* $NH_2OH.HCl$ adjusted to pH 2.0 with HNO_3 for 16 hours (overnight), centrifuged as before, filtered

and weights recorded as described above. This step extracted mainly iron and manganese oxides bound forms (Reducible).

3. To the residue from 2) were added carefully 10 cm^3 of 30% H_2O_2 to avoid losses due to violent reaction. The mixture was allowed to digest in the cold for 1 hour and was then taken to dryness on a water bath heated to 85 ± 2°C. A second 10 cm^3 aliquot of H_2O_2 was then added in order to complete the oxidation of organic matter and sulfides, and again taken to dryness on a water bath at 85 ± 2°C with intermittent manual shaking. After cooling, 25 cm^3 of 1.0*M* NH_4OAc adjusted to pH 5.0 with HOAc were added to the dry residue. The mixture was extracted by shaking for 16 hours (overnight), followed by centrifugation and filtration as before. The NH_4OAc was added to prevent the readsorption of extracted metals on to the oxidised solid residue[16]. This step extracted primarily organically bound and sulfide metals (Oxidisable).

The second sequential extraction scheme involved the same steps as the modified Ure method described above apart from the second step which was replaced by the third step of Tessier's method[24], but using 20 cm^3 (instead of 30 cm^3) of 0.04*M* $NH_2OH.HCl$ in 25% (v/v) HOAc at 96 ± 3°C for 5 hours.

The concentrations of Fe, Mn, Cu and Zn in the extracts were determined using a Perkin Elmer model 5000 flame atomic absorption spectrophotometer. The calculation of the amount of each metal fraction followed Luo and Christie[26]. Metal concentrations were calculated on a soil DM basis. The results reported are the mean values from four blocks of each treatment. Data were tested by analysis of variance. Individual means within each variable were compared by least significant difference (LSD $\alpha = 0.05$). The concentrations of the metals in the reducible and oxidisable fractions were compared by linear correlation.

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RESULTS

Reducible Fe and Mn

The concentrations of Fe and Mn in the ten soils extracted by a solution of 0.04*M* $NH_2OH.HCl$ in 25% (v/v) HOAc at 96 ± 3°C (referred to as $NH_2OH.HCl$/HOAc reducible) and by a solution of 0.10*M* $NH_2OH.HCl$ at pH 2.0 ($NH_2OH.HCl$-reducible) are presented in Table III. The concentrations of Fe and Mn in the sludge-amended and unamended soils were much higher in the $NH_2OH.HCl$/HOAc-reducible fraction than in the $NH_2OH.HCl$-reducible fraction, by about 5.9 fold for Fe and 1.4 fold for Mn on average. Moreover, Fe concentrations were much higher than Mn concentrations in the reducible fractions by both methods. The overall percentage of total Fe and Mn concentrations determined by XRF (Table II) in the reducible fractions of the unamended soils is shown in Figure 1. The percentage was higher after extraction with the $NH_2OH.HCl/HOAc$ compared to the $NH_2OH.HCl$ method, by about 500% for Fe and 36% for Mn. $NH_2OH.HCl/HOAc$-reducible Fe and Mn were correlated with total Fe ($r = 0.775$, $P < 0.01$) and with total Mn ($r = 0.914$, $P < 0.001$), respectively. $NH_2OH.HCl$ extractable Mn was also correlated with total Mn ($r = 0.798$, $P < 0.01$). In addition, significant relationships were found between the two methods for Mn ($r = 0.974$, $P < 0.001$) and for Fe ($r = 0.464$, $P < 0.05$).

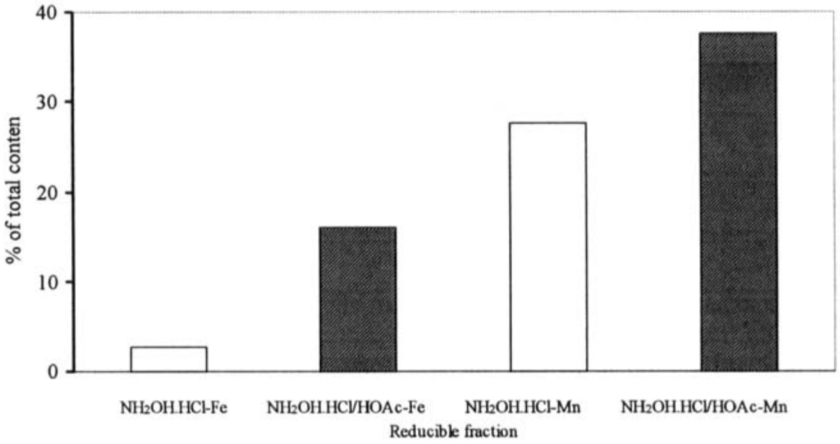

FIGURE 1 Overall percentage of total Fe or Mn in the reducible fraction of the soils extracted by the two methods

