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Articles

Distribution of Cd, Cu and Zn in a Sewage Sludge-treated Calcareous Soil

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The distributions of Cd, Cu, and Zn concentration in soil treated with one (1988) or two (1988 and 1993) applications of sewage sludge at rates of 0, 25, 50, and 100 Mg ha^{-1} (dry weight basis) were determined to assess the accumulation and mobility of the heavy metals. The heavy metals accumulated almost entirely in 0 to 15 cm soil depths. Small amounts of the metals moved out of the tillage zone (0-15 cm depth) into the subsoil, but even at the high rate of sewage sludge, little movement of heavy metals occurred below 100 cm depth. The water-extractable Cd, Cu, and Zn concentrations were very low regardless of the rate of sewage sludge application. Availability of metals as determined by DTPA extraction showed the percentage of DTPA-extractable/total concentration increased with sewage sludge application. In the 0-15 cm depth of sewage sludge treated soil, the percentage of DTPA-extractable/total concentration was higher than 46% for Cd, but the value was less than 27% and 17% for Cu and Zn, respectively. The Cd, Cu, and Zn added to this calcareous clay soil by sewage sludge application were not very mobile, and the amount of plant available form was very small.

Key words : *heavy metals, sewage sludge, land application, metal accumulation, metal mobility.*

The application of sewage sludge on agricultural land can be beneficial to the soil by improving its physical condition and supplying nutrients to plant. Sewage sludge provides major nutrients such as N, P, K as well as many of the trace elements required by plants[1] However, there are certain environmental concerns associated with the use of sewage sludge for agricultural purposes. It is a potential source of NO_3-N which could leach into groundwater,[2] toxic heavy metals such as Cd,[3] toxic synthetic organics such as pesticides and polychlorinated biphenyls (PCBs),[4] and pathogenic micro-organisms such as *Salmonella*.

Sewage sludge application rates on land may be based on the fertilizer value (N, P and K) and limited by the concentrations of heavy metals present in sewage.[6] Several countries have established loading rate limits for heavy metals present in sewage sludge. The maximum annual loading for Cd on agricultural land is 60 - 167 g ha^{-1} for EC, 90 g ha^{-1} for Canada, and 500 g ha^{-1} for the USA.[7] For the City of Winnipeg, this limit has been set at 56 dry Mg ha^{-1} on an annual basis. The buildup of heavy metals in the soil profile may constitute a hazard not only to plants but also to consumers of the harvested crops. The most important factor in determining plant uptake of heavy metals is sewage sludge application rate.[8] This understanding was used to develop regulations for land application of municipal sewage sludge that restrict the annual and cumulative sewage sludge application rates.

As land application is a natural way to recycle components of sewage sludge back to the environment, efforts should be made to use sewage sludge efficiently so that there is little adverse impact on the environment. Quantifying the levels of heavy metals in sewage sludge-treated soils is the first step towards protecting the soil environment from excessive sewage sludge amendments. It is necessary to examine the possibility of heavy metal contamination of the soil and groundwater through sewage sludge disposal. The objective of this study was to conduct soil profile monitoring of Cd, Cu, and Zn to establish whether such sewage sludge application rates (0, 25, 50, and 100 dry Mg ha^{-1}) would have any impact on the soil and groundwater contaminations due to heavy metals originating from the sewage sludge.

Materials and Methods

Experimental site and soil sample collection. The soil at the experimental site was calcareous Lakeland clay (Gleyed Carbonated Rego Black). The sewage sludge was anaerobically digested from North End Water Pollution Control Center of the City of Winnipeg. Sewage sludge was incorporated into the soil on May of each year, and

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Abbreviations: DTPA, diethylene triamine pentaacetic acid; PCBs, polychlorinated biophenyls.

Table 1. Selected properties of soil (sludge-untreated, 0-15 cm) and municipal sewage sludge from the City of Winnipeg.

