Solid Phase Forms of Heavy Metals in Sewage Sludge-Treated Soils[1]

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ABSTRACT

A sequential extraction procedure was used to fractionate Cd, Cu, Ni, and Zn in sludge-treated soils into the designated forms of exchangeable, adsorbed, organically bound, carbonate, and residual. Samples were obtained from a soil column study where anaerobically digested sewage sludge in either liquid or air-dried form was mixed into the top 15 cm of three reconstructed soil profiles and leached for 25 months with Colorado River water. The applied sewage sludge and uncontaminated soil samples were also sequentially extracted. The metals added into the soil had not moved out of the sludge-soil layers during the course of leaching. The chemical forms present in the sludge-soil layers at the termination of the leaching process were compared with those initially present in the soil and sludge. Most of each of the metals studied in the columns were found in the organically bound, carbonate, or residual forms, with the relative distribution among these forms depending on whether samples were taken in or below the sludge-soil layer. Less than 36% of each metal in the sewage sludge was in the residual form, while, except for Cd, the soils contained >65% of each metal studied in this form. It appeared that Cd, Ni, and Zn were all shifting to the residual form. The chemical forms of Cu had not changed significantly during the study. The occurrence of metals in the stable organically bound, carbonate, and residual forms in the sludge, coupled with a shift toward the more stable form (residual) after soil incorporation, contributed to the lack of metal movement in the soil profiles.

Additional Index Words: cadmium, copper, nickel, zinc, sequential extraction.

Heavy metals in the solid phase of soils or sewage sludge-treated soils occur in many chemical forms. These include normal exchange sites, specific adsorption sites, occluded or adsorbed-onto soil oxide materials, biological residues and living organisms, and substituted-into primary and secondary minerals. The chemical forms of heavy metals in soils can greatly influence their fate in terms of plant uptake or soil profile migration. Heavy metals in soils are usually expressed in terms of total concentrations, and the distributions among chemical forms remains unknown.

Precise separation of heavy metals in soils into all specific chemical forms is not possible with current analytical procedures. However, attempts have been made to partition solid phase metals into chemically similar forms through the use of sequential extractions with selective chemical reagents. McLaren and Crawford (1973) fractionated Cu in a number of soils into exchangeable, weakly bound to specific sites, organically bound, occluded by oxide material, and residual forms. It was assumed that residual Cu was bound in the clay lattice structure. They found that Cu seldom occurred in the exchangeable and weakly bound forms. Approximately half the Cu was in the residual form with the remainder divided between the organically bound and occluded forms. Silviera and Sommers (1977) used another sequential extraction procedure to determine exchangeable, available, and residual forms of heavy metals in different sewage sludges and in soil-sludge mixtures incubated for 28 days. They found that for the sludges, there was large variability in the percentages of metals in each fraction. This variability is an indication that the metals in different sludges may be in different chemical forms. For the soil-sludge mixtures, the distribution of metals in each fraction was also time-dependent. This indicates that there are probably interactions between some metals and soils with time. The relatively short period of incubation for the sludge-soil mixtures was probably not long enough for metals

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added into the soil to stablize into the final form of the metals. The final chemical equilibrium of heavy metals could be important in affecting plant uptake and migration.

The objective of this study was to determine the solid phase chemical forms of heavy metals in sludge-soil mixtures after they were subjected to long-term incubation and leaching by a sequential extraction procedure, and to assess the importance the chemical forms may have had on the magnitude of metal movement in the soil profiles.

MATERIALS AND METHODS

Sludge-soil mixture samples were taken from the sludge-soil layers of soil columns where anaerobically digested sewage sludge in either a liquid (wet) or air-dried (dry) form had been incorporated into the top 15 cm of the soil profiles, which were leached with approximately 5 m of water over a period of 25 months. Details on the complete experimental design are given by Emmerich (1980) and Emmerich et al. (1982). After leaching, the column profiles were sectioned. The sectioning consisted of dividing the sludge-soil layer into two equal increments; starting at the sludge-soil layer interface, the soil portions of the columns were sectioned into 5-cm increments. Saturation extracts (Richards, 1954) were prepared for each increment to remove the soluble metals and the samples for the sequential extraction were taken from the saturation extract cake. For simplicity in designating sample location, A and B will be used for the top and bottom halves of the sludge-soil layers, respectively, and 5, 10, and 15 for the first, second, and third 5-cm increment below the sludge-soil layer interface, respectively. The sequential extraction procedure used in this study is a modification of a procedure developed by Stover et al. (1976) for use on sewage sludges. The basis for the modification to Stover's procedure is discussed elsewhere (Emmerich, 1980). The sequential extraction consisted of placing triplicate, 2-g samples (oven-dried basis) of soil, sludge, or sludge-soil mixture into a polypropylene centrifuge tube and extracting sequentially according to the procedure outlined in Table 1. The samples were equilibrated on a reciprocating shaker, centrifuged, decanted, and filtered through Whatman no. 42 filter paper after each extraction. The supernatant liquids were analyzed by atomic absorption spectrophotometry (AAS, Perkin-Elmer model 5000) for Cd, Cu, Ni, and Zn using standards with the extractant to form the background matrix. All values given are averages of triplicate samples. A complete weight balance system was used to calculate the amounts of metals extracted by each extractant. The calculation included a correction for the carry over of metals from one extraction to the next and an assumption that the mass of soil or sludge or sludge-soil mixture remained constant. A more complete explanation of the sequential extraction procedure along with a computer program used to calculate the metal extracted in each form is given by Emmerich (1980).

