Agric. Chem. Biotechnol. 42(2), 85-91(1999)

Speciation of Cd, Cu and Zn in Sewage Sludge-Treated Soils Incubated under Aerobic and Anaerobic Conditions

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Received June 1, 1999

The incubation study was conducted under aerobic and anaerobic conditions to study the release of the kinetically labile forms (i. e. chelating ion or anion forms) of Cd, Cu and Zn in sludge-untreated soil ("Control"), sludge 50 and 100 dry Mg ha^{-1} treated soils ("Soil-Sludge mixtures"), and sewage sludge ("Sludge"). The chelating ion and anion exchange membranes were embedded into the samples and incubated for 16 weeks under aerobic and anaerobic condition. The total amounts of chelating ion or anionic forms of Cd were too little to be measured during both aerobic and anaerobic incubation. On the other hand, the total amounts of chelating ion or anionic forms of Cu and Zn slightly increased throughout the incubation period under both incubation conditions. For "Control" and "Soil-Sludge mixtures" treatments, the total amounts of Cu and Zn in chelating ion and anion exchange membrane were little difference between aerobic and anaerobic condition, and the total amounts of chelating ion form of Cu and Zn were not different from the those of anionic form of Cu and Zn. However, for "Sludge" treatment, the total amounts of Cu and Zn in anion and chelating ion exchange membrane were greater under aerobic condition than under anaerobic condition, and the total amounts of chelating ion form of Cu and Zn were greater than those of anion form of Cu and Zn under both incubation conditions.

Key words : *sewage sludge, heavy metals, speciation, aerobic-anaerobic conditions, ion exchange membrane.*

Sewage sludge can have a beneficial effect on plant growth and yields of crops are usually increased due to the presence of nitrogen and phosphorus in the sludge. Utilization of sewage sludge on agricultural land is increasing because it offers economic and nutrient recycling advantages over alternative disposal methods. However, several agronomic and environmental considerations have to be evaluated before sewage sludge is applied to agricultural land. Foremost among the potential problems are the enrichments of ground-water with nitrate[1)] and the accumulation of toxic heavy metals in soils.[2)] Land application of sewage sludge is governed by the level of pollutants that become concentrated in the sludge during treatment process. Municipal sewage sludges differ greatly in their content of trace metals, depending upon the nature and degree of industrial activity. Therefore, it has been difficult to establish general loading limits for agricultural application of sewage sludge because the heavy metal concentrations vary immensely.[3)]

Heavy metals may exist as free ionic species or as complexes with various ions in solution. The problems of identifying the fate of heavy metals in soils are that the retention reactions and transport of the various species in the soil environment must be accounted for.[4)] With respect to disposal of sewage sludge to land, heavy metal speciation is important because it influences bioavailability and will determine metal mobility. Reports on the chemical species of heavy metals in soil solutions are limited. This may be due to the complex nature of these types of samples as well as to the limitations of analytical techniques available as regards constraints imposed by interference, selectivity, and sensitivity.[5)] In addition, studies on soil solutions are rendered difficult by the very low concentrations of most metals in them.[6)] It is apparent that no comprehensive or reliable speciation schemes for determining discrete heavy metal species in sludge-treated soils have yet been developed.

Various chromatographic techniques have been employed in the speciation of metals in soil solution, including ion exchange, adsorbent resin, gel permeation, and high performance liquid chromatography (HPLC).[7)] The ion exchange membrane method offers a fast and convenient alternative to column and batch ion exchange resin methods. The ion exchange membranes eliminate the cumbersome process of packing a resin column, allow faster sample processing and regeneration than ion exchange re-

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Abbreviation: DTPA, diethylenetriamine-pentaacetic acid.

sin packing, and can provide results equivalent to those produced using a packed column. The membranes are also porous, to allow simultaneous separation and filtration.

A better understanding of the chemistry of release of metals from sewage sludge is necessary to predict the potential for contamination by sludge-borne metals. Therefore, the purpose of this investigation was to quantify the kinetically labile forms (chelating ion and anion forms) of heavy metals in sludge-treated soils. The incubation study under aerobic and anaerobic condition was conducted with the ion exchange scheme using chelating ion and anion exchange membranes. The chelating ion exchange membrane was used to estimate heavy metals complexed by organic molecules and the anion exchange membrane was used to measure the existence of the anionic forms of the heavy metals.

