Environmental Pollution **50** (1988) 225–242

The Use of Model Compounds to Elucidate Metal Forms in Sewage Sludge

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(Received 5 June 1987; revised version received 17 August 1987;
accepted 18 August 1987)

ABSTRACT

Model phases of metal precipitates and organically bound metal were used to corroborate the nature of metal species found in sewage sludge by a sequential chemical extraction scheme. Model phase extractions supported the identification of the major species of Cd and Ni as carbonate (EDTA-extractable), Zn as organically-bound ($Na_4P_2O_7$*-extractable) and Pb as organically-bound or carbonate, although considerable overlap of fractions was apparent. Identification of the major species of Cu as sulphide (*HNO_3*-extractable) could not be confirmed. The selectivity and efficiency of certain reagents was found to differ when used in sequence with other reagents, as opposed to being applied individually to model metal phases. Sample preparation was found to influence metal fractionation profiles in a model organic phase.*

INTRODUCTION

A wide variety of chemical extraction schemes has been developed for the determination of heavy metal forms in mineral and organic matrices. One of the major objectives of such schemes is to identify the proportion of total

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Environ. Pollut. 0269-7491/88/$03·50

metal which is readily mobile, as for instance from sediments, or available to plants, as from soils. The techniques originally devised for soils have been subsequently applied to sewage sludges in order to assess metal bioavailability following sludge disposal to land. Discussion of such methods is included in reviews by Lake *et al.* (1984) and Kirk *et al.* (1985).

The forms of metals solubilised by chemical extraction schemes are commonly referred to in terms of particular species; for example, metal carbonates, exchangeable metal or organically bound metal. However, compared to the number of studies which report results of chemical extractions (see Kirk *et al.*, 1985) those which provide empirical data to support the solubilisation of these individual metal species by their designated extractant reagents are limited.

One approach has involved the use of model metal compounds to evaluate extractant selectivity for target phases. Stover *et al.* (1976) compared the efficiency of seven reagents, designated to extract metals which were precipitated, bound to organic matter or associated with Fe, Mn and Al compounds, for extracting metal carbonates and sulphides. Meguellati *et al.* (1983) synthesised a wider range of model phases; exchangeable, carbonate, oxide-hydroxide and organic, and tested a series of reagents designed by Tessier *et al.* (1979) for use on sediments. An evaluation of the specificity of these same extractants was also made using well-defined mineral phases of metal carbonates, sulphides, Fe oxides (geothite and haematite), Fe phosphate (vivianite), chloritic clay minerals and Fe/Mn nodule material (Forstner, 1985). More recently, Miller *et al.* (1986) have assessed the solubility of basic Cu carbonate, Cu oxide and Cu sulphide in reagents ranging from water to hydrogen peroxide. These studies indicated that extractant reagents were not uniformly specific in attacking a single metal species, but that a degree of overlap may occur between fractions.

The current study was designed to elucidate the nature of the predominant metal forms identified by one sequential chemical extraction scheme, that of Stover *et al.* (1976). In this study metal forms are identified at three levels: the term "fraction" refers to the portion of metal present which is extracted by a specific reagent; a "phase" is the discrete metal species or group of species which a particular reagent is intended to extract; the "species" themselves correspond to the ions, complexes and compounds of individual metals. As part of a larger programme on the characterisation of metal forms in sewage sludges, it was intended to interrelate more closely the extraction characteristics of Cu, Cd, Ni, Pb and Zn to the forms of metal present, by utilisation of synthetic metal phases as test compounds. A comparison was also made between discrete and sequential application of the reagents in the extraction scheme, to determine whether the former can predict the behaviour of metals under sequential extraction.

MATERIALS AND METHODS

Sewage sludge samples

Samples of raw, activated and digested sludge were obtained from a major UK sewage treatment works. Analytical data for the sludges are given in Table 1. On collection, the samples were dried at 105°C, ground to pass a 0·5 mm mesh and stored over silica gel.

Model compounds

Model metal precipitates were obtained commercially at purities of >92%. These were carbonates, sulphides, phosphates and hydroxides (hydrous oxide for Pb) of Cu, Cd, Ni, Pb and Zn. Six precipitates which were commercially unavailable were prepared individually from Analar grade reagents according to standard chemical procedures (Sneed & Brasted, 1955; Parkes, 1967; Cotton & Wilkinson, 1980). After formation, the precipitates were rinsed, dried at 30°C *in vacuo* and ground to pass a 0·5 mm mesh. The experimentally determined purities of these precipitates were $Cd_3(PO_4)_2$, 80%; $Cd(OH)_2$, 75%; NiS, 62%; $Ni_3(PO_4)_2$, 69%; $PbO(OH)_2$, 96%; $Zn(OH)_2$, 72%. Potential contamination of one metal salt by the addition of another during extractions was generally <1% of the total, except for Zn where up to 15% of the total measured may have been contributed by other precipitates.

