

# Content and Fractionation of Heavy Metals in Water Treatment Sludges

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## ABSTRACT

The composition and distribution of Cd, Cu, Cr, Ni, Pb, and Zn in eight alum and FeCl<sub>3</sub> coagulation sludges were investigated using a five-step chemical fractionation procedure to assess potential impacts following soil incorporation. The mean total metal levels (mg kg<sup>-1</sup> dry wt.) for these sludges were Cd (<2), Cu (234), Cr (187), Ni (102), Pb (230), and Zn (557), which are well below maximum allowable levels for land-applied wastes. Two individual FeCl<sub>3</sub> sludges had Ni levels slightly above maximum allowable concentrations. Mean total Cr and Ni concentrations in the FeCl<sub>3</sub> sludges were, respectively, 5.4 and 3.1 times the corresponding alum sludge levels, reflecting elevated concentrations in the FeCl<sub>3</sub> coagulant. The Cu, Cr, Ni, Pb, and Zn in sludges were predominantly bound within the oxide or silicate components. A small portion of the sludge Cd was in a readily exchangeable form, whereas the dilute acid extractable and organically bound fractions contained the majority of non-residual Cd. Fractionation results suggest sludge Cd would potentially be mobile under acidic soil conditions, but the total Cd levels were very low (1–2 mg kg<sup>-1</sup> compared with an allowable maximum of 25 mg kg<sup>-1</sup>). Although fractionation data must be interpreted cautiously, the results suggest most metals in water treatment sludges occur predominantly in weakly mobile, nonbioavailable forms.

WATER UTILITIES, once concerned almost exclusively with finished water quality, are increasingly aware of the importance of treatment by-product disposal. Water treatment commonly involves addition of alum or ferric chloride for coagulation and removal of suspended solids present in the raw water. The sludges produced consist primarily of the precipitated hydroxide of the coagulant [e.g., Al(OH)<sub>3</sub>] along with material (sand, silt, clay, humic compounds) removed from the raw water. These water treatment sludges (WTS) have circumneutral pH, low BOD<sub>5</sub> (< 100 mg/L), and Al, Fe, Ca, and Si as major elemental components. For years, standard disposal procedures involved direct discharge of WTS to a watercourse. In most cases, this practice is no longer permissible. Sanitary landfilling is becoming increasingly difficult, expensive, and unattractive in view of potential liability for landfill cleanup and closure. Codisposal with municipal sewage is possible but requires a nearby facility with the capacity and willingness to accept the WTS. Land treatment of water plant wastes, which includes spreading on agricultural lands and strip-mined areas, and disposal in monofills—landfills that accept only WTS—is becoming increasingly attractive.

Sources for potable water supplies should represent the purest water available at reasonable cost. This generally means that toxic organics and pathogens are not concentrated in raw waters and therefore not important constituents of water treatment residuals. Toxic metals, however, are common contaminants of raw

water and certain water treatment chemicals. As a result, WTS, like sewage sludges, invariably contain measurable quantities of heavy metals. Yet a review of the literature yields very limited data regarding the total concentrations of toxic metals in WTS, and no information on metal fractionation in these sludges.

Toxic metals can be mobilized in soils by biogeochemical processes, causing water pollution or contamination of food crops. The extent to which metals are solubilized depends on a variety of reactions involving the waste, soil, and specific metal of interest. The fate and interactions of metals in soil–food chain systems from land application of municipal sewage sludge have been extensively studied (e.g., Page et al., 1987; Chaney, 1988). However, the few published studies on metals in WTS provide compositional data for only one or two sludges (Schmitt and Hall, 1975; Elliott and Singer, 1988; Lin, 1988). There is a need for more comprehensive characterization of metals in WTS, because levels vary with the raw water quality and the nature and source of chemical additives.

Additionally, there are no data available regarding the chemical fractionation of metals in WTS. Evaluation of “total” metal levels following a strong acid digestion of the sludge may be useful as a gross index of contamination, but it provides little insight into potential mobility of the metals under field conditions (Gibson and Farmer, 1986). Less aggressive reagents (e.g., electrolyte or chelating agent solutions) have been used in an attempt to quantify the plant-available or readily mobile metal forms in soils (Pickering, 1986). Multistep sequential extraction schemes provide a more complete picture for predicting the heavy metal distribution, mobility, and bioavailability in sediments, sludges, and waste-amended soils. Such techniques partition metals into two to nine separate fractions, beginning with the least aggressive reagents to determine easily soluble metals and proceeding to total decomposition of the solid matrix.