RESULTS AND DISCUSSION

The use of chemical reagents to extract a specific form of a metal is not exact. It is probably more appropriate to say these extractants extract a chemically similar form with some overlap of other forms. A procedure of sequential extraction by specific reagents, though not exact, can result in useful qualitative to semiquantitative estimates of the chemical forms of heavy metals in the solid phase of soil, sludges, and sludge-treated soils. The designated chemical forms extracted by specific reagents given in Table 1 are not meant to imply specific forms of the metal, but to say that the metal forms are chemically similar and extractable with specific reagents. Therefore, throughout this discussion the designated chemical form extracted and the metal extracted with a specific reagent will be used

Table 1—Order of sequential extraction sequence and designated chemical form extracted.

Extractant	Concentration of extractant	Density	Equilibrating time on shaker	Designated chemical form extracted[†]
	M	g/ml	hours	
KNO_3	0.5	1.03	16	Exchangeable
X-H_2O[‡]	55.5	1.00	2	Adsorbed
NaOH	0.5	1.02	16	Organically bound
Na_2-EDTA	0.05	1.00	6	Carbonate
HNO_3 (70–80°C)	4.0	1.12	16§	Residual

[†] The terminology, "chemical form extracted," is not meant to imply that the metal is in only absorbed, carbonate, etc., form, but extractable with that reagent. The terminology is used to be consistent with the literature.
[‡] Ion exchange water, extracted three times.
§ Extracted in oven, not on shaker.

interchangeably to denote a chemically similar fraction of the metal.

The results of extracting air-dried sewage sludge by the modified procedure and the percentages of Cd, Cu, Ni, and Zn recovered in each form are given in Table 2. Nickel was the only metal that showed any appreciable percentage in the exchangeable form. There were almost no metals present in the adsorbed form in the sludge. All of the metals occurred in significant amounts in the organically bound form, with the majority of the Cu being in this form. The occurrences of metals in the carbonate form were quite substantial. Nearly half of the sludge Cd and Zn were in the carbonate form. The residual form also contained significant amounts of the metals, with Zn having the lowest percentage present in this form. The total percentage for the different forms of Cd was 110%. The >100% recovery in the different forms of Cd was believed to be due to the low total concentration of Cd in the sludge and when it was fractionated, any small error in the analysis caused a large error in the total percent recovered. The same situation also existed in the fractionation of the heavy metals in the soils (Table 3).

The percentages of each metal in the different forms in the sewage sludge were significant in that for each metal <36% were in the residual form. The residual form was considered the most stable form because it required the most drastic extracting reagent for its removal. With the large percentages of the metals in other than the most stable form, the possibility existed for the forms of the metals in the sludge to shift to more stable forms once incorporated into the soil.

The surface layer of soils used in this study were sequentially extracted and the percentages of each metal in each fraction are given in Table 3. Zinc was the only metal that occurred in detectable amounts in the ex-

Table 2—Metal recovered with each extractant from the sewage sludge used in the study.

Extractant	Cd	Cu	Ni	Zn
			%	
KNO_3	<0.1	<0.1	10.9	0.1
H_2O	<0.1	1.5	0.5	<0.1
NaOH	22.4	60.4	24.3	27.9
EDTA	51.6	23.2	31.9	57.5
HNO_3	35.6	16.0	26.4	9.8

Table 3—Metal recovered with each extractant from the surface layer (0–15 cm) of the soils used in the study.