A model organic phase was prepared by dosing a laboratory scale activated sludge unit fed on synthetic settled sewage with influent metal concentrations of 0·02 mg litre^{-1} Cd, 0·2 mg litre^{-1} Cu, Ni and Pb and 1·0 mg litre^{-1} Zn. The unit was operated at a sludge age of 6 days. Mixed liquor suspended solids, withdrawn from the unit, were separated by centrifugation and washed three times in distilled water to remove soluble and colloidal forms of metals. Samples were used in either liquid or air-dried form; the solids were resuspended in distilled water and used within 48 h of collection or otherwise dried at 70°C, ground to pass a 1 mm mesh and

TABLE 1
Total Solids, Volatile Solids and Heavy Metal Content of Sewage Sludges Provided by WRc

Sludge type	*Original total solids (TS) content (% w/v)*	*Volatile solids content (% TS)*	*Heavy metal content (mg kg^{-1} dry weight)*				
			Cu	*Cd*	*Ni*	*Pb*	*Zn*
Raw	3·65	67	540	22	67	620	3 100
Activated	1·55	75	740	25	120	580	3 200
Digested	1·65	59	760	27	107	960	4 000

stored over silica gel prior to use. Unlike municipal activated sludge, this biomass was entirely biological in origin and contained 90% (w/w) volatile matter, compared to 59–75% (w/w) for the sewage sludges described in Table 1.

Extraction procedure

Fractionation of the metals present in each sample was undertaken using a modified version of the sequential extraction procedure described by Stover *et al.* (1976). This scheme comprises a sequence of 16-h extractions, using 1M KNO_3 to remove metal forms designated as soluble and exchangeable; 0·5M KF (pH 6·5) for adsorbed metals; 0·1M $Na_4P_2O_7$ for organically-bound metals; 0·1M EDTA (pH 6·5) for carbonate species and 6·0M HNO_3 for sulphide species. The solids to reagent volume ratios are 1:50 for steps 1 and 5 and 1:80 for steps 2, 3 and 4. Modifications to the original technique incorporated the use of a single 16-h EDTA extraction as opposed to a double 8-h extraction and the replacement of 1·0M HNO_3 with 6·0M HNO_3 (Oake *et al.*, 1984) in addition to centrifugation at 2500 × *g*, which was found to be as effective in solids separation as the 10 000 × *g* used by Stover *et al.* (1976). Triplicate samples of 0·4 g dry solids or preconcentrated liquid equivalent were extracted directly in 50 ml polypropylene centrifuge tubes. After each extraction, the supernatant was filtered and stored at 1% (v/v) HNO_3, while the pellet was washed and treated with the next reagent. For discrete extractions each reagent was applied to a fresh sample.

In addition to the Stover extraction, an alternative scheme was devised based on the use of $MgCl_2$ for the exchangeable fraction (adapted from Tessier *et al.*, 1979) and a CH_3COONa reagent for organically-bound metals (adapted from Meguellati *et al.*, 1983). The $MgCl_2$ extractant was used at pH 5, rather than neutral, since it was suggested that this may result in removal of adsorbed, in addition to exchangeable, metal (Tessier *et al.*, 1979).

A range of extractants reported to be selective for organic matter was also compared by means of discrete extractions of the model organic phase. These extractants were 0·5M NaOH (Emmerich *et al.*, 1982; Chang *et al.*, 1984), 5·25% (w/v) NaOCl pH 9·5, adjusted with concentrated HCl (Cavallaro & McBride, 1984), 1M $CH_3COONa + 0{\cdot}25$M $NH_2OH.HCl$ (pH 5·0) and 30% (w/v) H_2O_2 + concentrated HNO_3 at a ratio of 20:1 (adapted from Meguellati *et al.*, 1983). All reagents were of Analar or Aristar grade.

Analytical procedures

The total metal content of the sludges was determined by X-ray fluorescence spectroscopy. The residual metal content of samples was determined following HNO_3-H_2O_2 digestion (Krishnamurty *et al.*, 1976). Heavy metals in the extracted fractions were determined by flame or flameless atomic absorption spectrophotometry. All standards used for metal determinations in the extracted fractions were prepared in the respective reagents to compensate for any reagent interference. A comparison of metal determinations in each of the extractants by flame and flameless atomic absorption indicated no significant difference in the analyses at the 0·05 significance level, therefore where metal concentrations were above the practical limit of determination, flame atomic absorption was used.

All polypropylene and glassware (borosilicate) was cleaned by immersion in a 5% (v/v) solution of Decon 90 detergent (BDH Chemicals Ltd., UK) for 24 h, followed by leaching in 10% (v/v) Analar HNO_3 for 24 h.

RESULTS

Discrete and sequential chemical extraction of model metal precipitates

A comparison of discrete and sequential application of extractants to model metal precipitates was made in an attempt to elucidate both the specificity of reagents for a particular metal form and the possible effects of progressive interaction of the sequentially applied reagents. The discrete extractions should theoretically allow 100% solubilisation of each metal precipitate by each extractant, whilst the sequential extractions should give 100% solubilisation by summing all the extracted fractions for one precipitate. Examples of the fractionation profiles obtained with the Stover extraction method for the twenty metal salt combinations are shown in Figs 1 and 2. The residual fraction in column 6 of each fractionation profile was obtained by subtraction of all of the metal extracted in the sequential procedure from the total. Consequently, there is no corresponding residual fraction for the discrete extraction procedure. Relative standard deviations for replicate extractions were < 10% for $Na_4P_2O_7$, EDTA and HNO_3 fractions, but up to 15% for the minor fractions extracted by KNO_3 and KF.

