

Fractionation of Copper, Nickel, and Zinc in Metal-Spiked Sewage Sludge

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ABSTRACT

The enrichment or *spiking* of sewage sludge with heavy metals for experimental purposes is a fairly widely used, although sometimes controversial, technique. A study was undertaken, using a sequential fractionation scheme, to assess the degree of incorporation of Cu, Ni, and Zn into sewage sludge samples spiked with these metals and incubated for 6 mo. For all three metals, substantial proportions of the metals were incorporated into the sludge matrix, particularly as evidenced by their occurrence in the *oxide-bound*, *organic-bound*, and *residual* fractions. In particular, for Cu very little of the added copper remained in the sludge supernatant solution after 6 mo of incubation and, apart from at the highest level of Cu addition, there was very little difference in the fractional distribution of Cu between the Cu-spiked and non-Cu-spiked sludges. For Ni and Zn, however, although there was substantial incorporation of these metals into the sludge, the higher levels of Ni and Zn addition resulted in greater proportions of the metals in the most soluble fractions (*soluble*, *exchangeable*, *specifically sorbed*) compared with nonspiked sludges. The fractionation data for Ni also showed that large additions of Cu and Zn can affect the fractional distribution of Ni in the sludge. The drying of sewage sludge prior to analysis was shown to increase metal solubility in the sludge samples, and the potential implications of this finding for the prediction of sludge metal bioavailability are discussed.

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THE enrichment or *spiking* of sewage sludge with heavy metals for experimental purposes is a fairly widely used technique (for example, Davis and Carlton-Smith, 1981; Street et al., 1977; Coppola et al., 1988; Forge et al., 1993; Obbard et al., 1993). Spiking may be undertaken to (i) increase the rate of buildup of metals in soils treated with sludge without having to apply excessive amounts of sludge to the soil, or (ii) distinguish the effects of increasing amounts of a single metal from the effects of other metals or other types of contaminants present in the sludge. Unfortunately, in the absence of small-scale treatment plants, metal-spiking of sludge is often carried out using the final digested sludge materials produced at local municipal treatment plants. This of course means that the metals added as a spike do not undergo the same processes as those metals already present in the sewage entering the treatment plant. For this reason, the spiking of sewage sludge with simple metal salts is controversial, since there is no certainty that the added metals will be present in the same forms as those metals already present in the sludge. This is important because there is evidence that the bioavailability of metals added to soil as metal salts may differ from the bioavailability of metals added in nonspiked sewage sludge (Bell et al., 1991). In an attempt to overcome this problem, before they are used, sludges spiked with additional metals are commonly incubated for a

period of time, to allow the metals to react with, and become incorporated into the sludge matrix (Davis and Carlton-Smith, 1981; Coppola et al., 1988). One possible way of assessing the effectiveness of the spiking procedure is to subject the spiked sludge to a chemical sequential extraction procedure.

Sequential extraction (or fractionation) procedures have been developed predominantly to determine the amounts and proportions of metals present in different forms in soil or sediment samples (e.g., McLaren and Crawford, 1973; Tessier et al., 1979; Shuman, 1985). However, such procedures have also been used quite widely to fractionate metals in sewage sludge and sludge-treated soils (e.g., Stover et al., 1976; Lake et al., 1984; Dudka and Chlopecka, 1990; Pérez-Cid et al., 1996; McLaren et al., 1999). Fractionation procedures are often criticized because of their complexity and difficulty in interpretation, arising from potential problems such as lack of specificity of extractants and readsorption of metals during extraction (Beckett, 1989; Kersten and Förstner, 1995). Nevertheless, providing that such limitations are recognized, sequential fractionations can provide extremely useful information on metal distribution in sludges, particularly for comparative purposes.

This paper describes the fractionation of copper (Cu), nickel (Ni), and zinc (Zn) in samples of a sewage sludge spiked separately with increasing amounts of these three metals added as sulfate salts. The objective was to determine whether the spiking procedure had resulted in a similar distribution of metals between fractions to that determined for a nonspiked sludge sample. We also examine the effect of sample preparation on metal fractionation. Work with sediment samples has indicated that the type of sample preparation (e.g., air-drying, freeze-drying, freezing, wet storage at 1–4°C) can strongly influence the partitioning of metals obtained by sequential extraction procedures (Tessier and Campbell, 1988). To date, all metal fractionations carried out on sewage sludge appear to have used air-dried or oven-dried samples.

