

## Movement of Heavy Metals in Sewage Sludge-Treated Soils<sup>1</sup>

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### ABSTRACT

A controlled column study was conducted to evaluate the potential for Cd, Cu, Ni, and Zn movement through three reconstructed soil profiles from surface applied sewage sludge. Anaerobically digested sewage sludge was mixed into the top 15 cm in either liquid or air-dried form three times for a total rate of 476 metric tons/ha. The soil columns were leached with 5 m of Colorado River water over a 25-month period. After leaching, columns were sectioned and analyzed for metal movement by a complete metal mass balance. Analysis of the soils below the sludge-soil layers indicated that essentially no metals moved below the depth of incorporation. The mass balance calculation for the metals in the sludge-soil layers confirmed that movement had not occurred, in that close to 100% of the added metals were recovered in the sludge-soil layers. Although no metal movement was observed, a situation conducive to metal movement was noted. Greatly lowered pH of the soil profiles beneath the sludge-soil layers was attributed to the mineralization and nitrification of the added organic N. A subsequent pH reduction in the sludge-soil layer could increase the solubilization of the metals and induce movement in the soil profiles, but this was not observed within the time frame of this study.

*Additional Index Words:* cadmium, copper, nickel, zinc, soil columns, waste disposal.

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One of the constraints often associated with land application of sewage sludges is that they contain varying amounts of heavy metals (Sommers, 1977; Page, 1974). Once heavy metals are introduced into crop lands, they can be taken up by plants and subsequently become incorporated into the food chain. If heavy metals leach through the soil, they may also contaminate ground water. In recent years, the plant uptake of heavy metals has received a great deal of attention due to its potential health effects on humans. Research in the area of possible contamination of ground water by heavy metals from land application of sewage sludge has not been extensive.

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The potential for heavy metals to leach out of a sewage sludge was clearly demonstrated when Lagerwerff et al. (1976) extracted a sludge from Baltimore with tap water and observed removal of 11, 2, and 36% of the Cd, Cu, and Zn, respectively, from the sludge. They also subjected the sludge to an artificial oxidation treatment with various concentrations of H<sub>2</sub>O<sub>2</sub> and found that with increasing oxidation the metals became more water-extractable. When sewage sludge is incorporated into soil, it is subjected to oxidation by microorganisms and could possibly release heavy metals to the soil solution for movement.

At disposal sites (drying beds and lagoons) where large quantities of sewage sludges have been deposited the potential for movement of metals into the soil is greatest. Lund et al. (1976) found enrichment of Cr, Cu, and Zn to a depth of 2 m underneath a sewage sludge drying bed that had been in use for more than 20 years. Elevated soil Ni and Cd contents were detected to a depth of 3.5 m. Kirkham (1975) has also observed movement of Cd, Cu, Ni, and Zn to 61 cm in soil below a sludge-holding lagoon that had been used for 3 years.

Agricultural lands have and will probably continue to receive sewage sludges. Hinesly et al. (1972) reported the movement of Cd, Cr, Cu, Ni, and Zn to a depth of 30-45 cm in an agricultural soil after application of 136 metric tons/acre total of sludge over a 4-year period. Boswell (1975) reported Zn movement to a depth of 30 cm and Cd, Cr, and Cu to 15 cm after the application of 168 metric tons/ha during a 2 year study. Sidle and Kardos (1977) added 27 metric tons/ha of sewage sludge to a forest soil and after 17 months observed that 6.6, 0.3, and 3.2% of the applied Cd, Cu, and Zn, respectively, had moved below 120 cm in the soil profile.

In these agricultural situations where sewage sludges have been applied to soils and movement of metals measured, pH of the soils could have been a factor (Boswell, 1975; Hinesly et al., 1972). Boswell applied a sewage sludge that had a pH of 5.6 to a soil that had been limed to a pH of 6.2. Hinesly et al. (1972) started with a soil pH of 5.6, which at the end of 2 years had dropped to 4.9. These lowered pH's could have increased the solubility of the metals and contributed to the movement.

The studies discussed above all reported metal movement below the sludge-amended soil layer, but they were not designed to determine the sludge or soil characteris-

Table 1—Ranges of selected properties for the increments of the Holland, Ramona, and Helendale profiles used in the study.