Materials and Methods

Soil and sewage sludge. The soil used for the incubation study comprised the top 0-15 cm of the A horizon of a Lakeland series soil (Gleyed Carbonated Rego Black). The Lakeland soil was selected because it is one of the soils presently used for sludge disposal site by the City of Winnipeg (Manitoba, Canada). The soil was air-dried and passed through a 2 mm sieve.

The wet sewage sludge was obtained from the City of Winnipegs North End Water Pollution Control Centre on April 19, 1995. It originated from domestic waste-water and had undergone anaerobic digestion, followed by centrifugation. The moisture content of the wet sludge was 250% (w/w). To improve the handling and storage conditions of the sludge, the sludge was air-dried and sieved through a 2 mm polyethylene sieve. The moisture content of air-dried sludge was 4.0%. The saturation moisture content of the air-dried sludge was 170%. Selected properties of the soil and sewage sludge are given in Table 1.

Table 1. Properties of the soil and sludge.

Properties	SOIL	sludge
pH(1:2)	7.9	6.8
Organic C (g kg^{-1})	39.6	251.3
CEC (cmol(+) kg^{-1})	36.5	50.0
Carbonates (CCE %)*	30.3	20.0
Water-extratable Cd (mg kg^{-1})	nd	nd
Water-extratable Cu (mg kg^{-1})	0.37	2.7
Water-extratable Zn (mg kg^{-1})	0.04	1.5
DTPA-extratable Cd (mg kg^{-1})	0.14	4.5
DTPA-extratable Cu (mg kg^{-1})	6.7	95.0
DTPA-extratable Zn (mg kg^{-1})	5.0	307
Total Cd (mg kg^{-1})	0.33	6.5
Total Cu (mg kg^{-1})	45.5	935
Total Zn (mg kg^{-1})	88.5	970
Texture	Clay	-
sand(%)	15.8	
silt(%)	19.2	
clay(%)	65.0	

*CCE%: Calcium Carbonate Equivalent Percent

Incubation study. The incubation study consisted of 4 treatments, which were sludge-untreated soil ("Control"), 2 sludge-treated soils ("Soil-Sludge mixtures") and sewage sludge ("Sludge"), which were incubated individually in bottles for up to 16 weeks. The Soil-Sludge mixtures were prepared in the ratios of 40:1 (equivalent to sludge 50 dry Mg ha^{-1}) and 20:1 (equivalent to 100 dry Mg ha^{-1}) with air-dried soil and sewage sludge. The 16 week duration was chosen to simulate one growing season for spring wheat. All treatments were triplicated.

Five grams of sample were added to bottles (d=1.8 cm, l=4.5 cm). The chelating ion exchange membrane (d=1.8 cm, wt.=0.05 g, exch. capacity=0.08 meq.) and anion exchange membrane (d=1.8 cm, wt.=0.10 g, exch. capacity =0.16 meq.) were placed over the samples and another 5 g of sample were added to bottles, respectively. The membranes used were Bio-Rex ion-exchange membrane. The membranes are composed of uniformly dispersed particles of Chelex chelating ion exchange resin (sodium form) and AG 1-X8 anion exchange resin (carbonate form) in a polytetrafluoroethylene (PTFE) membrane.

The "Control" and "Soil-Sludge mixtures" treatments were wetted to moisture contents of 60% (w/w) (aerobic condition) and 110% (anaerobic condition) with deionized water. The Sludge treatments were wetted to moisture contents of 120% (aerobic condition) and 250% (anaerobic condition). The aerobic samples were opened to the air and stored in container with 100% of relative humidity to maintain the moisture contents. The anaerobic samples were tightly closed with cap. All sample bottles were incubated at 20±2°C. After the required incubation time of 1, 4, 8, 12, and 16 weeks, the embedded membranes were collected and analyzed for the total Cd, Cu and Zn. The soil was oven dried and analyzed for total and DTPA-extractable Cd, Cu and Zn. Ten gram samples were shaken with 20 ml of 0.005 M diethylenetriaminepentaacetic acid(DTPA) extracting solution (0.005 M DTPA, 0.1 M triethanol amine and 0.01M $CaCl_2$ with a pH of 7.3) for 2 hrs. All the filtrates were collected and analyzed for DTPA-extractable Cd, Cu and Zn.