MATERIALS AND METHODS

Sewage Sludge Treatment and Sampling

The samples of sewage sludge used in this study were prepared for application to field plots of soil in an experiment designed to examine the effects of increasing amounts of sludge-applied Cu, Ni, and Zn on various soil biological and biochemical properties (Speir et al., 2000). Anaerobically digested sewage sludge (approximately 8% solids), obtained from the Christchurch (New Zealand) city sewage treatment works at Bromley, was placed in a series of large polypropylene tanks, each tank containing approximately 250 L of sludge. Four of the tanks of sludge were treated with increasing amounts of Cu (samples Cu-1, Cu-2, Cu-3, Cu-4), four with increasing amounts of Ni (samples Ni-1, Ni-2, Ni-3, Ni-4), and four with increasing amounts of Zn (samples Zn-1, Zn-2, Zn-3, Zn-4), all metals being added as sulfates ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$). A final (thirteenth) tank was kept as a control and received no additional metals.

Following addition of the metal salts, the samples of sludge were thoroughly stirred and the tanks tightly sealed. The

sludge samples were held in this condition for 6 mo at ambient temperature with occasional additional stirring. Although stirring would have introduced some air into sludge, its very thick consistency, small surface area to volume ratio, and the tight sealing of the container lids ensured that the samples remained in a predominantly anaerobic condition during incubation. The amounts of metals added to the sludge samples were calculated so that when the contents of the tanks were applied to field plots and incorporated into the top 10 cm of soil, metal concentrations in the topsoil would be increased by between 20 to 70% (approximately) of the current New Zealand limits for sludge-amended soils (New Zealand Department of Health, 1992). After the 6-mo incubation, the treated sludges were again thoroughly stirred and samples removed from each tank for analysis. This was done using a specially designed sampling tool that could take samples of approximately 200 mL volume from any position within the tank. Ten subsamples were removed from random positions in each tank and bulked, giving a final sample size of approximately 2 L.

Sample Preparation

The sludge samples removed from the tanks were thoroughly mixed before subdividing into two portions. One portion was immediately oven-dried at approximately 50 to 60°C for 1 wk and then finely ground. The second portion was centrifuged at 10 000 rpm for 1 h and the supernatant solution decanted and filtered through a 0.45- μm filter before storing at 4°C prior to analysis. The residue from centrifuging was also stored at 4°C prior to analysis. Subsamples of the residues were taken for dry matter determination. The residues contained approximately 30% solids compared with 8% solids in the original sludge sample received from the treatment works.

Analysis

Sludge Supernatant

The sludge supernatant solutions were analyzed for Cu, Ni, and Zn by flame or graphite furnace atomic absorption spectrophotometry. Dissolved organic carbon was determined using a Shimadzu (Kyoto, Japan) TOC-5000A total carbon analyzer.

Dried and Wet Sludges

The sequential extraction technique described by Tessier et al. (1979) was used to fractionate Cu, Ni, and Zn in both the dried and wet sludge samples. The extractants used, the extraction conditions, and the nominal forms of metal considered to be extracted are outlined in Table 1. In the case of the wet samples, the amount of material used was determined from the moisture content to provide 1 g of solid material. The volume and concentration of the first extractant [$\text{Mg}(\text{NO}_3)_2$] was then adjusted so that the extraction conditions were identical to those used for the dried samples.

In addition to the metal fractionation, both the dried and wet sludges were extracted with water. Samples (1 g equivalent dry weight) were shaken with 25 mL deionized water for 1 h, centrifuged at 20 000 rpm for 30 min, and then filtered through a Whatman (Maidstone, UK) No. 42 filter paper. "Total" metal concentrations in the dried sludge samples were determined using a nitric acid digestion method (USEPA SW 846-Method 3051; USEPA, 1995), and total carbon determined using a LECO (St. Joseph, MI) CNS-2000 analyzer. All carbon was assumed to be organic in nature since the sludge is not treated with lime, and no calcium carbonate has been determined in sludge from the Christchurch treatment works. The

Table 1. Sequential extraction procedure (Tessier et al., 1979).

Step	Nominal fraction	Extractant	Conditions
1	Soluble plus exchangeable	1 M Mg(NO ₃) ₂ , pH 7.0	1 g biosolids, 8 mL extractant; 1 h shaking
2	Specifically sorbed	1 M sodium acetate, adjusted to pH 5.0 with acetic acid	Residue from Step 1 shaken for 5 h with 8 mL extractant
3	Oxide bound	0.4 M NH ₂ OH·HCl in 25% (v/v) acetic acid, ~pH 2	Residue from Step 2 heated for 6 h at 96°C with 20 mL extractant
4	Organic bound (also sulfides)	H ₂ O ₂ adjusted to pH 2 with HNO ₃	Residue from Step 3 heated for 2 h with 8 mL extractant then 3 mL extractant added and heated for further 3 h
5	Residual	Microwave digestion with HNO ₃	Residue from Step 1 dried and 0.5 g subsample digested according to USEPA 3501†

† USEPA (1995).

pH of the samples was measured in a water suspension (sludge to water ratio of 1:2.5) after the suspensions were shaken and left to stand overnight.

