

Evidence for Movement of Heavy Metals in a Soil Irrigated with Untreated Wastewater¹

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ABSTRACT

A Vertisol irrigated for over five decades with an untreated municipal wastewater had elevated levels of DTPA extractable Cd, Co, Cu, Mn, Ni, and Zn in the cultivated layer of the soil as compared to lower layers. Total Co, Ni, and Zn were uniformly distributed in the 150-cm depth of the soil profile, total Cu increased with depth and total Cd, Cr, and Mn had higher concentrations in the cultivated layer than in some deeper layers. Assuming that the added metals had accumulated in the cultivated layer of the soil and assuming uniform distributions of metals in the soil profile at the start of irrigation with wastewater, the amounts of metals added would have produced increased concentrations in the cultivated layer. These expected differences were not found, except for Mn. These results suggest that the metals Cd, Co, Cr, Cu, Ni, and Zn may have migrated downward from the cultivated layer and are now distributed throughout the soil profile or leached below the depth of sampling.

Additional Index Words: cadmium, cobalt, chromium, copper, manganese, nickel, zinc.

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The application of wastewaters to croplands has been practiced for centuries (Iskander, 1978) and the accumulation of heavy metals in soils treated with raw municipal wastewaters, or the sludges separated from these waters, is now widely recognized (McKim, 1978; Rohde, 1962; Page, 1974; Johnson et al., 1974; Mattigod and Page, 1983; Chang et al., 1984). But the movement of heavy metals in soils has been considered to be so slow as to be practically nonexistent. Recent reports, however, have shown that heavy metals do move (Mattigod et al., 1984; Kirkham, 1975; Reddy and Dunn, 1984; Dowdy et al., 1984), suggesting that substantial amounts might flow into subsoils or beyond the root zone over a period of decades with constant input of metal-containing wastewaters.

The objective of this paper is to present data for heavy metals in a soil located in an arid area that had been irrigated exclusively with untreated municipal sewage for over 50 yr along with indirect evidence of the downward movement of these metals. Although data from this experimental area have been presented (Schalscha et al., 1978, 1979), the results of a detailed analysis of the heavy metals in the soil profile have not been presented.

MATERIALS AND METHODS

The experimental area is located adjacent to Santiago, Chile, where a mixture of domestic and industrial wastewaters from the city are available from the Zanjón de la Aguada (ZA) Canal. A general description of the area is given by Schalscha et al. (1979). The average rainfall is 340 mm yr⁻¹ with most of it falling in the winter months of June through September. Irrigation with raw wastewater in the area started about 1900 and has continued to the present. No other water has been available. There is no sewage treatment of any kind. The wastewater is diverted directly from the ZA Canal which is open after it leaves the City of Santiago. The city has grown from a population of

300 000 in 1900 to over 4 million inhabitants in 1985, with a tremendous increase in industrialization since 1945.

The cultivation history of the experimental site over the past 50 yr is not well known but it had been used for vegetable crops during the 30-yr period previous to soil sampling. The farm is owned by an old, established landowner who rents it to small farmers. There are serious problems with enteric pathogens in the irrigation water, largely because the farmers wash the harvested crops in the raw sewage water. The pathogen problem, however, is not the main subject of this paper.

A total of eight samples of the ZA wastewater was taken in spring, summer, and fall of 1977, in spring and summer of 1979 and 1983, and in summer of 1981. Each sample was a composite of 5-L subsamples collected between 1000 h and 1600 h, the time preferred by farmers for irrigation with the ZA water. A total of 27 subsamples were collected. Samples were filtered through 0.45 µm micropore filters and the filtrates and residues were analyzed separately. Heavy metals in the filtrate were analyzed by atomic absorption spectrophotometry (AAS) after extraction with the ammonium pyrrolidinedicarbodithioate-methyl isobutyl ketone (APDC-MIBC) method described by Brooks et al. (1967) and Koirtiyohann and Wen (1973). Heavy metals in the suspended solids were determined by AAS after digestion with 0.3 kg kg⁻¹ H₂O₂ and concentrated HNO₃. The total concentrations of heavy metals in the original water were then calculated from the amounts in filtrate and residue.