Profile	pH (1:1)	CEC meq/100 g	Organic C %	Trace metals			
				Cd	Cu	Ni	Zn
				µg/g			
Holland	6.4-5.8	8.8-6.1	1.24-0.35	0.24-0.21	36.1-33.3	21.3-19.8	142-136
Ramona	6.7-5.2	9.7-4.4	0.43-0.16	<0.1	17.6-16.3	14.5-13.2	54.3-51.3
Helendale	8.0-7.4	15.5-5.4	0.25-0.05	<0.1	20.7-16.5	17.2-12.7	57.2-44.4

tics that were important in determining the amount of movement. Therefore, this study was conducted to measure the depth and amount of movement of Cd, Cu, Ni, and Zn out of a surface sludge-soil layer and through three soil profiles of varying characteristics under controlled conditions of a column study.

### MATERIALS AND METHODS

Six soil columns (120 cm) made from PVC pipe (10 cm i.d.) were constructed and maintained in a greenhouse where the air temperature was controlled between 25 and 30°C. A porous ceramic plate was mounted in the bottom of each column and connected to a 1/3-bar vacuum to extract the leachate from the columns. Nine mercury-manometer-type tensiometers were installed in the side of each column at a depth of 10 cm below the soil surface and 10 cm thereafter down the column to measure soil matric potential and to determine the direction of water movement in the column.

Soil profiles representing three taxonomic families were sampled in 10-cm increments to a depth of 1 m. Clods were also collected from each increment for bulk density determinations (Blake, 1965). The three profiles were classified as: Holland sandy loam—fine-loamy, mixed, mesic Ultic Haploxeralf; Ramona sandy loam—coarse-loamy, mixed, thermic Typic Haploxeralf; and Helendale loamy sand—coarse-loamy, mixed, thermic Typic Haplargid. The soil profile increments were air-dried and crushed to pass a 2-mm sieve. Duplicate columns were incrementally packed for each soil series to approximate the field bulk densities of each increment with ranges of 1.3-1.4, 1.6-1.7, and 1.6-1.7 g/cm<sup>3</sup> for the Holland, Ramona, and Helendale soils, respectively. The surface 10-cm increment, as collected in the field, was packed into the columns to a thickness of 15 cm for an overall column profile depth of 105 cm. The initial soil samples were extracted by 4.0M HNO<sub>3</sub> digestion (Lund et al., 1976) and analyzed for Cd, Cu, Ni, and Zn by using a Perken-Elmer model 5000 atomic absorption spectrophotometer (AAS). Heavy metal concentrations in the 10-cm increments of the soil profiles were uniform with depth (Table 1). Ranges of other selected properties for the increments of the soil profiles are also given in Table 1.

Anaerobically digested sewage sludge was collected from the Joint Wastewater Pollution Control Plant of County Sanitation Districts of Los Angeles County at three different times and mixed into the top 15 cm of the soil profiles in either liquid (wet; i.e., 8% total solids) or air-dried (dry) form. The mixing was accomplished with a rod and was repeated before each irrigation. The sludge was applied after initial wetting of the columns and after 4 and 8 months for a total of three applications and a total rate of 476 metric tons/ha (air-dried basis). The ranges of concentrations of Cd, Cu, Ni, Zn, and N were 64-69, 1,141-1,375, 425-519, 4,080-4,258 and 22,000-23,300 µg/g (air-dried basis), respectively, for the three sludge applications. On a kg/ha basis a total of 32, 608, 236, 1,984, and 10,780 kg/ha for Cd, Cu, Ni, Zn, and N, respectively, were added to each column.

The columns were drip-irrigated with Colorado River water from intravenous feeding bottles to prevent ponding or saturation at the surface. The Colorado River water had a pH of 8.2 and TDS between 700 and 800 µg/ml; the chemical analysis is given by Emmerich (1980). Irrigation consisted of 500-1,000 ml every 10-18 days depending on the readings of the tensiometers installed in the columns. The irrigations continued for 25 months. Over the duration of the study between 4.8 and 5.1 m of water was applied to the columns. The leaching fractions varied from 0.5 to 0.7 and between 6 and 10 pore volumes of water were leached from the columns. The leachates were analyzed for

Cd, Cu, Ni, Zn, and NO<sub>3</sub>-N, the metals by AAS, and NO<sub>3</sub>-N colorimetrically using a Technicon AutoAnalyzer II.

After 25 months, the columns were dismantled, sectioned, and sampled to facilitate complete analysis. Starting at the sludge-soil interface and moving down the columns, 5-g samples were taken across the column every centimeter for 10 cm and thereafter every 5 cm. The sludge-soil layer (top 15 cm) of each column was sectioned into two equal increments and below the sludge-soil interface the columns were sectioned into 5-cm increments. From each half of thoroughly mixed sludge-soil increments five samples were taken, and one sample was taken from each 5-cm increment. All the samples were analyzed for metals by methods described previously and a complete mass balance calculation performed. The remaining soil or sludge-soil mixture from each increment was used to make a saturation extract (Richards, 1954) with the appropriate weights being recorded so the concentrations of the constituents could be calculated on a soil-solution basis. The saturation extracts were analyzed for metals and pH.