Properties	Soil	Sludge* (1988)	Sludge* (1993)
pH	7.9	6.2	7.1
Organic C (g kg^{-1})	40	228	653
CEC (cmol(+) kg^{-1})	36.5	-	-
Total Cd (mg kg^{-1})	0.33	11.6	17.6
Total Cu (mg kg^{-1})	46	716	1400
Total Zn (mg kg^{-1})	89	1990	1650
Texture	Clay	-	-

*Data supplied by the City of Winnipeg.

Table 2. Descriptions of the field study plot.

Plot No.	Rates of Sludge (dry Mg ha^{-1})	Year Applied
1	0	-
2	25	1988
3	50	1988
4	100	1988
5	0	-
6	25	1988 & 93
7	50	1988 & 93
8	100	1988 & 93

uniformly mixed with the soil to a depth of 15 cm. Table 1 presents some of the selected properties of the soil and sewage sludge used in field study. Soil was sampled from the City of Winnipegs sewage sludge research plots located at Oak Hammock Marsh, Manitoba. Spring wheat (*Triticum aestivum* L.) was grown annually. The soil samples were collected on June 6, 1995 from plots which received one (1988) or two (1988 and 1993) applications of 0, 25, 50, and 100 Mg of sewage sludge (dry weight basis) per hectare. The description of field study plot is shown in Table 2. Soil samples were taken from five depths (0-15, 15-30, 45-55, 95-105, and 145-155 cm) from five randomly selected locations in each plot (45 × 61 m). The samples were combined, air-dried, and ground to pass a 2 mm sieve.

Analysis of Cd, Cu and Zn. The pH of the soil samples was measured in a 1 : 2 (soil : water).[9] The total concentrations of Cd, Cu, and Zn were determined using a nitric-perchloric acid digestion procedure in which 0.5 g of soil was digested with 2.5 mL concentrated HNO_3 and 5.0 mL $HClO_4$ acid.[10] The digests were filtered and underwent a clean-up process with dithizone ($C_{13}H_{12}N_4S$)-methylene chloride (CH_2Cl_2) to prevent interference for Cd determination[11] prior to measurement by atomic absorption spectroscopy (Perkin Elemer 1100B). Ten grams of soil was shaken with 20 mL of either deionized water (water-extractable) or DTPA extracting solution (DTPA-extractable) for 2 hours. The DTPA extracting solution consisted of 0.005 M DTPA, 0.1 M triethanolamine, and

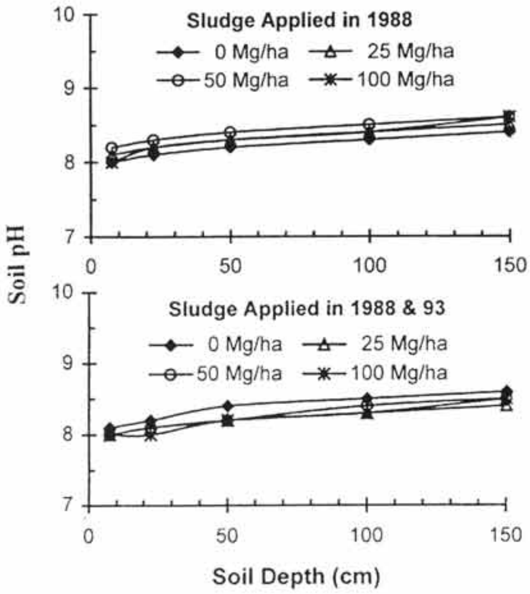

Fig. 1. Soil pH with depth.

0.01 M $CaCl_2$ with a pH of 7.3.[12] The extracts were filtered and analyzed for Cd, Cu, and Zn by atomic absorption spectrophotometer.