Analysis for Cu, Ni, and Zn in extracts was carried out by flame or graphite furnace atomic absorption spectrophotometry. Dissolved organic carbon in the water extracts was determined using a Shimadzu TOC-5000A total carbon analyzer. Results for both the dried and wet sludge samples were calculated on an oven-dried solids basis.

Replication and Quality Assurance

All analyses were carried out in duplicate and the values reported are the mean values of the replicate analyses. Analytical quality was maintained by the regular analysis of standard reference sludge samples within sample batches, inclusion of solutions of known concentrations within analytical runs, and the random repetition of analyses.

RESULTS AND DISCUSSION

Total Cu, Ni, and Zn concentrations and the pH of the sludge samples are shown in Table 2. The organic C concentration was constant across all samples with a mean of 31.6% C (CV 3.8%). However, application of Zn decreased the pH of the sludge, with the pH of the Zn-4 treatment nearly 1 pH unit below that of the control (Table 2). The Cu and Ni applications had no effect on sludge pH. The samples that received no additional Cu had a mean Cu concentration of 450 mg kg⁻¹ (CV 12.4%), a mean Ni concentration of 97 mg kg⁻¹ (CV 9.8%), and a mean Zn concentration of 1378 mg kg⁻¹ (CV 6.9%). These values are typical for sewage sludge from the Christchurch sewage treatment works. The small CV values for the three metals give some confidence that, in spite of the problems of working with such large volumes of sewage sludge and its inherent

Table 2. Total metal concentrations (mg kg⁻¹ dried sludge) and pH values of the sewage sludge samples.

Sample	mg kg ⁻¹ dried sludge			pH
	Copper	Nickel	Zinc	
Control	490	93	1 484	7.4
Cu-1	8 086	96	1 492	7.2
Cu-2	13 180	109	1 402	7.2
Cu-3	17 366	91	1 329	7.3
Cu-4	22 060	92	1 200	7.3
Ni-1	535	2 115	1 354	7.4
Ni-2	477	4 234	1 465	7.6
Ni-3	503	6 231	1 343	7.4
Ni-4	446	8 276	1 298	7.3
Zn-1	429	107	13 154	7.3
Zn-2	396	95	18 726	6.9
Zn-3	412	96	30 263	6.7
Zn-4	361	96	40 616	6.5

variability, the initial metal concentrations were pretty uniform across all containers.

As required for the purpose for which they were prepared, concentrations of Cu, Ni, and Zn in the spiked sludges were extremely high. Certainly the concentrations are well above current USEPA regulations that set limits of 4300 mg kg⁻¹ Cu, 420 mg kg⁻¹ Ni, and 7500 mg kg⁻¹ Zn for sludges applied to agricultural land. However, sludges applied to land in the past have had metal concentrations comparable with those in the spiked sludges. For example, Zn concentrations as high as 27 600 mg kg⁻¹ have been reported in a survey of sludges used on agricultural land in the UK (Smith, 1996), and up to 49 000 mg kg⁻¹ in an earlier UK survey reported by Berrow and Webber (1972). In the USA, sludge Zn concentrations as high as 28 850 mg kg⁻¹ have also been reported (Sommers et al., 1976). Similarly, sludge Cu concentrations of up to 8000 mg kg⁻¹ (Berrow and Webber, 1972) and 11 800 mg kg⁻¹ (Sommers et al., 1976), and Ni concentrations up to 5300 mg kg⁻¹ (Berrow and Webber, 1972) and 4000 mg kg⁻¹ (Sommers et al., 1976) have also been reported. It should be emphasized, however, that such concentrations are much higher than would normally be expected in most modern-day sludges produced in developed countries such as the USA and the UK.

An initial assessment of the degree of incorporation of the added metals into the sludge was carried out by determination of the concentrations of Cu, Ni, and Zn remaining in the sludge supernatant solution. Supernatant concentrations of the three metals are shown in Table 3. In the case of Cu, supernatant concentrations in the control and non-Cu-spiked samples were extremely low and accounted for approximately 0.01% of the total

Table 3. Metals in sludge supernatant solutions.

Sample	Copper		Nickel		Zinc	
	µg L ⁻¹	%†	µg L ⁻¹	%†	mg L ⁻¹	%†
Control	4.8	0.01	0.3	4.0	0.17	0.14
Cu-1	118.7	0.02	0.3	3.5	0.06	0.05
Cu-2	193.5	0.02	0.3	2.7	0.05	0.04
Cu-3	383.0	0.03	0.2	3.1	0.05	0.04
Cu-4	155.6	0.01	0.2	3.2	0.03	0.03
Ni-1	4.8	0.01	1.4	0.8	0.05	0.05
Ni-2	3.4	0.01	3.0	0.9	0.07	0.05
Ni-3	2.1	<0.01	3.6	0.8	0.05	0.05
Ni-4	1.0	<0.01	4.5	0.7	0.04	0.04
Zn-1	1.1	<0.01	0.3	3.5	0.19	0.02
Zn-2	16.2	0.04	0.6	6.3	17.79	1.03
Zn-3	5.8	0.02	1.1	12.2	193.62	6.82
Zn-4	1.2	<0.01	2.0	20.3	990.50	24.15

† Percent of total sludge metal content.