The total amounts of Cd, Cu and Zn in soil and membrane were determined using a modified acid digestion procedure with a 3:1 ratio of nitric/perchloric acid.[8] The digestion solution underwent a clean-up process with dithizone ($C_{13}H_{12}N_4S$)- methylene chloride (CH_2Cl_2) to prevent interference for Cd determination.[9] After clean-up process, the digests were filtered and analyzed by atomic absorption spectrophotometer (Perkin Elemer 1100B).

Results and Discussion

Changes in pH. The changes in soil and sludge pH

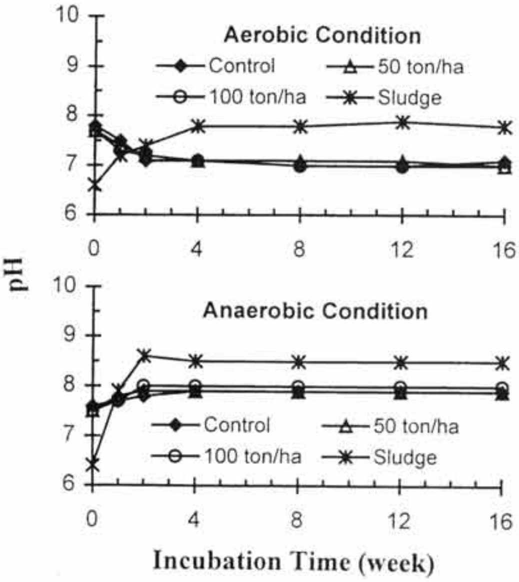

Fig. 1. Changes in pH during incubations.

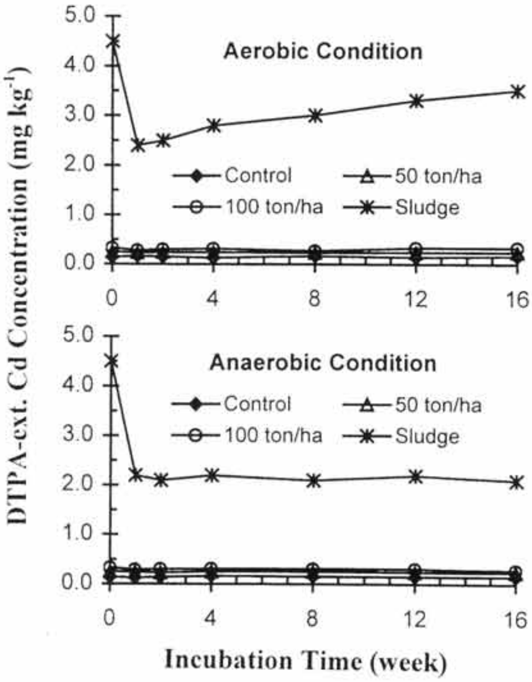

Fig. 2. Changes in DTPA-extractable Cd during incubations.

during incubation under aerobic and anaerobic condition are shown in Fig. 1. All values in this and subsequent figures are the means of triplicate incubations. During aerobic incubation, the pH of "Control" and "Soil-Sludge mixtures" treatments decreased in the first 2 weeks of incubation and then remained constant at a pH of about 7.1. The decrease in the pH may have been caused by the production of organic acids and hydrogen ions from the decomposition of organic matter.[10] The pH of "Sludge" treatment, however, progressively increased from 6.6 to 7.8 in the first 4 weeks of incubation and then stabilized.