The specific goal of this study was to evaluate the content and chemical fractionation of Cd, Cu, Cr, Ni, Pb, and Zn in WTS. These six metals are frequently monitored and regulated in waste land application systems. Eight coagulation sludges (three alum and five FeCl<sub>3</sub>) have been collected at different locations within Pennsylvania. A five-step chemical fractionation has been used to characterize the partitioning of heavy metals in the sludges. Implications for land treatment of drinking water sludges are discussed.

## MATERIALS AND METHODS

Coagulation sludges were collected from lagoons or sedimentation basins at eight water treatment plants. These facilities range in size from 15 to 570 L s<sup>-1</sup>, with an average of 150 L s<sup>-1</sup>. Solids production rates averaged 22 g of dry solids per m<sup>3</sup> of water treated (Dixon et al., 1988). Samples were oven-dried at 103 °C and ground prior to analysis. These treatment plants are all part of the Pennsylvania American Water Company and purchase treatment chemicals from common sources. Because sludge characteristics

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Table 1. Chemical extraction scheme for metal fractionation.

Fraction	Reagent conditions†	Shaking time, h
1. Exchangeable	16 mL 1 M MgCl <sub>2</sub> (pH 7.0)	1
2. Dilute acid-extractable	16 mL 1 M NaOAc adjusted to pH 5 with HOAc	5
3. Fe-Mn oxide bound	40 mL of 0.175 M (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> and 0.1 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	4
4. Organically bound	40 mL of 0.1 M Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	24
5. Residual	Dry (in oven) 0.1 g of material remaining after step 4. Add 4 mL HNO <sub>3</sub> , 1.0 mL HClO <sub>4</sub> , and 6.0 mL HF and heat at 140 °C for 3.5 h. Add 5.0 g boric acid and dilute to 100 mL volume.	

† These volumes are for 1.00 g oven-dried sludge. Extractions 1 through 4 were performed at room temperature for the stated times. Separation between steps was by decantation of the centrifugate after 20 min at 1500 rpm.

reflect properties of coagulants purchased at some prior time, analyses (Dixon et al., 1988) supplied by the parent company of treatment chemicals collected approximately 15 wk prior to sludge sampling were used in this study.

A five-step sequential fractionation scheme was used to partition the metals into exchangeable; dilute, acid-extractable; Fe-Mn oxide bound; organically bound; and residual fractions. The scheme (Table 1) was based on work by Tessier et al. (1979), Pickering (1986), and Gibson and Farmer (1986). Reagents were added to 1.0-g samples of oven-dried sludge, which were then agitated on a wrist-action shaker for the specified time, and then centrifuged at 1500 rpm for 20 min. The centrifugate was decanted into a plastic bottle and set aside for analysis. The next extracting solution was added and the extraction process repeated. After the first four extractions, 100 mg (dry wt.) of the remaining material was transferred to a Teflon decomposition bomb, and a hot triple-acid digestion was performed (Elliott and Shields, 1988). Total metal analyses were determined using this same digestion procedure on sludge samples not previously treated with any extracting reagents. Metal analysis was performed using flame atomic absorption spectroscopy (AAS). For the first four fractions, matrix effects were addressed by preparing AAS standards in solutions identical to the extracting solutions. For the residual fraction, interference of Fe in Ni analysis by AAS was minimized by adjusting the air/acetylene mixture.