Cu in the sludge. Supernatant concentrations were increased substantially by the added Cu, but still only accounted for a negligible proportion of the total Cu in the sludge. Nickel concentrations in non-Ni-spiked sludges were even lower than for Cu but accounted for significantly higher proportions of the total Ni. Addition of Ni did increase supernatant Ni concentrations but reduced the proportion of total sludge Ni present in the supernatant. However, addition of Zn at the higher levels clearly also had a major influence on supernatant Ni concentrations, causing displacement of Ni from the solid phase into the solution (Table 3).

In the case of Zn itself, supernatant concentrations in non-Zn-spiked samples were extremely low and, like Cu, accounted for negligible proportions of the total Zn in the sludge. Addition of Zn, however, caused substantial increases in both supernatant Zn concentrations and the proportions of total sludge Zn accounted for by

supernatant Zn. At the highest level of Zn addition (Zn-4), 24% of the total zinc was found in the supernatant (Table 3). The supernatant data overall suggest that at the levels of Cu and Ni addition used in this study, incorporation of these metals into the sludge matrix had been successful. However, with the Zn-3 and Zn-4 treatments in particular, substantial proportions of the added Zn remained in the supernatant solution, suggesting that the capacity of the sludge to incorporate the Zn had been exceeded. This may also have been due in part to the lower pH of these treatments (Table 2). The effect of these high Zn additions on the distribution of Ni between the supernatant and solid phases may also be of concern.

A more detailed assessment of the effectiveness of metal incorporation into the sludge is provided by the sequential fractionation data (Fig. 1-3). Experimentally, sequential extraction procedures, particularly ones with

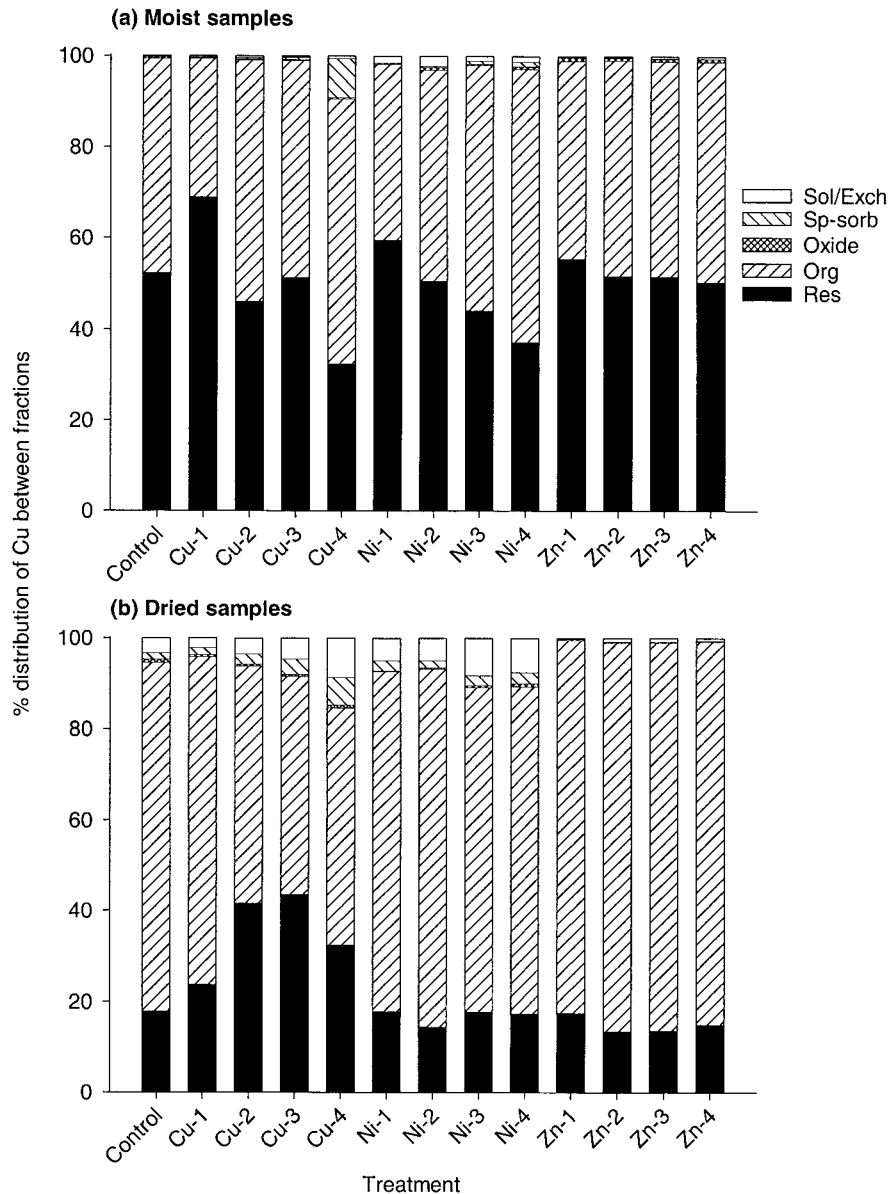


Fig. 1. Proportional distribution of Cu between fractions in moist and dried sewage sludge samples.