### RESULTS AND DISCUSSION

The concentrations of Cd, Cu, Ni, and Zn for the 10-cm increment below the sludge-soil interface before leaching the Ramona columns, and the concentrations of the metals from each centimeter for 10 cm after leaching the columns, are given in Table 2. The concentrations of the metals below the sludge-soil interface in the Ramona columns after leaching indicated that very little, if any of the metals had moved out of the sludge-soil layers. Data for the other soils indicated that even less metal movement took place and was limited to 2 or 3 cm. This could possibly have been caused by mixing of the sludge-soil layers and/or the difficulty in sampling in 1-cm increments. Analyses of samples further down the columns showed no increase in metal concentrations.

The results of this study seem to deviate from studies in the published literature in which movement of metals were shown, even though the magnitude may have been

Table 2—Metal concentrations below the sludge-soil interface before and after leaching the Ramona columns that had additions of wet or dry sludge.

Depth cm	Cd		Cu		Ni		Zn	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
	µg/g							
1	<0.1	<0.1	15.3	24.9	14.6	22.0	52.9	62.7
2	<0.1	<0.1	16.2	19.9	14.8	20.7	51.7	58.0
3	<0.1	<0.1	17.5	17.2	16.1	16.8	53.8	53.3
4	<0.1	<0.1	17.1	17.0	15.2	17.2	52.7	55.3
5	<0.1	<0.1	17.8	17.5	15.5	17.1	54.7	55.5
6	<0.1	<0.1	17.5	17.5	15.0	16.1	52.5	54.6
7	<0.1	<0.1	16.9	16.6	14.3	13.9	50.6	53.0
8	<0.1	<0.1	16.9	17.4	13.4	13.8	50.6	53.4
9	<0.1	<0.1	15.8	16.3	14.3	12.9	48.6	48.7
10	<0.1	<0.1	16.8	18.2	14.3	14.7	50.6	53.6
Soil†	<0.1		16.9		13.8		52.7	

† Concentration of metals in above layer before leaching.

small (Lund et al., 1976; Kirkham, 1975; Hinesly et al., 1972). Factors that may explain the absence of movement in this case could be the sludge-soil layer pH, the quantity of irrigation water applied, or the time involved for movement to take place.

Korte et al. (1976) has shown that pH is a factor in controlling the movement of heavy metals in soils under anaerobic conditions. The greatest reported depths of metal movement in soils has taken place over long periods of time (i.e., >20 years) at sludge disposal sites (Lund et al., 1976; Kirkham, 1975). Neither Lund nor Kirkham reported pH values of the soils at the depths they sampled, therefore, the possible effect pH could have had on the movement is unknown. In their studies, the soils were generally coarse-textured. Given the long periods of time, high hydraulic loadings, and soils that have large pores, the movement observed could have involved several commonly observed physical phenomena. Physical mechanisms of heavy metal movement could include colloidal precipitates and clay particles moving with the soil solution carrying the metals, or sludge moving through cracks in the soil created by repeated wetting and drying cycles. In the finer-textured soils used in this study, physical movement was less likely due to smaller pore sizes, destruction of soil structure and soil macropores because of reconstruction of the soil profiles, and repeated mixing of the sludge-soil layers to prevent cracks. The time factor and hydraulic loading were also much smaller in this study than those reported in the field studies.

An alkaline pH would induce a low solubility of heavy metals and probably played a role in the retention of the metals in the sludge-soil layers (Hem, 1972). The pH values in the sludge-soil layers in this study exceeded 6.7 in all columns at the termination of the experiment (Table 3). Sludge added into the sludge-soil layers seemed to have a buffering effect, regardless of the soil's original pH. The pH values for this layer were all within the range of 6.7-7.4 at the end of the experiment. For this pH range, low solubility of the metals in the sludge-soil layers would be expected and thus contributed to a lack of metal movement (Hem, 1972). In some of the columns there was a large pH change across the sludge-soil interface. Starting at the sludge-soil

Table 3—Saturation extract pH values for the Holland, Ramona, and Helendale columns after leaching, and for soil without leaching. "Wet" and "dry" designate form of applied sludge.