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Reducible Cu and Zn

The increased concentrations of Fe and Mn were accompanied by higher concentrations of Cu and Zn in the reducible fraction of amended and control soils (Tables IV and V). The concentrations of Cu and Zn in the reducible fraction were always markedly higher by the $NH_2OH.HCl/HOAc$ method than by the $NH_2OH.HCl$ method. Compared to the $NH_2OH.HCl$-reducible fraction the overall percentage in the $NH_2OH.HCl/HOAc$-reducible fraction increased by about 532% for Cu and 138% for Zn. The increases were usually more pronounced in the sludge-amended soils than in unamended soils. Linear correlation analysis revealed significant relationships between the two methods for Cu ($r = 0.622$, $P < 0.01$) and for Zn ($r = 0.975$, $P < 0.001$). Significant correlations were also found between reducible Zn and reducible Mn using the $NH_2OH.HCl$ method ($r = 0.603$, $P < 0.01$) and the $NH_2OH.HCl/HOAc$ method ($r = 0.553$, $P < 0.05$).

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TABLE III Concentrations of Fe and Mn in the reducible fraction of sludge-amended and control soils

Soil type	*Sludge-amended ($33.5\ t\ DM\ ha^{-1}$) or Control*	*Reducible Fe ($mg\ kg^{-1}$)*		*Reducible Mn ($mg\ kg^{-1}$)*	
		$NH_2OH.HCl$	*$NH_2OH.HCl/HOAc$*	*$NH_2OH.HCl$*	*$NH_2OH.HCl/HOAc$*
Silurian shale sandy loam	Control	1171	5350	150	220
	Amended	1227	5450	140	212
Basaltic clay loam	Control	1221	11150	429	655
	Amended	1160	10375	441	652
Old Red sandstone clay loam	Control	1295	5625	149	185
	Amended	1160	4950	141	167
Marine loamy sand	Control	972	3925	95	122
	Amended	873	3825	100	120
Comber sandy loam	Control	1018	5975	287	360
	Amended	1034	6475	282	362
Lough Neagh Clay sandy loam	Control	1730	8400	108	175
	Amended	2108	7975	102	160
Granite sandy loam	Control	1298	8225	106	208
	Amended	749	8175	105	230
Limestone sandy clay loam	Control	506	4700	558	643
	Amended	535	5100	538	700
Loughry sandy clay loam	Control	537	4950	220	280
	Amended	587	4900	202	275
Loughry sandy loam	Control	1147	5675	246	310
	Amended	1181	5750	299	368
LSD[†]		321.5		29.8	

Soil type	*Sludge-amended (33.5 t DM ha^{-1}) or Control*	*Reducible Fe (mg kg^{-1})*		*Reducible Mn (mg kg^{-1})*	
		$NH_2OH.HCl$	*$NH_2OH.HCl/HOAc$*	*$NH_2OH.HCl$*	*$NH_2OH.HCl/HOAc$*
Significance[‡] of:					
Extraction method			***		***
Soil type			***		***
Sludge application			ns		ns
Soil type × sludge application			*		**

[†] Least significant difference at the 5% protection level.

[‡] By analysis of variance: ***, $P<0.001$; **, $P<0.01$; *, $P<0.05$; ns, not significant.

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TABLE IV Concentrations of Cu in the reducible and oxidisable fractions of sludge-amended and control soils

Soil type	*Sludge-amended (33.5 t DM ha^{-1}) or Control*	*Reducible Cu (mg kg^{-1})*		*Oxidisable Cu (mg kg^{-1})*	
		$NH_2OH.HCl$	*$NH_2OH.HCl/HOAc$*	*$NH_2OH.HCl$*	*$NH_2OH.HCl/HOAc$*
Silurian shale sandy loam	Control	2.1	6.7	8.5	10.7
	Amended	1.5	7.3	9.0	11.8
Basaltic clay loam	Control	0.6	9.4	16.3	24.7
	Amended	0.5	9.6	16.9	25.5
Old Red sandstone clay loam	Control	0.3	1.4	4.8	8.3
	Amended	0.2	0.9	5.9	10.8
Marine loamy sand	Control	0.9	2.2	4.9	7.5
	Amended	0.7	2.6	5.1	8.3
Comber sandy loam	Control	0.4	2.8	6.0	9.3
	Amended	0.4	3.7	7.5	10.6
Lough Neagh Clay sandy loam	Control	2.0	7.9	18.5	27.3
	Amended	1.4	8.6	19.3	27.4
Granite sandy loam	Control	1.0	8.8	20.6	28.8
	Amended	0.8	8.8	20.0	32.0
Limestone sandy clay loam	Control	0.3	4.0	9.7	18.0
	Amended	0.3	4.4	10.6	20.8
Loughry sandy clay loam	Control	1.0	7.4	17.4	34.5
	Amended	0.9	7.5	18.1	32.5
Loughry sandy loam	Control	2.6	10.7	16.5	25.2
	Amended	1.8	11.2	18.3	25.6
LSD[†]		0.61		0.90	