Soil profile samples were taken from each corner of a 20- by 40-m plot of an irrigated field using an auger-type hollow probe. The soil was the El Recuerdo series (Typic Torrenets). Depth samples represented the 0- to 5-cm and 5- to 30-cm depths, and 30-cm depth intervals to the 150-cm depth. Air-dried samples were analyzed for heavy metals by AAS after digestion with concentrated HClO₄-HF (Linn and Jackson, 1982) to completely destroy organic matter and to dissolve inorganic materials. Organic C was determined by a Walkley-Black procedure and the cation-exchange capacity (CEC) was determined by Na saturation (Jackson, 1958). Soil samples from each site were analyzed separately so that statistical treatment by analysis of variance of the data was possible, using soil depths as main effects.

Metals extractable in diethylenetriaminepentaacetic acid (DTPA) were obtained by extracting 25 g of air-dried soil with 50 mL of 0.005 M DTPA solution which was also 0.020 M in CaCl₂ and adjusted to pH 7.3 using triethanolamine (Baker and Amacher, 1982).

RESULTS

The total concentrations of Cd, Co, Cr, Cu, Mn, Ni, and Zn in the ZA water are presented in Table 1. The mean concentrations represent eight samplings during

Table 1. Total concentrations of metals in the untreated municipal wastewater.

Year	Metal						
	Cd	Co	Cr	Cu	Mn	Ni	Zn
	µg L ⁻¹						
1977	6	5	460	440	140	50	290
1979	3	7	330	530	nd†	78	362
1981	8	2	425	553	330	142	332
1983	18	13	267	591	502	62	474
Mean	8.8	6.8	370	528	325	83	364

† Not determined.

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Table 2. Some properties of the El Recuerdo soil.

Depth	pH	CEC	Organic C	Texture
cm	(paste)	mol (+) kg ⁻¹	g kg ⁻¹	
0-5	6.4	0.23	28	silt loam
5-30	7.4	0.28	18	silt loam
30-60	7.6	0.36	6	silty clay loam
60-90	7.4	0.33	3	silty clay loam
90-120	7.2	0.32	2	silt loam
120-150	7.2	0.30	2	silt loam

the 1977 to 1983 period and each sample consisted of a composite of subsamples taken during the period of the day when most irrigation was performed.

A few properties of the El Recuerdo soil profile are presented in Table 2. The texture is a silt loam in the 0- to 30-cm depth with an increase in clay content in the 30- to 90-cm depth. The pH of the surface soil is slightly acid, probably as a result of continuous nitrification of the NH₄⁺ in the ZA water. The organic matter content is relatively high as a result of long use of the ZA water with its component of organic residues. Because of the uncertainty of the depth of cultivation and the depth of mechanical mixing of metals into the soil profile, the 0- to 5-cm depth was considered a safe sample to represent the cultivated layer. However, this means that the 5- to 30-cm depth was a mixture of the cultivated layer with a substantial amount of uncultivated material, perhaps 10 cm of the cultivated layer with 15 cm of uncultivated soil.

Data for the DTPA-extracted metals are presented in Table 3. In all cases except Cr, which was not detected in the DTPA extract, the amount extracted in the 0- to 5-cm depth was larger than in the rest of the profile. For Cd, Co, Mn, Ni, and Zn, the 5- to 30-cm depth was intermediate between the 0- to 5-cm and 30- to 60-cm depth. This intermediate level would be expected if this layer consisted of a mixture of the cultivated layer represented by the 0- to 5-cm depth and an uncultivated layer more like the 30- to 60-cm depth. The greater amounts of extractable metals in the cultivated layer of the soil is probably the result of yearly additions of metals from the ZA water. However, one must also consider that the cultivated layer has a lower pH, which would favor greater metal solubility, and that natural cycling of metals to the surface soil by vegetation would tend to keep metals in this surface layer in forms more easily extracted by DTPA.