The EDTA extractant was incorporated in the technique specifically to attack carbonate metal species. Although under discrete extractions the majority of the carbonates were successfully solubilised, the transition to sequential application of the reagents resulted in poor specificity of EDTA for carbonates of Pb and Ni in particular, giving extractions of 34% and 33%, respectively. The sulphides of Ni and Pb were also attacked by the EDTA reagent, thus ostensibly contributing to the carbonate species component. Sulphides were expected to be extracted most efficiently by the HNO_3 reagent and although this was observed in discrete extraction, the

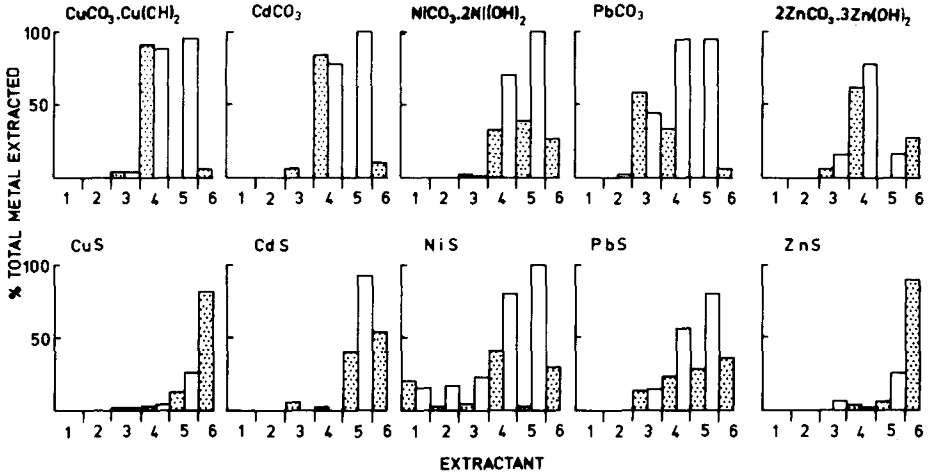

Fig. 1. Comparison of discrete (▭) and sequential (▨) chemical extractions of model metal carbonates and sulphides. Extractants were 1:KNO_3, 2:KF, 3:$Na_4P_2O_7$, 4:EDTA, 5:HNO_3, 6:Residual (by subtraction).

combination of reagents applied in the sequential extraction appeared to render the sulphides more resistant to extraction such that a significant residual phase was apparent. This was particularly marked in the cases of Cu and Zn, where even the discrete extraction efficiency of HNO_3 was low. In this respect it would seem that the sulphide and residual fractions may be more appropriately classified as a single phase.

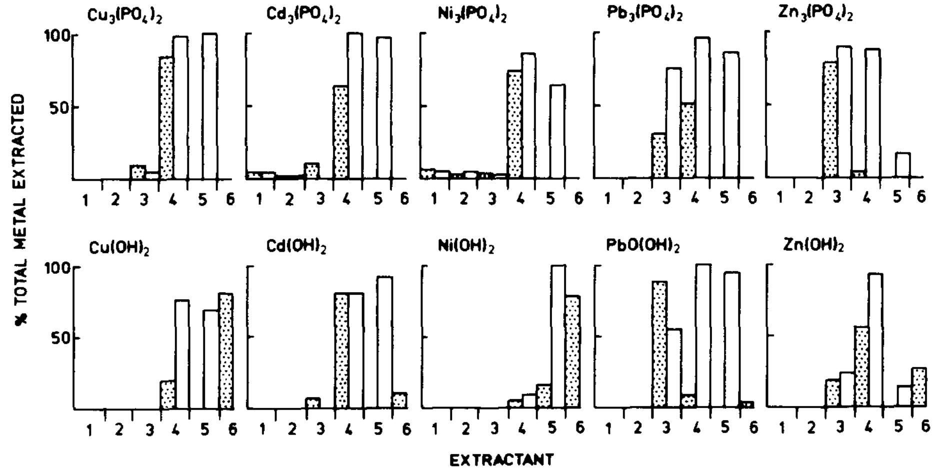

Fig. 2. Comparison of discrete (▭) and sequential (▨) chemical extractions of model metal phosphates and hydroxides. Extractants were 1:KNO_3, 2:KF, 3:$Na_4P_2O_7$, 4:EDTA, 5:HNO_3, 6:Residual (by subtraction).