Results and Discussion

Soil pH. Soil pH was not different between the control (sewage sludge-untreated soil) and sewage sludge-treated soils (Fig. 1). The pH of the soil used in the field study was high due to high carbonate contents (about 30 % as calcium carbonate equivalent). The risk of heavy metal toxicity resulting from sewage sludge may be very low because of high soil pH. At a high pH, metal uptake is minimized because of the reduced heavy metal availability.[13] Crop and soil management programs developed to regulate sewage sludge application to agricultural soils frequently recommend that the soil pH should be maintained at >6.5 to reduce the availability of heavy metals for plant uptake and leaching.[14] Continued crop production requires a near neutral soil pH, even years after sewage sludge application is discontinued, in order to reduce mobility of heavy metals that are added to the soil.

Distribution of total Cd, Cu and Zn. The total concentrations of Cd, Cu, and Zn in different soil depths are shown in Fig. 2 to 4. In control plot (sewage sludge-untreated plot), the range of the total Cd concentration was 0.12-0.31 mg kg^{-1}. This range was consistent with the Cd concentrations of < 1.0 mg kg^{-1} for uncontaminated soil. The total Cd concentration of uncontaminated soils in Canada generally falls within the range of 0.09 to 1.0 $mgkg^{-1}$.[15] On the other hand, in sewage sludge-treated plots, the total Cd, Cu, and Zn concentrations increased with increasing rates of sewage sludge application. The distribution patterns of the total Cd, Cu ,and Zn concentrations in the soil profile were

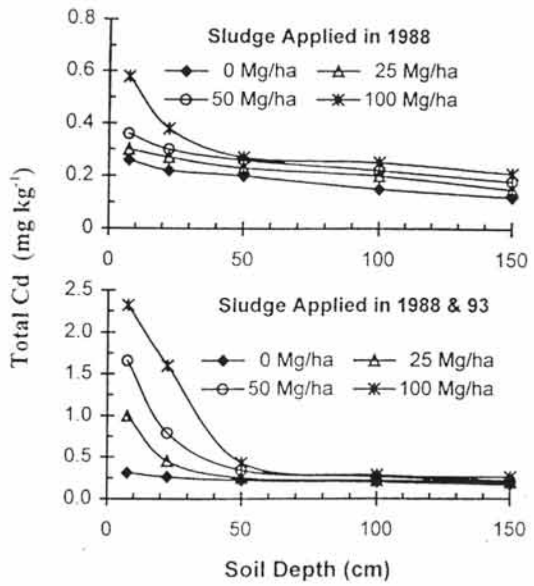

Fig. 2. Distribution of total Cd.

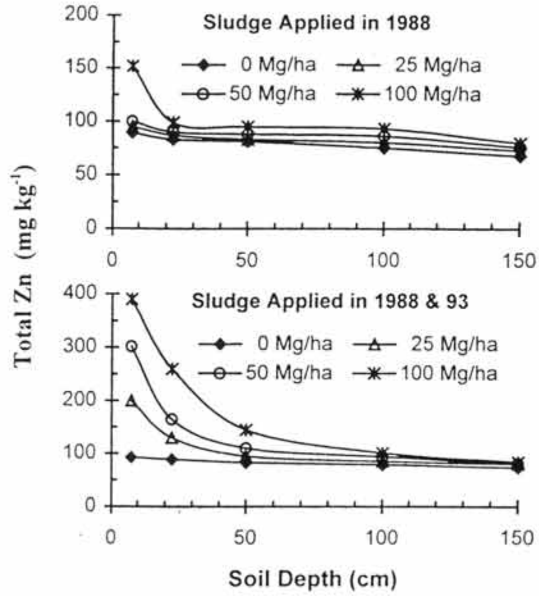

Fig. 4. Distribution of total Zn.