Data for total contents of heavy metals in the El Recuerdo soil are presented in Table 4. When compared

Table 4. Total concentrations of metals in the El Recuerdo soil.

Depth	Element						
	Cd	Co	Cr	Cu	Mn	Ni	Zn
cm	mg kg ⁻¹						
0-5	3.8	54	73	653	1574	66	328
5-30	3.6	57	42	732	1536	62	291
30-60	3.5	58	21	732	1283	68	271
60-90	3.3	52	23	731	1385	59	264
90-120	3.5	57	21	1016	1408	61	314
120-150	3.6	59	19	1204	1459	65	369
Least significant difference at 0.05 level	0.29	4.7	13.8	247	169	5.3	109

Table 3. Metals extracted by DTPA from samples of the El Recuerdo soil.

Depth	Cd	Co	Cr	Cu	Mn	Ni	Zn
cm	mg kg ⁻¹						
0-5	0.39a†	1.27a	nd‡	106a	186a	2.47a	19.2a
5-30	0.32b	0.74b	nd	84b	87b	0.82b	5.6b
30-60	0.14c	0.55c	nd	77b	51c	0.27bc	1.21c
60-90	0.14c	0.81b	nd	74b	65bc	0.38bc	1.57c
90-120	0.14c	0.85b	nd	42c	46c	0.27bc	2.35bc
120-150	0.16c	0.83b	nd	48c	53c	0.20c	3.07bc

† Not detected.

‡ Means within each column not followed by the same letter are significantly different at the 0.05 probability level by Duncan's Multiple Range Test.

with the data presented by Mattigod and Page (1983) the concentrations of Cd and Cu were above the usual range, that for Co was near the top of the usual range and those for Cr, Mn, Ni, and Zn were well within the normal range for uncontaminated soils. For Cd, Cr, and Mn, the amounts in the 0- to 5-cm depth were greater than in the 30- to 60-cm depth whereas for Co, Cu, Ni, and Zn there were no significant differences. In the case of Cr the difference was highly significant, indicating a large accumulation in the cultivated layer. The weighted mean for the 5- to 30-cm depth from 10 cm of soil at 73 mg Cr kg⁻¹, representing the cultivated layer, and 15 cm of soil at 21 mg Cr kg⁻¹, representing soil below the cultivated zone assumed to have the same concentration of Cr as the 30- to 60-cm depth, is 41.8 mg Cr kg⁻¹. This assumes that the bulk densities are the same which is unlikely. However, the agreement does suggest that the 5- to 30-cm depth might have consisted of about 10 cm of cultivated and 15 cm of uncultivated soil.

For Co, Cu, Ni, and Zn there were no significant accumulations in the cultivated layer. For Co, Ni, and Zn there were no differences in the profile. For Cu the 90- to 150-cm depth had significantly greater contents than the overlying layers. For Cd the cultivated layer had a higher concentration than in some of the underlying depths. Thus, the total concentrations presented different depth distribution patterns than the DTPA extractable metals.

DISCUSSION

The data for total metal contents, particularly Co, Cu, Ni, and Zn could suggest downward movement to produce a fairly uniform distribution of the added metals throughout the soil profile. To analyze this possibility in greater detail several assumptions were made.

Table 5. Concentrations of total Cr, Cu, Mn, Ni, and Zn in three depths of a nonirrigated noncultivated soil similar to the El Recuerdo soil.