The behaviour of metal phosphates under sequential extraction was largely as indicated by discrete extraction, with those of Cu, Cd, Ni and Pb emerging in the EDTA fraction and Zn phosphate in the $Na_4P_2O_7$ fraction. Discrete extractions of the metal hydroxides gave predominant removals in the EDTA and HNO_3 fractions. In contrast, the sequential extraction of Cu and Ni hydroxides indicated that a large percentage was retained in the residual phase, while Pb hydrous oxide, like Pb carbonate and sulphide, was attacked by $Na_4P_2O_7$. Any hydroxide precipitates in a sample would probably contribute to either the residual, carbonate or organic phases. Overemphasis of the importance of the $Na_4P_2O_7$ fraction seemed likely to occur as a result of the efficiency of this reagent for dissolving Pb precipitates. In terms of predicting metal solubility under sequential extraction from the results of discrete reagent application, it appears that for only six out of the twenty precipitates were the differences in metal solubility obtained by the two methods for the predominant fraction within 10% of each other.

In an optimised scheme, where individual extractants were specific to a particular metal form, each sequential histogram would be composed of a single bar. Determination of the specificity of individual extractants for model precipitates requires not only that one reagent extracts the majority of the metal present, but also that the other reagents with which it is associated leave the metal relatively unaffected. Using an arbitrary limit of extraction efficiency such that any extractant should remove $>75\%$ of the total metal, while the other reagents extract $<10\%$, specific sequential extractants for the metal precipitates could be identified. The results are shown in Table 2, and suggest that only eight metal precipitates are likely to be extracted specifically, five of which were predicted to within 10% total

TABLE 2

Specific Fractions ($>75\%$ Total Metal, Other Fractions $<10\%$) in which Metal Precipitates are Extracted by Sequential Application of Reagents

Metal	*Specific extractants*			
	CO_3	*S*	*PO_4*	*OH*
Cu	EDTA[a]	—	EDTA[a]	—
Cd	EDTA[a]	—	—	EDTA[a]
Ni	—	—	EDTA	—
Pb	—	—	—	$Na_4P_2O_7$
Zn	—	Res.	$Na_4P_2O_7$[a]	—

[a] As predicted by discrete extraction.

metal by the discrete extractions. It would appear that EDTA is liable to extract more than just carbonate phases of metals, while HNO_3 may not be a suitable extractant for metal sulphides.

Fractionation of model metal precipitates spiked into sewage sludge

In order to determine whether the precipitates under investigation exhibited constant extraction characteristics when present in the sludge matrix, a comparison was made between observed and expected fractionation profiles of sludge/precipitate admixtures. The observed profile was produced by extracting triplicate samples of a mixture of 0·35 g of raw, activated or digested sludge containing 0·01 g of the same precipitate of each metal, thus metal originating from the model compounds was in excess compared to the sludge derived metal. The expected profile was obtained by combining data obtained for extraction of the sludges alone with those of the model precipitates alone in the correct proportions. The results of the comparison are shown for Cu as an example in Fig. 3.

Extraction of the carbonates of Cu, Cd and Ni appeared to be consistent,

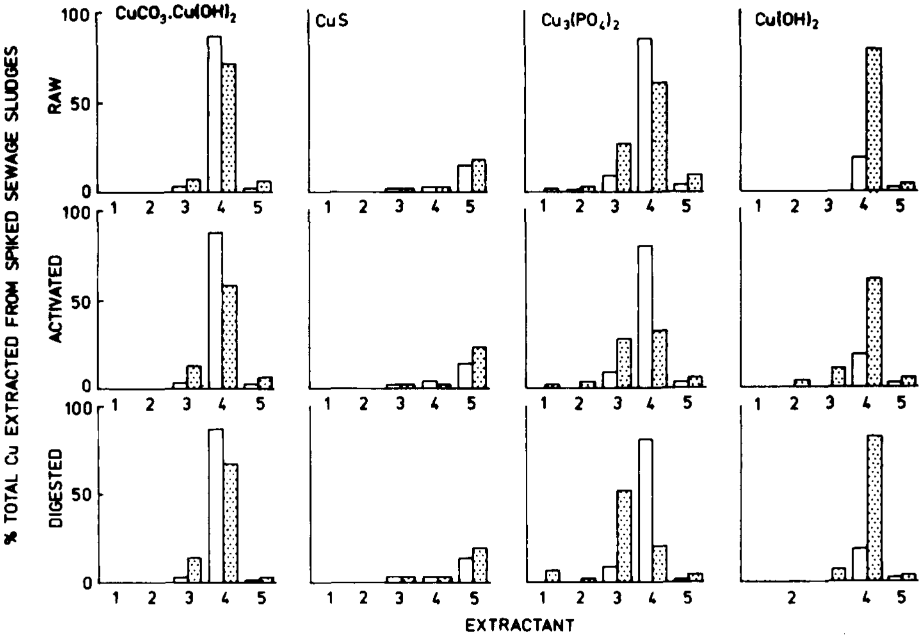

Fig. 3. Comparison between observed (▨) and expected (☐) fractionation profiles of Cu model precipitates spiked into raw, activated and digested sewage sludge subjected to sequential chemical extraction. Extractants were 1:KNO_3, 2:KF, 3:$Na_4P_2O_7$, 4:EDTA, 5:HNO_3.