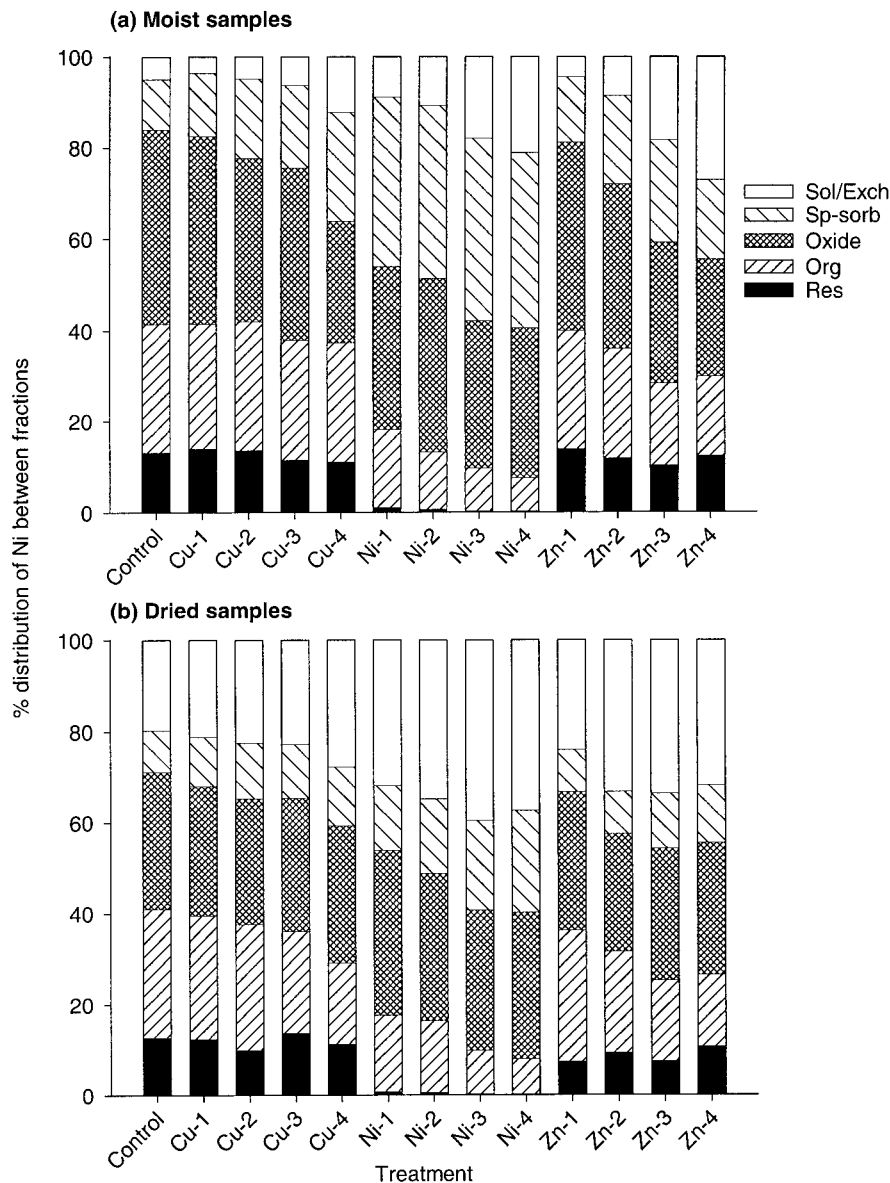


Fig. 2. Proportional distribution of Ni between fractions in moist and dried sewage sludge samples.

five or more fractions, are tedious and time consuming to undertake. They involve numerous weight, volume, and analytical determinations, and losses of small amounts of material at each stage during centrifugation and decantation are common. Without due care, the errors at each stage accumulate and can result in a substantial lack of precision and accuracy in the final results. A good check on the reliability of sequential fractionation data is whether, within acceptable error, the sum of the metal in the individual fractions agrees with a single total metal determination. In the present study, the metal concentrations recovered during fractionation were considered acceptable although, with a few exceptions, they were generally lower (by approximately 10–15%) than the single total metal determinations (Table 4). This was considered mainly due to small cumulative losses of material during fractionation caused by the highly organic nature of the sludge. Agree-

ment between the total metal recoveries for the dried and wet samples was generally good (within $\pm 10\%$). To make comparisons easier, the data in Fig. 1 through 3 are presented on a proportional basis. For the moist sample data, supernatant metal concentrations have been added to the *soluble plus exchangeable* fraction to make the data comparable with that for the dried samples.