Element	Total concentrations, mg kg ⁻¹		
	0- to 5-cm depth	5- to 0-cm depth	30- to 60-cm depth
Chromium	6.6	9.4	9.8
Copper	112	99	102
Manganese	868	667	605
Nickel	19	19	18
Zinc	112	94	102

Table 6. Estimated metals deposited from the ZA water and the calculated increases in concentration in the 0- to 15-cm depth of soil assuming the elements deposited over a 30-yr period were retained in this depth of soil.

	Element						
	Cd	Co	Cr	Cu	Mn	Ni	Zn
Yearly deposition, kg ha ⁻¹	0.19	0.15	8.1	11.6	7.2	1.8	8.0
Deposited in 30 yr, kg ha ⁻¹	5.7	4.5	243	348	216	54	240
Increase in concentration							
Bulk density = 1.1, mg kg ⁻¹	3.4	2.7	147	211	131	33	145
Bulk density = 1.4, mg kg ⁻¹	2.7	2.1	116	166	103	26	114
Bulk density = 1.7, mg kg ⁻¹	2.2	1.8	95	146	85	21	94
Difference in concentration †, mg kg ⁻¹	0.4	-1.0	51	-79	240	2.5	61

† Concentration in the 0- to 5-cm depth minus that in the 30- to 90-cm depth. The 0- to 5-cm depth represents a sample of the cultivated zone which is assumed to be no deeper than 15 cm.

The first is that the mean concentrations of metals in the ZA water during the 1977 through 1983 period (Table 1) can be used to estimate the amounts of elements added during the more than 50 yr this soil has received ZA water. Industrial development has been part of growth in the city of Santiago for the past 50 yr, but, during the 30 yr previous to soil sampling, industries have been in full production and have grown as the city has grown so that the ratio of industrial to nonindustrial discharge is judged to have been fairly constant. Because of the uncertainty of projection back in time, the elements added were calculated for a 30-yr period representing the time from about 1949 to 1977.

The second assumption is that the El Recuerdo soil had a uniform depth distribution of heavy metal contents at the time irrigation with ZA water started. The most critical part of this assumption is that the cultivated layer did not have lower concentrations than layers immediately below. This is not likely because of centuries of accumulation of metals in the surface as a result of deposition from vegetation. There is no way to verify this assumption, but data from a similar soil in the same area that had not been irrigated with the ZA water showed that the total concentrations of Cr, Cu, Ni, and Zn in the 0- to 5-cm, 5- to 30-cm, and 30- to 60-cm depths were essentially the same (Table 5). The concentrations of total metals in this so-called control soil are much lower than in the El Recuerdo soil, but these differences have no meaning because we do not know the distribution of these metals in soils in the Santiago Valley.

A third assumption is that the soil had lost relatively small amounts of metals by erosion and by removal in harvested crops. The area has flat topography and shows no signs of erosion. Also, calculations show that removal in crops represents only a few percent of the amounts of metals added in the ZA water.

Using these assumptions the data in Table 6 were calculated. The amounts deposited in a 30-yr period were calculated from the mean values presented in Table 1. The increase in concentration in the 0- to 15-cm depth that would have occurred, if the added elements had accumulated in this depth, were calculated for three bulk densities because the bulk density at time of sampling was not known. The data for calculated increases in the 0- to 15-cm depth compared to the actual increases in concentration in the 0- to 5-cm depth, which could represent the 0- to 15-cm depth, suggest downward movement of metals with the exception of Mn.

Another comparison of the DTPA extractable and total metals in the El Recuerdo soil is presented in Table 7. The relative topsoil enrichment (RTE) for the 0- to 5-cm depth, representing the cultivated layer, and the 30- to 60-cm and 60- to 90-cm depths show some enrichments as measured by DTPA, but little or no enrichment, except for Cr, as measured by total contents. For all metals, except for Mn, the RTE ratios measured were less than those calculated by assuming that the added metals had accumulated in the cultivated layer, using a bulk density of 1.4.