with the majority of the metal solubilised by EDTA. Lead was extracted in the $Na_4P_2O_7$ fraction as expected, although this reagent was designed to be specific for organically bound metal. Zinc was the only metal to behave differently in the sludge matrix, with the majority of the carbonate solubilised by $Na_4P_2O_7$ instead of EDTA. The observed sulphide profiles were qualitatively similar to the expected profiles, although they differed quantitatively. Much higher percentages of the sulphide salts of Cd and Zn were apparently extracted from the sludge admixture, indicating a matrix effect. This was slightly more pronounced in the raw sludges than the digested sludges. Copper solubilisation was low in both extractions, at $<23\%$. The observed Ni profile indicated an increase in $Na_4P_2O_7$-extractable metal.

The metal phosphates were the only precipitates to show pronounced variations with sludge type, being less easily extracted from an admixture with digested than activated or raw sludges, respectively. Although predicted to dissolve in the EDTA fraction, Ni, Cd and Cu were extracted more effectively by the $Na_4P_2O_7$ reagent in the raw and activated sludges. Zinc, however, was extracted largely as expected, by $Na_4P_2O_7$. The presence of the sludge matrix also affected hydroxide extraction, as although Cu and Ni were solubilised by the predicted reagent, the quantity extracted increased by up to 66% and 55%, respectively. This may possibly have indicated a change in speciation on addition of these metal salts to the sludge. The observed profiles for Cd, Pb and Zn differed qualitatively from those expected, with Cd and Zn appearing more amenable to extraction and Pb more resistant.

Results from the spiked extractions were comparable with those obtained from the model precipitates alone, insofar as the solubilisation of Cu, Cd and Ni carbonates and Pb phosphate in the EDTA fraction, Pb carbonate and Zn phosphate in the $Na_4P_2O_7$ fraction and Cd and Pb sulphide in the HNO_3 fraction were concerned.

Comparison of discrete and sequential chemical extraction of a model organic phase

Experiments similar to those on the model precipitates were undertaken to determine the predictability and specificity of reagents for organically-bound metals, using the model organic phase of metal-dosed activated sludge. Results of the comparison of discrete and sequential application of the Stover extraction scheme reagents to both air-dried and liquid forms of the model organic phase are given in Fig. 4.

Poor reagent specificity for the organic phase was evident from the discrete extractions, particularly for Cu and Ni. Generally higher

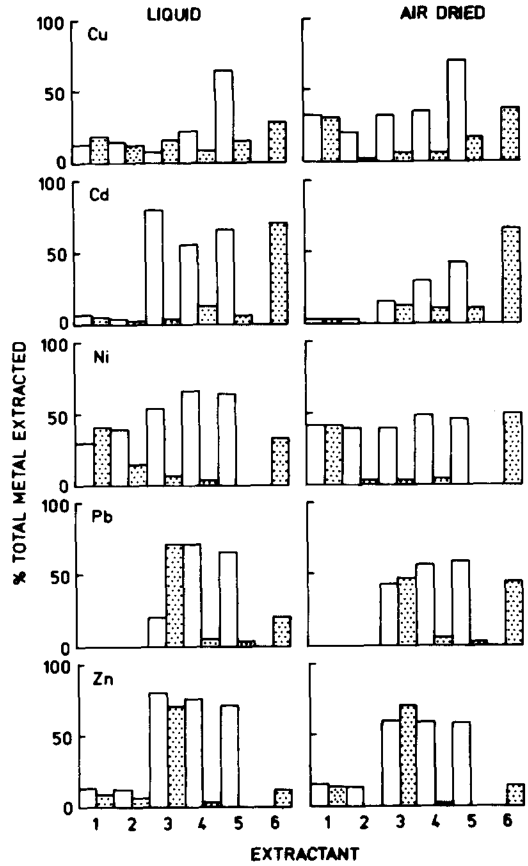

Fig. 4. Comparison of discrete (□) and sequential (▨) extraction of liquid and air-dried forms of a model organic phase. Extractants were 1:KNO_3, 2:KF, 3:$Na_4P_2O_7$, 4:EDTA, 5:HNO_3, 6:Residual (by subtraction).

concentrations were extracted from liquid than air-dried forms of the organic phase, although the predominant fraction identified by sequential extraction was similar in both cases. Nitric acid gave a solubilisation of >60% Cu by discrete application, but the sequential Cu fractionation profile was less clearly defined, with the KNO_3 and residual fractions predominating. Despite >50% extraction of Cd from the liquid organic phase by $Na_4P_2O_7$, EDTA and HNO_3 the sequential profile showed a strong residual phase. This suggested that cumulative treatment with the reagents altered the nature or reactivity of the indigenous Cd species.