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Soil type	*Sludge-amended (33.5 t DM ha^{-1}) or Control*	*Reducible Cu (mg kg^{-1})*		*Oxidisable Cu (mg kg^{-1})*	
		$NH_2OH.HCl$	*$NH_2OH.HCl/HOAc$*	*$NH_2OH.HCl$*	*$NH_2OH.HCl/HOAc$*
Significance[‡] of:					
Extraction method		***		***	
Soil type		***		***	
Sludge application		ns		***	
Soil type × sludge application		ns		**	

[†] Least significant difference at the 5% protection level.

[‡] By analysis of variance: ***, $P<0.001$; **, $P<0.01$; ns, not significant.

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TABLE V Concentrations of Zn in the reducible and oxidisable fractions of sludge-amended and control soils

Soil type	*Sludge-amended (33.5 t DM ha^{-1}) or Control*	*Reducible Zn (mg kg^{-1})*		*Oxidisable Zn (mg kg^{-1})*	
		$NH_2OH.HCl$	*$NH_2OH.HCl/HOAc$*	*$NH_2OH.HCl$*	*$NH_2OH.HCl/HOAc$*
Silurian shale sandy loam	Control	2.7	9.7	7.6	10.9
	Amended	4.5	12.1	7.8	11.4
Basaltic clay loam	Control	8.5	23.2	16.9	21.6
	Amended	10.4	26.4	18.2	22.9
Old Red sandstone clay loam	Control	3.8	11.1	11.0	19.7
	Amended	7.5	14.5	13.1	23.8
Marine loamy sand	Control	4.9	12.2	9.7	13.8
	Amended	6.1	14.3	10.4	14.0
Comber sandy loam	Control	5.6	14.0	9.7	16.1
	Amended	7.9	18.7	9.8	16.6
Lough Neagh Clay sandy loam	Control	6.9	19.8	14.7	23.3
	Amended	8.0	21.3	15.4	24.0
Granite sandy loam	Control	2.9	9.6	9.9	16.8
	Amended	3.2	11.4	10.6	18.1
Limestone sandy clay loam	Control	15.0	28.4	15.2	20.4
	Amended	15.9	32.9	15.5	23.3
Loughry sandy clay loam	Control	17.9	35.9	20.4	28.8
	Amended	17.2	36.8	21.3	29.0
Loughry sandy loam	Control	10.1	24.9	14.8	19.3
	Amended	11.8	28.5	16.4	20.5
LSD[†]		0.96		0.76	

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Soil type	*Sludge-amended (33.5 t DM ha^{-1}) or Control*	*Reducible Zn (mg kg^{-1})*		*Oxidisable Zn (mg kg^{-1})*	
		$NH_2OH.HCl$	*$NH_2OH.HCl/HOAc$*	*$NH_2OH.HCl$*	*$NH_2OH.HCl/HOAc$*
Significance[‡] of:					
Extraction method			***		***
Soil type			***		***
Sludge application			***		***
Soil type × sludge application			***		***

[†] Least significant difference at the 5% protection level.

[‡] By analysis of variance: ***, $P<0.001$; *, $P<0.05$; ns, not significant.

Oxidisable Cu and Zn

Concentrations of Cu and Zn in the subsequent step (oxidisable fraction) also increased significantly both in sludge-amended soils and in unamended soils following the $NH_2OH.HCl/HOAc$ method (Tables IV and V) compared to those following the $NH_2OH.HCl$ method, by about 57% and 47% on average. Close correlations were found between the two methods for Cu ($r = 0.958$, $P < 0.001$) and for Zn ($r = 0.912$, $P < 0.001$).