Depth cm	Holland			Ramona			Helendale		
	Wet	Dry	Soil	Wet	Dry	Soil	Wet	Dry	Soil
0-7.5	7.1	7.2	6.6	7.2	6.9	5.1	7.1	7.0	7.7
7.5-15	6.7	7.3		7.4	7.2		7.2	7.0	
	Sludge-soil interface								
15-20	6.7	5.7	5.6	6.8	6.4	5.5	6.4	6.8	7.5
20-25	6.6	4.8		6.0	5.3		6.3	5.7	
25-30	4.9	4.4	5.5	5.0	4.7	5.9	6.2	5.2	7.3
30-35	4.8	4.4		4.8	4.6		6.3	5.0	
35-40	4.7	4.3		4.7	4.5		6.4	4.7	7.2
40-45	4.7	4.2	5.6	4.6	4.4	6.3	6.5	4.9	
45-50	4.7	4.3		4.6	4.4	6.6	6.5	4.9	7.2
50-55	4.6	4.2	5.6	4.6	4.4		6.5	4.8	
55-60	4.6	4.3	5.8	4.6	4.4	6.7	6.6	4.8	7.2
60-65	4.6	4.2		4.6	4.4		6.5	4.7	
65-70	4.6	4.2		4.6	4.4	6.6	6.5	4.8	7.2
70-75	4.4	4.2	5.7	4.6	4.4		6.3	4.7	
75-80	4.4	4.2		4.6	4.4	6.5	6.2	4.9	7.1
80-85	4.4	4.2	5.8	4.6	4.4		5.8	4.8	
85-90	4.4	4.2		4.7	4.4	6.5	5.0	4.8	7.1
90-95	4.4	4.2	5.8	4.7	4.4		4.8	4.7	
95-100	4.4	4.1	5.8	4.7	4.4	6.5	4.7	4.8	7.2
100-105	4.4	4.2		4.6	4.4		4.5	4.8	

interface, the pH of all soils decreased with depth and in general the dry columns had larger decreases than the wet columns. This decrease in pH was possibly due to mineralization and nitrification of sludge-added N. The sludge contained about 2.3% total N that through mineralization and nitrification processes produced H<sup>+</sup> ions, which could account for the decrease in soil pH. In leachates from the columns, the NO<sub>3</sub>-N concentrations were up to 450 ppm (Fig. 1) after sludge applications, indicating that significant mineralization of N was occurring. Iskandar (1978) observed a decrease in soil pH with high application of waste water and attributed the decrease to nitrification with subsequent movement of applied metals to a depth of 15-30 cm. Therefore, the possibility exists that the metals in the sludge-soil layer that did not move over the duration of this experiment could have become more mobile with increasing time.

Water quality criteria for drinking water for Cd, Cu, and Zn are 0.01, 1.0, and 5.0 ppm, respectively

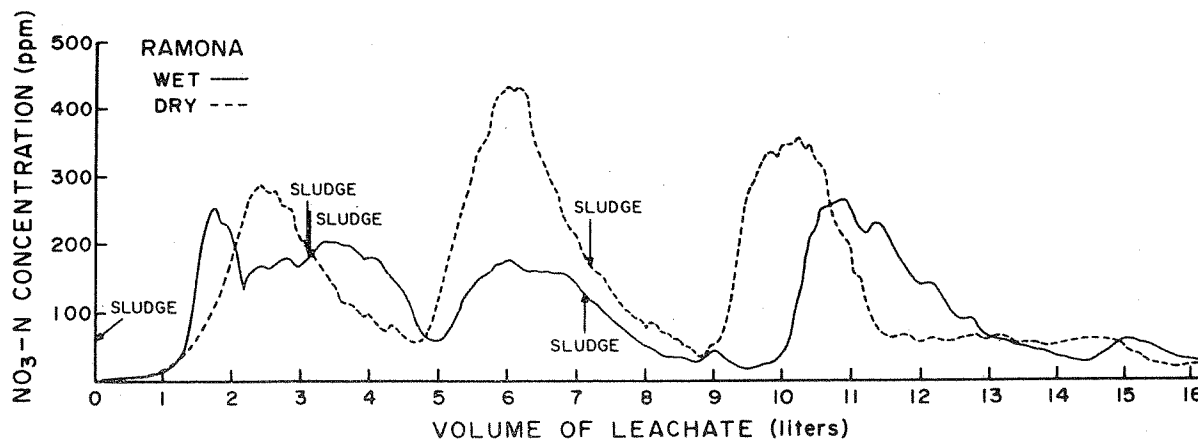


Fig. 1—Concentration of NO<sub>3</sub>-N in the leachate of the Ramona columns starting at the first sludge application and showing second and third sludge applications.

Table 4—Recovery of metals in the sludge-soil layer of the Ramona columns.