None of the reagents could be regarded as specific for Ni extraction, as all removed between 39 and 49% when applied individually. In the sequential scheme Ni was primarily extracted by KNO_3, the reagent designated for solubilisation of exchangeable metals. Low Ni extractions were observed for

TABLE 3

Values of Total Organic Carbon (TOC) Determined in Sequential Extracts of a Model Organic Phase

Fraction	*TOC (mg litre^{-1})*	
	Liquid organic phase	*Dried organic phase*
KNO_3	581	2 701
KF	470	105
$Na_4P_2O_7$	354	37·8
EDTA	—	—
HNO_3	788	657

subsequent reagents, suggesting that, like Cd, a modification of Ni extractability occurred through the effects of successive reagents. A high degree of solubilisation of Pb and Zn by $Na_4P_2O_7$, the reagent designated to extract organically bound metal, was evident, indicating that the extraction scheme was appropriate for organically associated forms of these metals. The discrete extractions furthermore allowed prediction of this behaviour.

In summary, it would appear that although the $Na_4P_2O_7$ reagent, which is supposed to extract organically-bound metal, is appropriate for Pb and Zn, it is less effective for the other metals. Copper, Cd and Ni were either solubilised rapidly by KNO_3, which is included in the scheme for extracting exchangeable metals, or left as insoluble forms within the residual phase. Determinations of total organic carbon (TOC) in the samples resulting from sequential extraction (Table 3) indicated that the KNO_3 fraction contained considerable organic carbon, particularly in the case of the dried sample. The $Na_4P_2O_7$ reagent appeared to extract very little organic carbon from the model organic phase.

Comparison of proposed organically bound metal extractants applied to a model organic phase

Since $Na_4P_2O_7$ exhibited variable extraction efficiency, a range of reagents proposed to solubilise organically bound metals were applied to the model organic phases to determine both their extraction efficiency and selectivity. The results are shown in Table 4. The H_2O_2/HNO_3 reagent proved efficient for all five metals, with removals ranging from 63% to 100%. Recoveries by this reagent were higher from the air-dried sludge than from the liquid samples, but the reverse was generally found for the other reagents. Other reagents performed less consistently; the CH_3COONa reagent solubilised only a small proportion of Cu while NaOCl produced low recoveries of Zn

TABLE 4
Metal Extracted from Liquid and Air-dried Forms of a Model Organic Phase using Reagents Proposed for Extracting Organically-bound Metals

Extractant	*% Total metal solubilised by discrete extraction*									
	Cu		*Cd*		*Ni*		*Pb*		*Zn*	
	Liquid	*Dried*	*Liquid*	*Dried*	*Liquid*	*Dried*	*Liquid*	*Dried*	*Liquid*	*Dried*
H_2O_2	70·5	78·6	63·0	82·7	66·9	73·1	69·8	86·4	95·1	100
NaOH	61·0	60·8	65·6	40·5	55·6	43·7	37·0	27·0	73·3	44·9
NaOCl	72·6	64·9	48·5	49·2	71·9	68·2	5·4	2·5	13·1	5·6
$Na_4P_2O_7$	7·8	32·7	79·5	13·8	53·5	39·3	21·7	47·0	8·0	60·1
CH_3COONa	4·7	10·8	74·0	34·1	69·4	42·4	75·7	47·3	82·6	57·6

and Pb. NaOH was consistent but only gave a mean percentage removal of 51% for the five metals.

Although the H_2O_2/HNO_3 reagent was the most effective extractant for the organically-bound metals, it was considered likely to be poorly specific in sequence, with the possibility of dissolution of carbonates through the pH effect and of sulphides by oxidation. Sodium hypochlorite was limited by the number of metals it could extract. Despite a poor extraction of Cu, the CH_3COONa reagent generally evinced a higher extraction efficiency than NaOH and was thus employed in an alternative extraction scheme to determine its behaviour under sequential application.

Sequential extraction of a model organic phase using an alternative extraction scheme

The results for extractions performed on both liquid and air-dried forms of the model organic phase using an alternative scheme are shown in Table 5. Total recoveries were generally high, with only the extraction of Ni from the liquid phase producing a value of $<70\%$. Metal solubilisation by CH_3COONa in the sequential extraction was similar to that obtained by discrete application, other than where $MgCl_2$, designated for exchangeable and adsorbed metals, had already effected a significant extraction.

The largest fraction of Cu was extracted by $MgCl_2$, although all four reagents removed significant quantities of the metal in both the liquid and air-dried samples. Magnesium chloride also solubilised the largest proportion of Cd and Ni for both sludge types. In the case of Ni, $>90\%$ of the non-residual metal was removed by this reagent. Cadmium was recovered particularly well by this scheme, with a mean extraction of $>97\%$ for both liquid and air-dried samples. The predominant fraction was that of

TABLE 5
Metal Extracted from Liquid and Air-dried Forms of a Model Organic Phase by an Alternative Sequential Extraction Scheme

Extractant	*% Total metal solubilised by sequential extraction*									
	Cu		*Cd*		*Ni*		*Pb*		*Zn*	
	Liquid	*Dried*	*Liquid*	*Dried*	*Liquid*	*Dried*	*Liquid*	*Dried*	*Liquid*	*Dried*
$MgCl_2$	38·4	46·4	52·9	73·0	54·3	70·1	5·8	11·5	36·6	58·8
CH_3COONa	13·4	11·8	43·7	18·8	<1·0	<1·0	69·5	71·8	43·9	30·2
EDTA	24·4	13·7	3·2	<1·0	3·2	3·0	4·9	11·8	3·9	2·7
HNO_3	7·2	15·9	<1·0	5·7	2·9	<1·0	<1·0	<1·0	<1·0	<1·0
Res.[a]	16·6	12·2	<1·0	2·5	39·6	29·9	14·8	4·9	15·6	8·3

[a] By subtraction.