DISCUSSION

All the soil samples used for the comparison were first extracted with HOAc, and there was no difference between the two sets of soil samples in HOAc-soluble metals (data not shown). We then compared two different extraction solutions for the second step, the dissolution of reducible Fe and Mn oxides. One solution was $0.10M$ $NH_2OH.HCl$ at pH 2.0 used by Ure et al.[8] and the other was $0.04M$ $NH_2OH.HCl$ in 25% (v/v) HOAc at 96 ± 3°C used by Tessier et al.[24]. Distinctive differences between the two solutions in their ability to extract reducible Fe and Mn oxides bound metals were clearly demonstrated (Table III). The latter solution dissolved much more Fe and Mn than the former solution and the difference was more pronounced for Fe than for Mn. This suggests that the $0.10M$ $NH_2OH.HCl$ solution at pH 2.0 is a mild reagent that attacks Mn oxides strongly and attacks Fe oxides weakly and may have dissolved the easily reducible Fe and Mn oxides only. In contrast, the solution of $0.04M$ $NH_2OH.HCl$ in 25% (v/v) HOAc at 96 ± 3°C is a more strongly reducing reagent that aggressively dissolved both Fe oxides and Mn oxides and may have dissolved both the easily and the moderately reducible Fe and Mn oxides. The Fe and Mn solubility results obtained using these reducing reagents are in good agreement with previous reports[15,24,27,28].

The higher concentrations of Fe and Mn using the stronger reducing solution were accompanied by higher concentrations of Cu and Zn in the reducible fraction in sludge-amended and unamended soils. It is very likely that more Cu and Zn were released from the dissolution of the moderately reducible Fe and Mn oxides. However, it appeared that Fe oxides made a more important contribution to the increased metal concentrations than did Mn oxides. This supports earlier reports that $0.10M$ $NH_2OH.HCl$ at pH 2.0 is a weak reducing solution for dissolving trace metals adsorbed on or occluded in Mn oxides[5,28] and from partly amorphous Fe oxide[17,18]. The metal extracted by this mild extractant may not represent the reducible Fe-Mn oxide fraction. The concentrations of reducible Fe

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oxides were always much higher than the concentrations of reducible Mn oxides in the soils (Table III). The importance of Fe oxides in binding and retaining trace metals in soils and subsequently in controlling metal mobility and bioavailability has been emphasised[19,21,28]. It is necessary to use an extractant which can effectively extract trace metals adsorbed on or occluded in both reducible Fe and reducible Mn oxides. The reducing solution used by Tessier et al.[24] may be better than the solution used by Ure et al.[8] in representing the trace metals removed from the reducible Fe-Mn oxides in the sequential extraction scheme . Earlier researchers reported that that 0.04*M* $NH_2OH.HCl$ in 25% HOAc at 96–100 °C extracted trace metals bound to Fe-Mn oxides of a range of crystallinities[29] or reducible Fe-Mn oxides without dissolving organic matter or sulfides[24].

The metal fraction extracted after the reducible fraction is operationally defined as an oxidisable fraction or organic matter and sulfide bound fraction. It appeared that extraction of the moderately reducible Fe and Mn oxides also resulted in a significant increase in the subsequent oxidisable fraction in sludge-amended and unamended soils. The good correlations found between the oxidisable and reducible fractions for Cu and Zn support this association. This increase may be a result of the removal of an Fe and/or Mn coating on particles and the subsequent exposure of oxidisable organic matter and sulfides. We have not seen any report on the changes in subsequent oxidisable metal concentrations resulting from previous removal of reducible Fe-Mn oxides using these two reducing solutions in sequential extraction schemes.

Clearly, different reducing solutions have different capacities to dissolve the reducible metal fraction in soils and have different effects on the subsequent dissolution of the oxidisable metal fraction. Differences in the residual metal fraction (which cannot be extracted by the previous extractants) must also be expected. Consequently, using reducing reagents with different capacities to extract reducible Fe-Mn oxides will lead to different distribution patterns of trace metals in sludge-amended and unamended soils. Selection of reducing extractant is therefore important not only for extracting the reducible Fe-Mn oxide bound metal fraction itself but also for the subsequent metal fractions. Using a solution 0.10*M* $NH_2OH.HCl$ at pH 2.0 to dissolve reducible Fe/Mn oxides underestimated the concentrations of trace metals in both reducible and oxidisable fractions. The reducible metal fraction may be solubilised by soil acidification and reduction and the oxidisable metal fraction is likely to be biologically degradable. Both metal fractions are likely to be potentially mobile and bioavailable in soils.

Therefore the data obtained from a sequential chemical extraction scheme involving a reducing solution such as 0.10*M* $NH_2OH.HCl$ at pH 2.0 should be interpreted with care, particularly when metal mobility and bioavailability are being assessed in relation to metal distribution in metal-contaminated soils.

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