## RESULTS AND DISCUSSION

The total concentrations of the six metals in water plant sludges and uncontaminated soils varied considerably (Table 2). For comparative purposes, the

Table 3. Total concentrations of metals in treatment chemicals.†

Metal	Liquid ferric chloride	Liquid alum	Cat-floc® polyelectrolyte	Powdered activated carbon
	mg L <sup>-1</sup>			
Cd	<0.5-79	<0.5-10	<0.5	<5.0
Cu	43-1132	<0.2-7	<0.2	<5.0
Cr	200-765	21-32	<0.5	<5.0
Ni	2.0-154	<5.0	<5.0	<50
Pb	<0.5-447	<0.5	<0.5	<5.0
Zn	93-10760	<0.5-3	<0.5	<5-8
No. of samples	8	6	1	1

† Data for treatment chemicals collected approximately 15 wk prior to sludge sampling (Dixon et al., 1988).

maximum levels permitted for wastes applied to agricultural cropland in Pennsylvania are included. Mean levels for both sludge types are well below maximum values. The Cd, Pb, and Cr, which are restricted because of potential animal toxicity, all have mean values less than 27% of the maximum. Except for Ni in the FeCl<sub>3</sub> sludges, similarly low values were found for Cu, Ni, and Zn, which are limited primarily because they are toxic to commercially important crops. These mean metal levels in WTS range from 10% (for Cd) to 35% (for Zn) of the typical mean values in municipal sewage sludges, which are routinely land applied.

The Cd content was comparable for the alum and FeCl<sub>3</sub> sludges, but the mean concentrations of Cr, Cu, Ni, Pb, and Zn were all higher in the FeCl<sub>3</sub> sludges. This suggests the composition of the added coagulant plays an important role in metal contamination of the resulting sludge. This is confirmed by the chemical analyses of the coagulants (Table 3). The ranges shown indicate that the FeCl<sub>3</sub> coagulant has substantially higher metal content than other treatment additives.

The FeCl<sub>3</sub> sludges were enriched in Ni and Cr, with mean levels being 3.1 and 5.4 times those in the alum sludges, respectively (Table 2). In fact, two FeCl<sub>3</sub> sludges were at or above the 200 mg kg<sup>-1</sup> maximum allowable Ni value. Elliott and Singer (1988) reported a FeCl<sub>3</sub> sludge to be high in Ni (307 mg kg<sup>-1</sup>). In contrast, alum sludges generally have Ni levels below 60 mg kg<sup>-1</sup> (Cornwell and Westerhoff, 1981; Lin, 1988). One reason for this difference is the quality of the FeCl<sub>3</sub> coagulant used by some water utilities. Some FeCl<sub>3</sub> is produced from reprocessing of pickle liquor, a by-product of steel manufacturing. Such coagulants

Table 2. Metals in water treatment sludges and uncontaminated soils (mg kg<sup>-1</sup> dry wt.)

Metal	Sludges				Soils		Maximum levels†
	Alum		FeCl <sub>3</sub>		Range‡	Typical§	
	Range	Mean†	Range	Mean†			
Cd	1-2	1.6	<0.1-2	<1	0.01-0.7	0.4	25
Cu	135-230	171	135-485	272	2-100	12	1000
Cr	40-64	50	62-513	269	1-1000	50	1000
Ni	26-65	44	33-218	136	5-5000	25	200
Pb	47-439	204	18-840	245	2-200	15	1000
Zn	195-815	527	215-865	575	10-300	40	2500

† Means given are for three alum or five FeCl<sub>3</sub> sludges.

‡ Data from Lindsay, 1979.

§ Data from Berrow and Reaves, 1984.

† Maximum contaminant levels allowed in Pennsylvania for sludges used in agricultural production.

are characteristically high in metals. Of the eight liquid  $\text{FeCl}_3$  samples analyzed for the data in Table 3, six were produced from raw materials and had Ni levels of  $<5 \text{ mg L}^{-1}$ , whereas the two produced from steel industry by-products averaged  $135 \text{ mg L}^{-1}$  Ni. The Ni content of WTS may be the parameter limiting the annual application rate or the useful life of a disposal site. It is likely that utilities will require treatment chemical suppliers to meet maximum contaminant levels as a condition of purchase (Dixon et al., 1988).

It is important to understand that metals in land-applied wastes contribute to the pool of metals that exist naturally. Table 2 shows the common range and typical background concentrations of metals in soils where no wastes have been applied. Note that the mean sludge metals levels are generally within an order of magnitude of typical soil levels.