$MgCl_2$, although CH_3COONa solubilised a significant quantity of the metal, particularly from the liquid samples.

Similar extraction profiles were obtained for Pb from air-dried and liquid samples, indicating little change in extractability of metal phases caused by drying. The predominant Pb fraction was extracted by CH_3COONa, which removed >69% of the total metal in both forms. Significant, but very much lower, extractions were produced by $MgCl_2$ and EDTA. The first two extractants accounted for >95% of the Zn solubilised in the alternative scheme. Extraction by CH_3COONa was slightly higher than by $MgCl_2$ for the liquid phase, but only half that of $MgCl_2$ for the air-dried sample, demonstrating a clear difference in Zn extraction characteristics for the two sample types. In general, it appeared that $MgCl_2$ was an effective extractant for organically associated forms of Cd, Ni, Cu and Zn while the proposed organic extractant exhibited good selectivity for Pb and, to a lesser extent, Zn.

A comparison of results of the alternative and Stover extraction schemes indicated that total metal recoveries were generally better using the alternative scheme, with lower residual metal levels found for all samples except Ni and Zn extraction from the liquid phase. The alternative scheme generally supported the evidence obtained by the Stover extraction for the characteristic extraction behaviour of certain metals in the model organic phase. Copper exhibited varying degrees of resistance to all the extractants and hence no specific reagent could be identified for extraction of this metal. Nickel was retained either as a readily labile form or a highly resistant form, while Pb was strongly associated with the organic phase. A greater emphasis was placed on the more readily extractable, exchangeable and adsorbed forms of Cd and Zn in the alternative extraction scheme, as compared to the Stover scheme, although organically associated Zn was an important fraction in both.

DISCUSSION

Discrete and sequential extraction procedures are widely applied in studies of the association of heavy metals with solid phases in environmental samples, such as soil, sediment and sewage sludge (Kirk *et al.*, 1985). However, data obtained from such procedures are often not interpreted with full consideration of the assumptions inherent in the techniques. The following factors should be borne in mind. First, sequential and discrete extraction procedures are operationally defined and, therefore, comparisons between different procedures are, at best, tentative. Secondly, sequential schemes are often applied to study a range of elements whose chemistries are markedly different. Thirdly, it is essential to distinguish between a 'fraction' and a 'phase', a specific form of chemical interaction or association. Sequential extraction techniques provide information on fractions, data on specific phases have to be inferred.

The inference of chemical phases is often based upon experiments on extraction of pure mineral phases, such as clays, iron oxyhydroxides, carbonates, or model compounds. With the model compound approach, one is testing the solubility of elements of interest in a series of reagents. The solubility of a model precipitate will, of course, be concentration dependent, and unless the extractant is present in excess with respect to the model phase, the resultant data may be biased. Verification of a chemical extraction scheme is often carried out by a series of discrete extractions (Stover *et al.*, 1976; Meguellati *et al.*, 1983). These experiments will also indicate a preferred order for the extraction reagents under sequential application. Behaviour of the model phases under sequential conditions is assumed by extrapolation from the single reagent case. Although initial investigations of reagent specificity and efficiency have of necessity to be made by means of discrete extractions, it would seem that where possible it would be advisable to evaluate the chosen reagent in combination with others in the scheme, in order to confirm its extraction of a designated phase.

Differences in percentage metal extraction were observed when using liquid and air-dried forms of the model organic phase. Total sequential removals were higher for all metals in the liquid samples except Cd and Zn, which were similar in both forms. The KNO_3 fraction, designated as soluble/exchangeable metal by Stover *et al.* (1976) was significantly increased for Cu in the dried samples (31·1%) as compared to the liquid samples (18·1%) and to a lesser extent for Zn, at 15·1% and 9·2% total metal, respectively. Similar results were obtained by Miller *et al.* (1986) who compared the solubility of Cu in slurried, freeze-dried and oven-dried swine manure by means of chemical extraction. The process of drying was reported to increase Cu solubility and cause substantial changes in Cu speciation. Oake *et al.* (1984) found a similar ranking of extracted fractions for corresponding liquid and air-dried sludge samples, but the quantities of metals solubilised differed between the two forms. Such observations imply that the form of subsamples used for the determination of potential metal solubility should be consistent with that of the bulk material being tested.