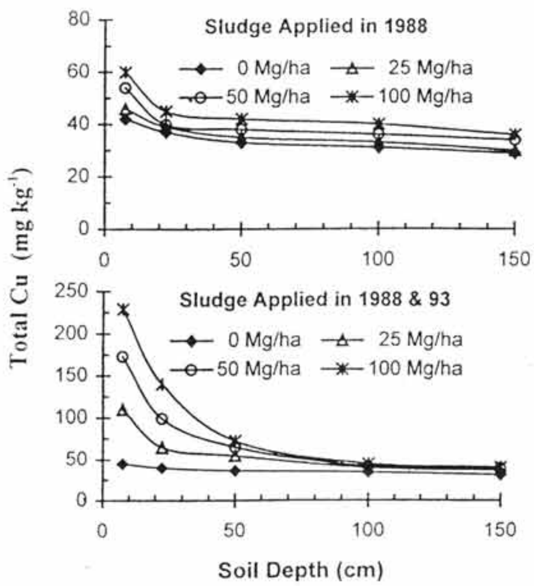

Fig. 3. Distribution of total Cu.

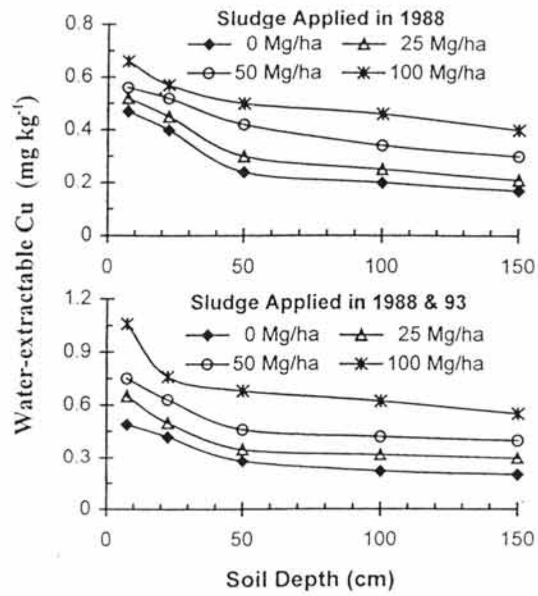

Fig. 5. Distribution of water-extractable Cu.

similar regardless of the rate of sewage sludge application. The heavy metals originating from sewage sludges accumulated almost entirely in the 0 to 15 cm soil depth and only small amounts moved out of the tillage zone (0-15 cm depth) into the subsoil. Williams et al. reported that heavy metals added to soil by sewage sludge application exhibited little mobility.[16] When sewage sludge is added to soils, heavy metals remain in the zone of application (0-15 cm depth) as a result of adsorption on hydrous oxides, clays, and organic matter or the formation of insoluble.[17,18]

Distribution of water-extractable Cd, Cu and Zn. Irrespective of the rate of sewage sludge application, the water-extractable Cd concentrations were below detection limit (about 0.02 mg kg^{-1}). The water-extractable Zn concentration was very low, around 0.05 mg kg^{-1} at 0-15 cm depth in sewage sludge-treated plots and decreased to below detection limit at 50 cm depth (about 0.02 mg kg^{-1}). On the other hand, the water-extractable Cu concentrations increased with sewage sludge application (Fig. 5). However, the water-extractable Cu concentration was less than 1.0 % of total Cu concentrations in sewage sludge-treated plots. This results indicated that most of the metals originally present in the soil are held in forms that are relatively immobile and unavailable to plants, and the added metals will also tend to become immobilized. Water soluble metals exist in the soil solution as free ions, soluble complexes or as ions adsorbed on suspended colloids. Lund et al. reported that the heavy metals moved as soluble metal-organic complexes.[19]

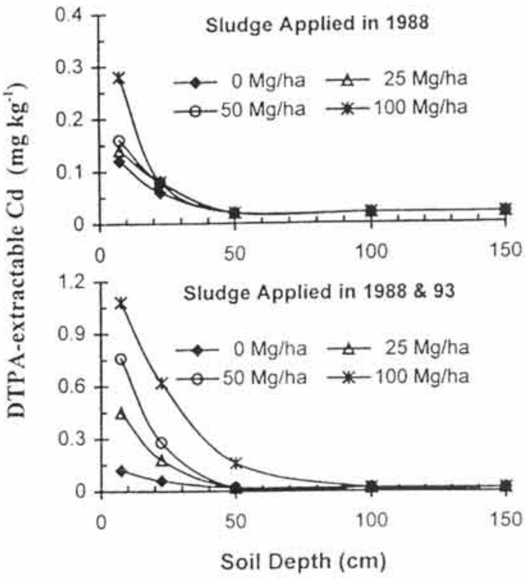

Fig. 6. Distribution of DTPA-extractable Cd.