It might be inferred from the low background soil levels of Cd that sludge addition will significantly impact its soil chemistry. Yet the values of Cd found in these sludges are substantially below the  $25 \text{ mg kg}^{-1}$  maximum concentration for land-applied wastes. Other researchers have similarly reported WTS Cd levels to be 1.9 (Lin, 1988), 1.3 (Elliott and Singer, 1988), and  $<1 \text{ mg kg}^{-1}$  (Schmitt and Hall, 1975), although Cornwell and Westerhoff (1981) reported an alum sludge to contain  $4 \text{ mg kg}^{-1}$  Cd. The significance of these Cd levels can be appreciated by noting that up to  $0.5 \text{ mg kg}^{-1}$  Cd is even permissible in livestock feed formulations (NRC, 1980). Moreover,  $20 \text{ Mg ha}^{-1}$  application of a water sludge containing  $2 \text{ mg kg}^{-1}$  Cd will increase the typical soil Cd level from 0.4 to 0.41, still well within the common range for native soils.

The distribution of the metals determined by chemical fractionation is shown in Table 4. Although sequential procedures vary in the number of fractions evaluated, it is conceptually convenient to consider two broad categories, distinguished by whether solid phase dissolution is required to release the metals. Metals displaceable without substrate dissolution are termed *nondetriral*, whereas solid phase dissolution is essential to solubilize *detriral* metals. Non detriral metals are those that are water soluble, exchangeable, or adsorbed onto solids phases and would correspond to the exchangeable and dilute acid-extractable fractions in Table 4. Exchangeable metals would likely represent those most readily mobilized in soil-water systems whereas low pH ( $<5$ ) would be required to release the dilute acid-extractable metals. The detriral fraction includes metals present as precipitated compounds (e.g., hydroxides, sulfides), fixed within the silicate matrix,

or bound to hydrous oxides through occlusion, chemisorption, or coprecipitation. Although caution is warranted in interpreting fractionation results, detriral metals are probably not significantly mobilized in the short-term under normal soil conditions. Researchers differ as to the lability of organically bound metals (Pickering, 1986), but because this fraction is evaluated after the oxide-bound metals in this scheme (Table 1), it will be considered as part of the detriral metals.

Two features of the data in Table 4 are obvious. A small percentage of the total metals in these sludges was in the easily mobile, exchangeable fraction. Except for Cd and Pb, 1% or less of the total metals were exchangeable. At the other extreme, 75% or more of the metals were found in the oxide-bound or residual form, Cd excepted. That the majority of the metals are tightly held by the sludge matrix likely reflects the nature of the coagulation process in water treatment. Normally the coagulant is dosed such that rapid formation of Al or Fe hydrous oxides occurs. These freshly precipitated hydrous oxides have a large capacity to occlude, coprecipitate, and sorb divalent metal ions from the surrounding aqueous media. The metals tend to be trapped or intermixed within the hydrous oxide solid phase as it forms. In relationship to the extraction scheme, these metals are probably retrieved in the oxide and residual fractions.

The coprecipitation and strong adsorption of heavy metals by amorphous Al and Fe hydrous oxides have been demonstrated in several studies. The ability of hydrous oxide surfaces to accumulate heavy metal cations despite an unfavorable surface charge (Forbes et al., 1974; Kinniburgh et al., 1976) indicates that specific adsorption mechanisms operate. On the basis of their strong sorption behavior, it is widely held that hydrous oxides play a major role in heavy metal immobilization by soils and aquatic sediments. Krauskopf (1956) concluded that Fe and Mn oxides are the major adsorbents governing soluble trace metal concentrations in seawater. Likewise, the percentage of free Fe oxides was felt to be one of the most useful parameters for estimating the migration of elements in soils (Korte et al., 1976).

Kinniburgh et al. (1976) studied the adsorption of heavy metals on freshly precipitated Fe and Al hydrous oxide gels, effectively the same materials formed in the coagulation treatment step. They found that heavy metal cations are strongly sorbed by Fe and Al gels even under slightly acid conditions, and at near neutral pH, adsorption approached 100%. The selectivity sequence for Fe gels was found to be  $\text{Pb} > \text{Cu} > \text{Zn} > \text{Ni} > \text{Cd}$ , whereas that for Al gels was  $\text{Cu} > \text{Pb} > \text{Zn} > \text{Ni} > \text{Cd}$  (Kinniburgh et al., 1976). The former sequence has been documented for mineral soils as well (Elliott et al., 1986) and corresponds closely with the pK for the first hydrolysis product of the particular metal (Forbes et al., 1974).