It is clear for all three metals that, although added as easily soluble salts, during the 6-mo incubation period, substantial proportions of the metals had become associated with the less readily extracted oxide-bound, organic-bound, and residual fractions (Fig. 1–3). In the case of Cu, most of the added metal (samples Cu-1 to Cu-4) was associated with the organic-bound and residual fractions and there was little Cu found associated with the soluble plus exchangeable, specifically sorbed, or oxide-bound fractions (Fig. 1a). The distribu-

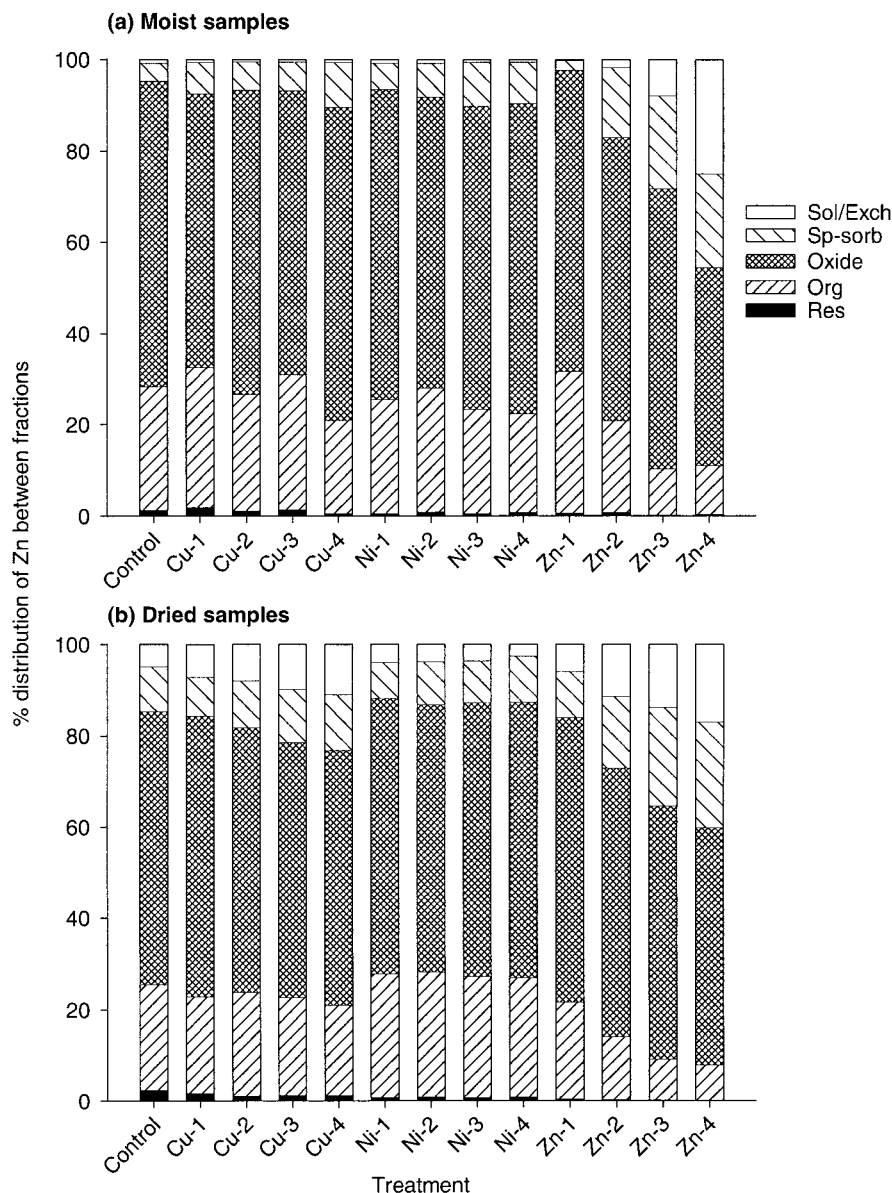


Fig. 3. Proportional distribution of Zn between fractions in moist and dried sewage sludge samples.

tion was very similar to that observed for Cu in the non-Cu-spiked sludges; however, the proportions of Cu present in the two most easily extracted fractions (soluble plus exchangeable and specifically sorbed) did increase with increasing Cu concentrations in the sludge (Fig. 1a). Oven-drying the sludge clearly had some effect on the distribution of Cu as determined by the sequential extraction. Compared with the samples maintained in a moist condition, drying appeared to increase the proportion of Cu found in the organic-bound fraction at the expense of Cu in the residual fraction (Fig. 1b). Drying also clearly increased the proportion of Cu found in the soluble plus exchangeable and specifically sorbed fractions.