Extractant	Cd	Cu	Ni	Zn
		%		
Holland soil†				
KNO₃	<0.1	<0.1	<0.1	0.1
H₂O	<0.1	<0.1	<0.1	<0.1
NaOH	<0.1	22.3	<0.1	<0.1
EDTA	73.0	3.9	3.4	1.2
HNO₃	16.5	73.3	79.8	93.9
Ramona soil‡				
KNO₃	<0.1	<0.1	<0.1	0.6
H₂O	<0.1	<0.1	<0.1	<0.1
NaOH	<0.1	32.7	<0.1	<0.1
EDTA	<0.1	7.0	3.9	5.3
HNO₃	<0.1	65.2	93.5	92.0
Helendale soil§				
KNO₃	<0.1	<0.1	<0.1	0.1
H₂O	<0.1	<0.1	<0.1	<0.1
NaOH	<0.1	12.7	<0.1	<0.1
EDTA	<0.1	5.4	8.1	2.1
HNO₃	<0.1	82.4	87.1	96.1

† Holland sandy loam: fine-loamy, mixed, mesic Ultic Haploxeralf.
‡ Ramona sandy loam: coarse-loamy, mixed, thermic Typic Haploxeralf.
§ Helendale loamy sand: coarse-loamy, mixed, thermic Typic Haplargid.

changeable form. No metals were present in the adsorbed form. Copper was the only metal that existed in the organically bound form. Except for the Holland soil, which had 73% of its Cd in the carbonate form, metal carbonate forms accounted for <10% of the heavy metals in the soils. For all the metals except Cd, >65% of the total was in the residual form in the soils. The Ramona and Helendale soils had an undetectable amount of total Cd in the soil, hence <0.1% in each of the forms. The important observation to be made from the percentages of metals in each form in the soils is the high percentage of each metal that was in the residual form. This obsevation indicates that the metals were present in the soils in a relatively stable form.

A comparison of the sludge and soil percentages for the organically bound metals indicates that Cu has a high affinity for organic matter; this was also confirmed by McLaren and Crawford (1973). Obviously, in the sludge there is ample organic matter for complexing the Cu, and this results in a large percentage of Cu being organically bound in the sludge (Table 2). Even in the soils where the percentage of organic matter was low, a significant percentage of the total soil Cu was organically bound, whereas the other metals were not (Table 3).

The percentages of the metals in the sludge-soil layer and below occurring in each form are given in Table 4 for the Holland wet column. The percentages in the other columns were similar to the Holland column. The percentages of metals in the exchangeable and adsorbed forms were very low in all the columns, with none being higher than 3%. The largest percentage of each of the metals in the columns was distributed among the organically bound, carbonate, or residual forms depending on whether they were in or below the sludge-soil layer. In the sludge-soil layers most of the Cu was in the organically bound form, and below the layers in the residual form. Most of the Cd and Zn in the sludge-soil layers was in the carbonate form. Below the sludge-soil

Table 4—Trace metals recovered with each extractant for samples from the Holland wet column.

Sample†	KNO₃	H₂O	NaOH	EDTA	HNO₃
			Extractant		
			%		
Cd					
A	<0.1	<0.1	0.7	46.1	42.0
B	<0.1	<0.1	1.3	51.3	30.2
Sludge-soil interface					
5	<0.1	<0.1	<0.1	62.1	30.7
10	<0.1	<0.1	<0.1	51.8	27.6
15	<0.1	<0.1	<0.1	65.9	17.2
Cu					
A	0.2	1.2	54.2	24.7	22.1
B	0.2	1.4	49.5	22.0	24.9
Sludge-soil interface					
5	<0.1	0.7	19.9	5.7	78.8
10	<0.1	0.5	20.8	5.7	77.3
15	<0.1	0.4	23.4	3.9	80.8
Ni					
A	<0.1	0.5	11.6	17.7	64.4
B	<0.1	0.6	14.1	23.9	57.0
Sludge-soil interface					
5	<0.1	<0.1	<0.1	3.9	84.9
10	<0.1	<0.1	<0.1	5.1	84.4
15	<0.1	<0.1	<0.1	5.7	93.1
Zn					
A	0.2	0.7	18.5	45.7	36.0
B	0.3	0.9	20.2	48.5	33.5
Sludge-soil interface					
5	<0.1	<0.1	<0.1	0.7	87.3
10	<0.1	<0.1	<0.1	0.7	87.1
15	<0.1	<0.1	<0.1	0.9	90.3

† A and B = top and bottom halves of the sludge-soil layers, respectively, and 5, 10, and 15 = first, second, and third 5-cm increment below the sludge-soil layer interface, respectively.

layers most of the Zn was in the residual form. Throughout the columns the dominant form of Ni was the residual form, and for Cd the carbonate form was dominant.