The predominant theoretical metal species identified in sewage sludges by workers using sequential extraction techniques are given in Table 6. Evidence from the model compound extractions made in the current study generally supported the identification of the major species of Cd and Ni as carbonate, Zn as organically-associated, and Pb as organically-bound or carbonate, although other precipitates may have contributed to these fractions for all four metals. This was particularly the case for Pb, where the efficiency of $Na_4P_2O_7$ solubilisation would seem likely to cause overestimation of the importance of organically-bound species. This may be due to the formation of lead pyrophosphate, $Pb_2P_2O_7 . H_2O$, which is soluble in alkaline solution (Greninger *et al.*, 1973).

Copper, however, has been predominantly identified by those workers employing the Stover extraction scheme in the HNO_3 fraction, which was originally designed to extract sulphide forms (Stover *et al.*, 1976). The predominance of sulphide forms of Cu in activated sludges in particular would appear to be anomalous, as sulphides are not generally formed under the aerobic conditions which prevail in the activated sludge system (Painter,

TABLE 6

Predominant, Theoretical Metal Species Identified in Sewage Sludges by Means of Sequential Chemical Extraction

Metal	*Predominant metal species*				
	Stover et al. (*1976*)	*Emmerich* et al. (*1982*)	*Legret* et al. (*1983*)	*Oake* et al. (*1984*)	*Lake* et al. (*1985*)
Cu	S	org.	org.	S	S
Cd	CO_3	CO_3	oxid.	CO_3	CO_3
Ni	CO_3	CO_3	org.	CO_3	exch./CO_3
Pb	CO_3	—	res.	org./CO_3	org./CO_3
Zn	org.	CO_3	oxid.	org.	org.

Abbreviations, S: sulphide; CO_3: carbonate; org.: organically bound; oxid.: oxidisable phase; exch.: soluble and exchangeable; res.: residual.

1983). Furthermore, the gradual aeration of anaerobic sludge, following withdrawal from a digester, is likely to oxidise sulphides and reduce the magnitude of the HNO_3-extractable fraction, as demonstrated for Cd by Feltz & Logan (1985). Evidence from the extraction of model compounds indicated that HNO_3 liberated a higher percentage of organically bound than sulphide forms of Cu, although neither model phase could fully account for the magnitude of the HNO_3 fraction reported for sewage sludges. The organically-bound fraction has been identified as the most significant for Cu by workers using other sequential chemical extraction techniques (Emmerich *et al.*, 1982; Legret *et al.*, 1983) and concurs with observations of its increased affinity for organic material in both activated (Rudd *et al.*, 1984*a*; Forster, 1985) and digested (Gould & Genetelli, 1984; Sterritt & Lester, 1984) sludges, in comparison to other metals. Since a significant proportion of Cu and other model metal sulphides were evident in the residual fraction following sequential extraction, it may be more appropriate to classify sulphide and residual forms as one combined phase, as has been done by Emmerich *et al.* (1982).

The fractionation profile of Ni in sewage sludges is characterised by a significant KNO_3-extractable (i.e. exchangeable) fraction, at approximately 14% total metal (Stover *et al.*, 1976; Oake *et al.*, 1984). Sequential extraction of the model organic phase indicated that such exchangeable forms of Ni were associated with organic matter. Although 'organically bound metal' is frequently categorised as one distinct phase, it is more likely to cover a broad spectrum of binding mechanisms, including adsorption (Ellis & Knezek, 1972), complexation (Stevenson & Ardakani 1972), and chelation (Worthington, 1979), and will thus overlap with the preceding phases in the extraction scheme. The weak associations of both Ni and Cu with organic matter, demonstrated by both the sequential extraction schemes employed here, probably involved ion-exchange processes, since Calmano & Forstner (1983) have stated that organic surfaces provide locations, such as amino and carboxyl groups, to which metals can bind via ion exchange. Furthermore, it has been observed that Ni has a particular affinity for readily soluble organic matter in activated sludges (Rudd *et al.*, 1984*b*), thus KNO_3, and possibly $MgCl_2$, may remove readily soluble Ni-organic complexes intact, rather than exchanging with the metal cation alone. Evidence from the TOC determinations in the KNO_3 extracts would seem to support this.

The observations above serve to highlight the problems inherent in attempting rigorous division of metal species within sludge, when such species are likely to be involved in a variety of interactions. Furthermore, given the probable continuum of metal solubility in natural materials (Miller *et al.*, 1986), it is recognised that problems are likely to exist in finding a reagent which will accurately separate out identical forms of disparate metals. In using chemical extraction methods, careful distinction must be made between a fraction, i.e. that portion of metal solubilised by a specific reagent, and a phase, i.e. the discrete metal species sought. This proves difficult when individual phases contribute to more than one fraction, as exemplified by the model compounds employed in the current study. Nevertheless, chemical extraction can prove useful as a semi-quantitative tool for assessing differences in potential metal solubility in sludges, and with further definition using model phases or other means, tentative identification of the species extracted within operationally defined fractions can be made.

ACKNOWLEDGEMENTS

The work was carried out under contract to WRC Environment, whose permission to publish is acknowledged. Acknowledgement is also made to the Science and Engineering Research Council for co-operative funding.

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