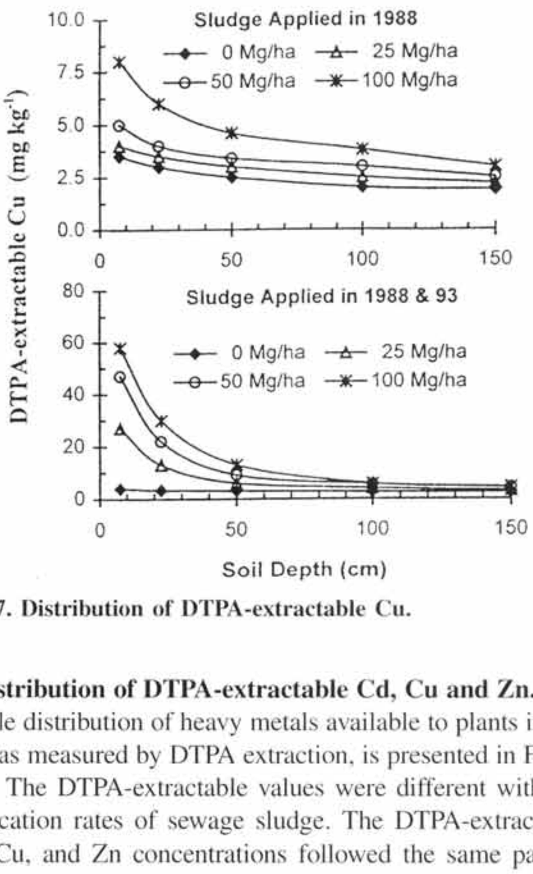

Fig. 7. Distribution of DTPA-extractable Cu.

Distribution of DTPA-extractable Cd, Cu and Zn. The profile distribution of heavy metals available to plants in the soil, as measured by DTPA extraction, is presented in Fig. 6 to 8. The DTPA-extractable values were different with the application rates of sewage sludge. The DTPA-extractable Cd, Cu, and Zn concentrations followed the same pattern observed with the total Cd, Cu, and Zn concentrations. The detectable concentration of DTPA-extractable Cd was restricted up to 30 cm depth except for the plot where 100 Mg ha^{-1} sewage sludge was applied in 1988 and 1993. Cadmium was not detected from the deeper soil layers (Fig. 6). The DTPA-extractable Cu and Zn concentration distribution showed that the relative increase in the Cu and Zn concentration was related to the rate of sewage sludge application (Fig. 7 and 8). The percentage of DTPA-extractable/total concentration increased with sewage sludge application rates (Table 3). A higher percentage (> 40 %) of total Cd was DTPA-extractable than Cu (< 25 %) or Zn (< 15 %) in sewage sludge-treated plots.

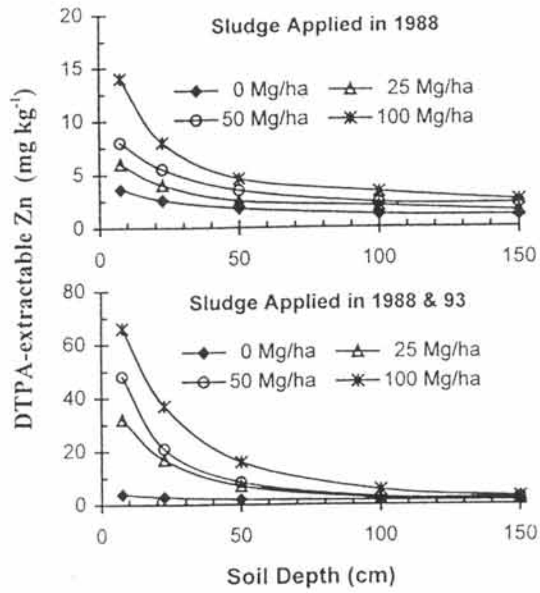

Fig. 8. Distribution of DTPA-extractable Zn.