Unlike for Cu, the distribution of Ni between fractions in the metal-spiked sludges differed considerably from that in the control. In the Ni-spiked sludges (Ni-1 to Ni-4), most of the added Ni appeared in the speci-

cally sorbed, oxide-bound, and organic-bound fractions, with virtually no Ni present in the residual fraction (Fig. 2a). The occurrence of a substantial proportion of Ni in both control and Ni-spiked samples in the nominal oxide-bound fraction raises questions as to the real nature of the Ni in this fraction. In the original procedure published by Tessier et al. (1979), this fraction was designed to extract metals bound to Fe and Mn oxides. However, since the sludge samples were maintained under predominantly anaerobic conditions, and the concentrations of Fe (1%) and Mn (300 mg kg^{-1}) were not high, the occurrence of oxides of these elements in the sludge seems rather unlikely. The reagent used to extract the oxide-bound fraction is extremely acid (Table 1), and it would seem more likely that the Ni extracted in this fraction has in fact been displaced from organic surfaces, or possibly by dissolution of sulfides. It is interesting to note that there was little Cu in this fraction

Table 4. Total recoveries of metals (%) during fractionation of sludge samples.

Sample	Copper		Nickel		Zinc	
	Moist	Dried	Moist	Dried	Moist	Dried
	%					
Control	84.1	84.1	88.6	92.5	86.1	83.5
Cu-1	87.5	87.2	108.8	86.7	95.8	85.1
Cu-2	82.6	84.9	83.6	91.9	88.5	85.6
Cu-3	102.1	85.6	102.7	92.3	82.8	94.0
Cu-4	83.7	85.9	88.3	86.3	83.4	85.3
Ni-1	92.1	82.7	92.9	106.1	84.2	84.5
Ni-2	94.2	112.2	100.3	91.2	89.2	85.3
Ni-3	83.7	86.7	86.8	93.7	85.7	89.4
Ni-4	84.4	89.3	86.5	97.0	96.3	85.6
Zn-1	85.9	107.1	80.4	80.9	87.8	99.1
Zn-2	105.2	115.5	115.2	83.7	114.5	97.2
Zn-3	108.4	92.2	99.7	83.6	101.7	100.9
Zn-4	98.6	90.8	108.2	80.9	107.3	98.3
Mean	91.7	92.6	95.5	89.8	92.6	90.3

(Fig. 1). Copper is bound much more tightly by organic matter than Ni (or Zn) and is much less likely to be displaced by the hydroxylamine hydrochloride reagent.

There were also significant proportions of Ni present in the soluble plus exchangeable fraction, which increased from approximately 5% in the control sample to more than 20% at the highest added Ni concentration (Ni-4). In the absence of added Ni, the distribution of Ni between fractions was also influenced by Cu and Zn additions. The effect of these metals was to increase the proportion of Ni in the soluble plus exchangeable fraction at the expense of Ni in the organic-bound fraction. As for Cu, drying the sludge had a marked effect on the distribution of Ni between fractions. For all samples, drying the sludge produced substantial increases in the proportion of Ni present in the soluble plus exchangeable fraction, predominantly at the expense of the specifically sorbed fraction (Fig. 2).

In the case of Zn, for all sludge samples a high proportion of Zn occurred in the oxide-bound fraction (approximately 60%) with smaller proportions in the organic-bound and specifically sorbed fractions. As discussed for Ni, however, the source of Zn in the oxide-bound fraction is open to debate, and may well be derived predominantly from organic-bound and sulfide sources. With the Zn-spiked samples (Zn-1 to Zn-4), the proportions of Zn recovered in the soluble plus exchangeable and specifically sorbed fractions increased substantially with the increasing amount of Zn added (Fig. 3a). Drying the sludge had a similar effect on Zn to that observed for Ni, that is, soluble plus exchangeable Zn was increased predominantly at the expense of the specifically sorbed fraction.

The fractionation data overall confirms a high degree of incorporation of the added Cu, Ni, and Zn into the sewage sludge matrix. However, for Zn and Ni, at the higher levels of metal addition, the proportions of metal occurring in the most easily extracted fractions are substantially higher than in nonspiked sludge. These trends observed with the Ni- and Zn-spiked samples, compared with the unspiked equivalents are fairly clear, even taking into account differences in metal recoveries between treatments (Table 4). The observed differences in metal