The sewage sludge applied to the soils seemed to be controlling the chemical forms of the metals that occurred in the sludge-soil layers in all three soils. The percentage of any metal in a certain chemical form in the sludge-soil layers was essentially independent of soil type and for all soils did not differ by >10%. The almost constant percentage of a metal indicated that soil properties did not influence the chemical forms of the metals in the sludge-soil layers. The physical condition of the applied sludge (i.e., wet or dry) also did not affect the chemical forms of metals present at the termination of leaching.

Analyses of soils below the sludge-soil interface indicated that the metals applied in the sewage sludge had not moved below this interface (Emmerich et al., 1982). Therefore, as expected, the percentages of the chemical forms of the metals extracted in the soil below the sludge-soil interfaces and the original soils are similar (Tables 3 and 4). This was further evidence that the metals in the soils were in stable forms and the leaching of the soils had not removed or changed the forms of the metals appreciably.

Table 5—Calculated and observed percent metals recovered with each extractant in columns where sludge was added in wet form.

Extractant	Cd		Cu		Ni		Zn	
	Calculated†	Observed‡	Calculated	Observed	Calculated	Observed	Calculated	Observed
				%				
				Holland§				
NaOH	22	1	58	52	21	13	24	19
EDTA	52	49	21	23	28	20	50	47
HNO₃	35	36	22	24	35	61	21	35
				Ramona				
NaOH	22	1	59	50	21	10	26	21
EDTA	52	53	22	29	29	23	54	49
HNO₃	36	38	19	21	35	69	15	30
				Helendale				
NaOH	22	1	57	50	21	9	26	28
EDTA	52	54	22	30	29	25	55	41
HNO₃	36	40	20	19	34	63	14	28

† Calculation based on amounts of metals extracted from soil and sludge separately, prior to leaching.
‡ Average of A and B increments (sludge-soil layer).
§ See Table 3 footnotes for identification of soils.

Mass-balance calculations of the sludge-soil layers indicated that metals added in the sewage sludge had remained in that layer (Emmerich et al., 1982). Because the metals remained in the sludge-soil layer, the percentages of metals in each chemical form could be calculated from the soil and the sludge by assuming that: (i) the metals added in the sewage sludge were extracted as if they were in sludge alone, (ii) the metals in the soils were extracted as if they were in the soil alone, and (iii) the metals in the sludge and the soil did not change forms during the study. The results for the wet columns are given in Table 5. The percentages actually recovered in each form are also given in Table 5 for comparison; exchangeable and adsorbed forms were not included because of their low percentages in the sludge and soils.

The large amounts of metals added to the sludge-soil layer with the sludge, as compared with the native soil metals initially present, dominated the calculated percentages of the forms in the sludge-soil layers. As previously stated, the percentages of metals in the sludge-soil layers were not dependent on the soils or the physical form (i.e., wet or dry) of the added sludge. Hence, any deviation from the calculated percentages would not be due to differences in soils or form of sludge, but to changes in the forms of the metals during the study.

A qualitative measure of the change in chemical forms of the metals can be made by comparing the calculated and observed percentages in Table 5. An indication of a change in the form of a metal would be a sizeable difference between the calculated and observed percentages. Possible changes in the forms of Cd were obscured by the 110% recovery of Cd in the sludge and its effect on the calculated percentages of the metals. There was an indication that Cd had shifted away from the organically bound form, but there was no subsequent increase in another form. Some of the forms of Cd may have been over- or underestimated in the original extraction of the sludge, and partially account for the 110%. Copper generally did not show any change in forms, with the added metal remaining in the organically bound form. The Ni percentages indicated that there were substantial changes in forms. The changes were from the organically bound and carbonate forms to the

residual form, with some of the metals coming from the exchangeable form in the sludge. The Zn also showed a similar type of change with increases of Zn in the residual form. The same general trends in shifts in chemical forms of the metals were observed for the dry columns.

Because most of the metals were in stable organically bound, carbonate, and residual forms in the sludge and shifted toward the most stable form, residual, when added to the soil, the reason for the lack of detectable movement of the metals out of the sludge-soil layers became obvious. The more stable the solid phase form of a heavy metal the less likely it will dissociate into the solution phase and become available for movement with the soil solution. The possibility that the metals would continue to slowly shift toward the residual form with time should not be an unreasonable expectation, as the dominant form (Table 3) in the soils was, except for Cd, the residual form.

ACKNOWLEDGMENTS

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