The solubility and, therefore, the bioavailability of heavy metal ions are variable because many factors affect their concentrations in soil solution. Soil chemical properties such as pH, clay content, organic matter content, cation sorption capacity and oxidation-reduction status are reported to influence the mobility and plant availability of heavy metals from organic wastes.[20] DTPA analysis of metal distribution in the soil profile revealed that the bulk of the added metal remained in the top 15 cm, the zone of its incorporation. Slow soil chemical processes over several years may change the forms, extractability, and bioavailability of metals. Follet and Lindsay stated that, with time, a slow reversion of metals occur, with a change from a readily available form to unavailable or immobile forms.[21] A small portion of Cu and Zn must have moved below 30 cm as the concentration distribution profile indicated. However, very little movement of metals had occurred below 100 cm in sewage sludge-treated soils. Kelling et al. found somewhat increased levels of DTPA-extractable Cd and Cu in the 15 to 30 cm depth of sludge amended soil, and attributed this to tillage practice.[22] However, they reported that the increase of the DTPA-extractable Zn at depths > 30 cm might be due to some movement of Zn in the soil.

Conclusions

The surface layers of the sewage sludge-applied, calcareous soil (above 15 cm) accumulated heavy metals with relatively little movement of the metals below the 30 cm depth. Because of the very slow rate of mobility of heavy

Table 3. Percent of DTPA-extractable/total concentration at 0-15, 15-30 and 45-55 cm depth.

	Year Applied	Soil Depth (cm)	Sewage Sludge Application Rates			
			0 dry Mg ha^{-1}	25 dry Mg ha^{-1}	50 dry Mg ha^{-1}	100 dry Mg ha^{-1}
			(%)			
Cd	1988	0-15	42.9	46.7	47.2	48.3
		15-30	25.0	28.6	26.7	21.1
		45-55	9.5	8.7	7.7	7.4
	1988 & 93	0-15	40.0	45.0	45.8	46.6
		15-30	23.1	38.7	35.4	38.8
		45-55	9.0	8.0	6.7	37.2
Cu	1988	0-15	7.5	8.7	9.3	13.3
		15 - 30	6.8	7.7	9.0	13.0
		45 - 55	7.6	8.6	8.9	11.0
	1988 & 93	0 - 15	7.8	24.5	26.9	25.3
		15 - 30	7.5	20.0	22.5	21.4
		45 - 55	8.6	10.9	14.2	18.1
Zn	1988	0 - 15	4.0	6.3	8.0	9.3
		15 - 30	2.8	3.4	6.1	8.1
		45 - 55	2.2	3.0	4.0	4.8
	1988 & 93	0 - 15	4.2	16.0	15.7	16.8
		15 - 30	3.3	13.1	12.4	14.2
		45 - 55	2.4	7.4	7.6	11.0

metals in this calcareous soil, the lower horizons of this soil (below 100 cm) and, thus, ground-water may not be readily contaminated by the heavy metals originating from this sewage sludge. It can be concluded that the sewage sludge application rate of 56 dry Mg ha^{-1} established by the City of Winnipeg is safe for sewage sludge disposal to agricultural land with a neutral to alkaline pH. However, repeated applications of sewage sludge under extended period may require further investigation including crop analysis. Long-term monitoring and evaluation of land application projects are needed to promote the safe use of sewage sludge on crop land. By monitoring the heavy metal contents of sewage sludge-treated soils, the concentration of heavy metals added to the soil can be regulated and, consequently, agricultural land can be prevented from contamination by heavy metals.

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