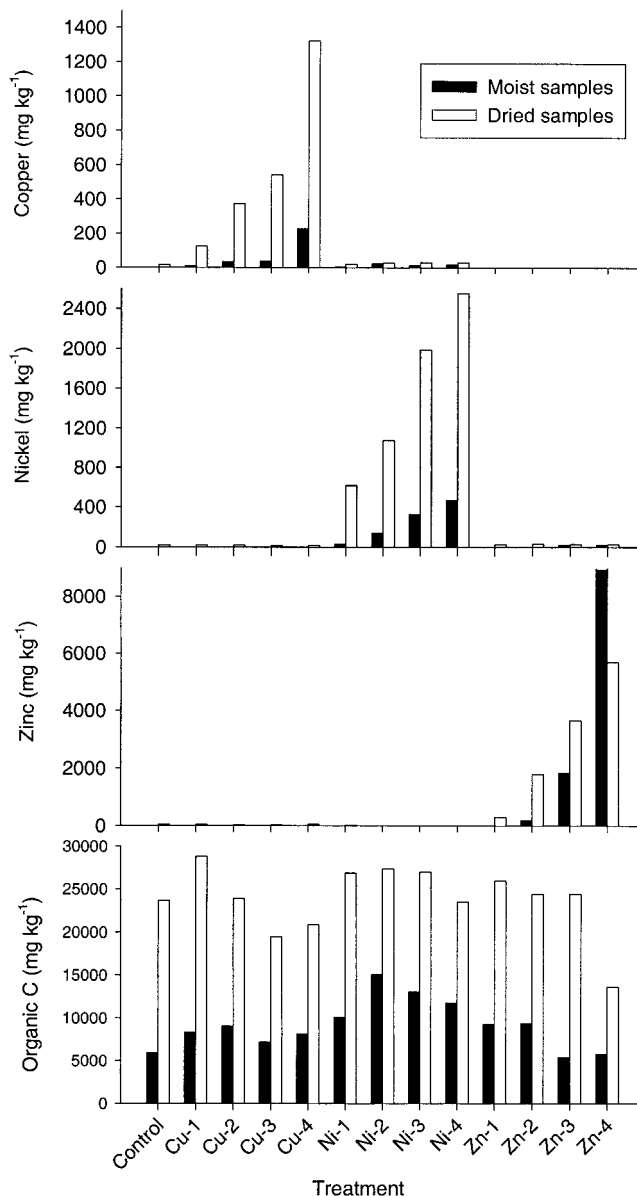


Fig. 4. Water-extractable Cu, Ni, Zn, and organic carbon concentrations in moist and dried sewage sludge samples.

distribution between fractions could well have implications for the mobility and/or bioavailability of these metals when the sludges are applied to the soil. The effect of Cu and Zn additions on Ni solubility could also have implications for Ni mobility and/or bioavailability. However, application to the soil is also likely to result in changes in the distribution of metals between fractions, and this possibility is currently being investigated.

Drying sludge clearly influences the distribution of metals between fractions as determined by sequential extraction, although the significance of this is difficult to predict. It could be argued that by drying samples, an overestimate of the most soluble forms of metals may be obtained. Conversely, it could also be argued that drying the sludge actually simulates what happens when sludge is applied to soil in the field (e.g., drying and oxidation). In order to examine the drying effect

in more detail, the concentrations of water-soluble Cu, Ni, and Zn were compared between the dried and moist samples (Fig. 4). In agreement with the fractionation data, with the exception of the highest Zn treatment, drying the sludge samples substantially increased the solubility of all three metals. The increases in water-extractable metals were paralleled by substantial increases in water-extractable organic carbon brought about by the drying process (Fig. 4). Thus it would seem likely that the increased solubility of metals observed after drying is related to this increase in soluble organic carbon. We speculate that the breakdown (oxidative) of organic components during the drying process could either (i) release associated (bound) metals from the solid phase organic matter and/or (ii) lead to greater complexing of metals by the increased concentrations of water-soluble organic components.

CONCLUSIONS

The results obtained from this study demonstrate that when sewage sludge is spiked and incubated with additional metals added as simple salts, substantial proportions of the metals become incorporated into the sludge matrix. In addition, for Cu, apart from at the highest level of Cu addition, there was very little difference in the fractional distribution of Cu between the Cu-spiked and non-Cu-spiked sludges. This was not the case for Ni and Zn, where, although there was substantial incorporation of these metals into the sludge, for the two highest levels of addition in particular, the fractional distribution of metals differed substantially between the spiked and nonspiked samples. For these higher levels of Ni and Zn addition, much greater proportions of the metals were present in the most soluble fractions. Such trends were much larger than could be explained simply by differences in metal recoveries between samples.

In addition, as evidenced by the Ni fractionation data, this study suggests that the effects of large additions of one metal on the fractional distribution of others may be of concern in spiking experiments. Results from this study also raise some concerns and problems of interpretation regarding the drying of sewage sludge samples prior to fractionation.

However, in spite of the issues discussed above, it would appear that even when sludge is spiked following completion of the digestion process, by restricting the concentrations of metals added, it is possible to produce sludges with metal distributions similar to those in unspiked sludges.

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