The fractionation data in Table 4 and the relative metal adsorption affinities observed for hydrous oxide gels both suggest relatively weak fixation of Cd by the sludge colloids. Note that there was no detectable Cd released with the oxide-bound fraction (Table 4). A substantial portion of Cd was organically bound. This

Table 4. Fractionation of the sludge metals (% of total metal in each fraction averaged for all sludges).

Metal	Fraction				
	Exchangeable	Acid soluble	Organically bound	Fe-Mn oxide bound	Residual
Cd	5.8	19	38	BD†	38
Cr	1.0	2.4	10	38	49
Cu	1.0	5.8	6.3	32	55
Ni	0.6	12	4.5	31.8	51
Pb	4.2	2.6	13	8.4	72
Zn	0.5	17	6	34	42

† Below detection.

preferential retention of Cd by organic matter has been previously documented for soils (Elliott et al., 1986). A small fraction of the Cd was found to be exchangeable whereas nearly one-fifth was retrieved by acid extraction.

The sum of these first two fractions (exchangeable plus dilute acid-extractable) has been used to reflect maximum availability of metals in contaminated soils (Gibson and Farmer, 1986). On the basis of relative amounts of each element released in the first two extraction steps (Table 4), Cd would have the greatest mobility in soil-water systems. This does not appear to be unique to WTS, as Sauerbeck and Rietz (1983), using 25 different extracting solutions on contaminated soils, found Cd consistently more labile than Zn or Pb. Gibson and Farmer (1986) also concluded that Cd was the metal most easily released from contaminated urban soils.

Insights into potential impacts on groundwater can be gained by extrapolating this data to field conditions. A sludge application rate of 20 Mg ha<sup>-1</sup> might be made to a field with a net infiltration of 50 cm yr<sup>-1</sup>. Assuming the sludge Cd content is 1.6 mg kg<sup>-1</sup> (Table 2) and 25% of this Cd can be brought readily into solution within the first year (Table 4), the Cd concentration in the leachate would be 1.6 µg L<sup>-1</sup>. This level is below the Cd drinking water standard of 10 µg L<sup>-1</sup>. This assumes acid soil conditions and that the metals leached from the sludge will not be attenuated to any extent in the soil profile before reaching groundwater. Readsorption of sludge metals by soil colloids will further delay their migration and reduce the impact on groundwater supplies.

### CONCLUSIONS

As surface spreading and subsurface burial continue to represent attractive WTS disposal options, questions regarding potential impacts of sludge-borne metals may be raised. Little information has been published on the concentration and environmental reactivity of WTS metals in relationship to soil-plant environments. The mean total levels of Cd, Cu, Cr, Ni, Pb, and Zn in WTS are generally 10 to 35% of their corresponding values in sewage sludges, which are routinely land applied. Only two individual WTS had total Ni levels near the maximum recommended levels for waste materials to be land applied. The source of these high Ni levels appeared to be the FeCl<sub>3</sub> coagulant produced from steel industry waste pickle liquor. To meet state land application regulations, water utilities will likely specify maximum contaminant levels in treatment chemicals they purchase.

Total analyses were supplemented by a five-step fractionation procedure to identify the main metal retention modes within the sludge. Although lack of reagent selectivity dictates caution when interpreting such fractionation schemes, useful information was obtained for assessing potential metal mobility under field conditions. Because of strong adsorption and coprecipitation by freshly formed Al and Fe hydroxides in the coagulation treatment step, most heavy metals in WTS are predominantly bound in forms not readily released into solution. From 76 to 87% of the Cr, Cu,

Ni, Pb, and Zn were bound within an oxide or silicate matrix. For each of the six metals, less than 6% of the total concentration was in the exchangeable fraction, which is considered to represent the immediately available metal reservoir.

If soil conditions were allowed to become acidic (pH < 5), roughly 28% of the sludge Cd could become mobile. However, total Cd levels are so small that leaching or crop uptake should be minimal. With moderate sludge application rates (20 dry Mg ha<sup>-1</sup>) and properly managed soils (pH > 6.0), metal movement to groundwater or translocation into edible crop tissues should not be significant.

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