Possible explanations for the data in Tables 6 and 7 are: (i) the amounts of elements deposited are greatly overestimated, (ii) the original metal contents increased with increase in depth so that accumulations in the cultivated layer did not show as increases in comparison to lower depths, (iii) metals moved into the soil profile and distributed themselves uniformly throughout the profile or were leached through the soil profile, or (iv) a combination of these. We feel that the most plausible explanation is that the metals have been moving into the lower depths of the soil profile. Of course, there is no

Table 7. Relative topsoil enrichment (RTE) ratios comparing the 0- to 5-cm depth with the 30- to 60-cm and 60- to 90-cm depths for DTPA-extractable and total concentrations of metals in the El Recuerdo soil.

Depth comparison	Element						
	Cd	Co	Cr	Cu	Mn	Ni	Zn
DTPA-extractable							
0- to 5-cm vs. 30- to 60-cm	2.78	2.31	-†	1.38	3.65	9.15	15.87
0- to 5-cm vs. 60- to 90-cm	2.78	1.57	-†	1.43	2.86	6.50	12.23
Total concentrations‡							
0- to 5-cm vs. 30- to 60-cm	1.09	0.93	3.48	0.89	1.23	0.97	1.21
0- to 5-cm vs. 60- to 90-cm	1.15	1.04	3.17	0.89	1.14	1.12	1.24
0- to 5-cm vs. 30- to 60-cm calculated‡	1.77	1.04	6.52	1.23	1.08	1.38	1.42
0- to 5-cm vs. 60- to 90-cm actual/calculated§	0.62	0.89	0.53	0.72	1.14	0.70	0.85

† Cr was not detected in the DTPA extract.

‡ Calculated assuming the metal added over the past 30 yr (Table 6) had accumulated in the cultivated layer, assuming a bulk density of 1.14.

§ Ratio of the RTE comparing the 0- to 5-cm to the 30- to 60-cm depth using the actual data of Table 4 to the RTE that would have been found if the metal added had accumulated in the cultivated layer assumed to be the 0- to 15-cm depth.

way to rule out the other explanations. The GEOCHEM program (Mattigod and Sposito, 1979), used by Mattigod et al. (1984) to simulate the downward migration of metals in this soil, indicated that small amounts of metals do move in solution, suggesting that with large volumes of drainage water over a long period substantial amounts of heavy metals do migrate downward. In the El Recuerdo soil the amount of irrigation water used was estimated as 2200 surface mm yr⁻¹ with a leaching fraction of 0.63 or a drainage volume of 1390 surface mm yr⁻¹. This volume of drainage water has provided ample opportunity for mobile elements to migrate to lower depths in the soil during the past five decades. The average annual rainfall of 340 mm, which is largely limited to the months of June, July, August, and September, contributes very little to the drainage volume.

Other workers have found evidence of movement of heavy metals into soil profiles. Kirkham (1975) reported substantial increases in Cd, Cu, Ni, Zn, and Pb in the 30- to 61-cm depth of soil in a plot that had received sewage sludge at an average rate of 28 Mg ha⁻¹ yr⁻¹ for a period of 35 yr. Dowdy et al. (1984) reported evidence that Cd and Zn had moved from the zone of incorporation to a depth of 0.8 to 1.0 m in plots that had received treatments over a 14-yr period. For example, they reported that Cd concentrations (extracted with 4 M HNO₃) were 10 times greater in sludge treated than in control plots (2.5 vs. 0.2 mg Cd kg⁻¹ clay) in the 50- to 60-m depth of soil. Reddy and Dunn (1984) reported significant movement of certain heavy metals along the profile of a soil treated with sewage sludge at rates up to 100 Mg ha⁻¹ yr⁻¹ for several years. Although these results were obtained with sludges rather than with untreated wastewaters, they do indicate that heavy metals added from organic materials do move in soil profiles. The difference is that the wastewater added to the El Recuerdo soil was undigested and the solids were added in a dilute form in small quantities at time of each irrigation during a 210- to 270-d period of each year for several decades.

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