Column	Cd	Cu	Ni	Zn
	Wet			
Initial + added (mg)	25.5	512.1	211.0	1,641.2
Recovered (mg)	24.7	479.1	197.8	1,626.6
Difference (mg)	0.8	33.0	13.2	14.6
Recovered (%)	97	94	94	99
	Dry			
Initial + added (mg)	25.5	512.1	211.0	1,641.2
Recovered (mg)	22.7	444.7	184.3	1,528.6
Difference (mg)	2.8	67.4	26.7	112.6
Recovered (%)	89	87	87	93

(USEPA, 1976). There is no drinking water criteria for Ni at this time. The concentrations of all these metals in the column leachates were always well below the drinking water standards. Cadmium concentrations were below the detection limit for our study (5 ppb) in all of the leachate samples, and the highest concentrations of Cu, Ni, and Zn in any of the leachate was 0.04 ppm. From a drinking water quality standpoint, the soils were able to retain the metals investigated and would have prevented the possible contamination of ground water at least for the duration of the experiment.

Analyses of the soils below the sludge-soil interfaces and the leachates of the columns demonstrated that metal movement in the soils had, essentially, not taken place. If metal movement did not occur, all of the metals added in the sewage sludge should be recoverable in the sludge-soil layer. The total amounts of metal present in the sludge-soil layers (ie., sludge + soil metal) and the amounts recovered from the sludge-soil layers are given in Table 4 for the Ramona columns. Recovery of metals from the sludge layer of the wet-sludge column was essentially complete. The recovery from the dry-sludge column was somewhat less consistent. The increased concentrations of Cu, Ni, and Zn for a few centimeters below the interface in the Ramona dry column (Table 2) could account for only a small percent of the recovered metals in the sludge-soil layer. The percentages of metals recovered in most of the other columns were closer to 100% than in the Ramona dry column, further evidence that metal movement did not occur.

The unaccounted-for metals (differences in Table 4) in the sludge-soil layer could be explained in at least two ways. First, there were problems with sampling the sludge-soil layer, and second, the metals had moved out of the sludge-soil layer. Both halves of the sludge-soil layers were thoroughly mixed before samples were taken, and after air-drying each sample was crushed and mixed. These precautions did not insure a homogeneous sample for analysis in every case (Table 5). The variability was probably due to the heterogeneous nature of the sludge-soil mixture. The five replicated samples from each increment helped reduce the variability in determining the total amount of metals in the sludge-soil layers. However, the remaining variability could easily account for the deviation from a complete recovery.

The second possible explanation for incomplete recovery of the metals is that they leached from the sludge-soil layer. This is unlikely in light of the analyses

Table 5—Variability of the samples used to determine total metal in the sludge-soil layer of the Ramona columns.

Sample	Cd	Cu	Ni	Zn
	μg/g			
	Wet			
Top half	17.6	329	138	1,195
	17.8	358	134	1,161
	18.5	344	144	1,200
	19.2	378	146	1,236
	18.5	358	141	1,187
Mean	18.3	353	140	1,196
S.D.	0.6	18	5	27
Bottom half	13.2	255	103	836
	13.4	259	108	947
	13.0	255	102	825
	15.1	284	120	973
	16.8	324	131	1,097
Mean	14.3	275	113	936
S.D.	1.6	30	12	112
	Dry			
Top half	18.1	344	139	1,197
	18.8	357	147	1,230
	19.1	390	140	1,262
	18.9	388	141	1,252
	18.4	356	141	1,220
Mean	18.7	367	141	1,232
S.D.	0.4	21	3	26
Bottom half	13.1	254	109	890
	13.7	265	114	929
	14.5	282	118	975
	14.4	279	117	982
	13.7	267	112	946
Mean	13.9	269	114	944
S.D.	0.6	11	4	37

of the soils below the sludge-soil interface and the column leachates. Making the assumption that the metals had moved out of the sludge-soil layer and were distributed equally throughout the column and using the Ramona dry column as an example, the concentrations of Cd, Cu, Ni, and Zn would be 0.23, 5.66, 2.23, and 9.45 μg/g, respectively, above the indigenous concentrations of the metals. These increases in the metal concentrations could have easily be detected above the variability in samples. Since these increases were not found, the unaccounted-for metals must not have been in the columns below the sludge-soil interfaces. If the metals had moved out of the Ramona dry column in the leachate, the minimum concentration for Cd, Cu, Ni, and Zn would have been 0.12, 2.29, 1.15, and 4.87 μg/ml, respectively. These concentrations again could have been easily detected in the leachates, but were not. Therefore, the unaccounted-for metals must still have been in the sludge-soil layer, and the inability to account for 100% of the initial plus added metals in each column must have been due to the sampling error.

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