During anaerobic incubation, the pH of "Control" and "Soil-Sludge mixtures" treatments slightly increased in the first 2 weeks of incubation and then remained fairly constant at a pH of about 7.9. However, the pH of "Sludge" treatment rapidly increased from 6.6 to 8.6 within the first 2 weeks of incubation and remained fairly stable during the incubation period. Generally, the pH increased under anaerobic condition because the hydroxyl ion was produced from the reduction reaction of $Fe(OH)_3$ $Fe^{2+} + 3OH$[11]

Total and DTPA-extractable Cd, Cu and Zn concentrations. For all of the treatments, the total Cd, Cu and Zn concentrations were fairly constant over the entire incubation period and were little different between aerobic and anaerobic conditions. The mean values of total Cd, Cu and Zn concentrations were 0.32, 46 and 90 mg kg^{-1} for "Control" treatment; 0.44, 63 and 108 mg kg^{-1} for 50 Mg ha^{-1} treated soil; 0.55, 74 and 118 mg kg^{-1} for 100 Mg ha^{-1} treated soil; 6.4, 933 and 979 mg kg^{-1} for "Sludge" treatment. The total concentrations increased with sludge addition. The total Zn concentration was higher than the total Cu concentration. The total concentration of heavy metal in soils does not correlate well with biological availability and gives no information on the chemical reactivity of the different forms of the metal found in soils.[12]

Fig. 2 to 4 show the changes in the DTPA-extractable Cd, Cu and Zn concentrations, considered to be an indication of plant available form, during the incubation period. In "Control" and "Soil-Sludge mixtures" treatments, the DTPA-extractable Cd, Cu and Zn concentrations ranged 0.13-0.16, 6.0-6.7 and 4.2-5.0 mg kg^{-1} for "Control" treatment; 0.23-0.25, 16.0-16.5 and 12.2-14.0 mg kg^{-1} for 50 Mg ha^{-1} treated soil; 0.27-0.33, 18.5-21.0 and 18.3-20.0 mg kg^{-1} for 100 Mg ha^{-1} treated soil. The addition of sewage sludge increased DTPA-extractable metals. The DTPA-extractable Zn differed little from DTPA-extractable Cu. The DTPA-extractable Cd, Cu and Zn concentrations changed very little during the incubation period and were little different between aerobic and anaerobic conditions. Metzger and Yaron reported that the organic carbon content of soil and sludge-treated soils changed very little over the 16 weeks incubation period, because the soil organic matter was stable.[13] However, Haghir stated that a gradual decomposition and loss of organic matter will take place in agricultural land for years, therefore this loss will result in the accumulation of metals up to high concentrations through sludge additions.[14]

The fate of heavy metals in soil is affected by soil physicochemical as well as biological factors. Slow soil chemical processes may change the chemical forms and soil microbial activity is responsible for both binding of metals and its subsequent release from soil. Lagerwerff et al. reported that chelates released from microorganisms may have allowed the heavy metal to remain in soil

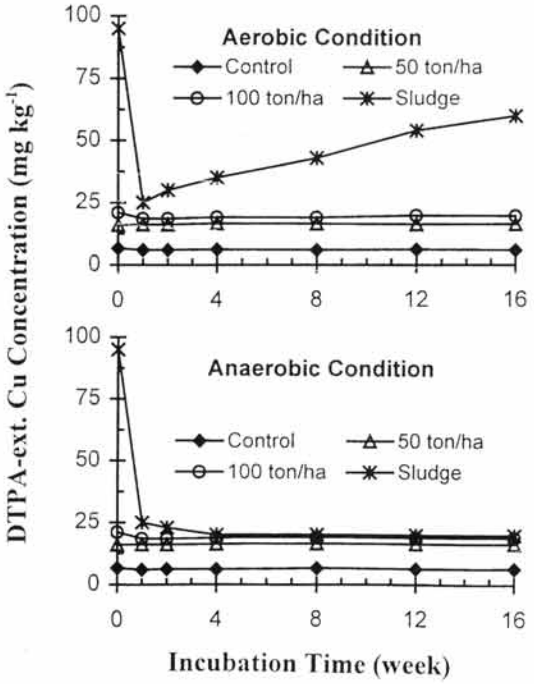

Fig. 3. Changes in DTPA-extractable Cu during incubations.

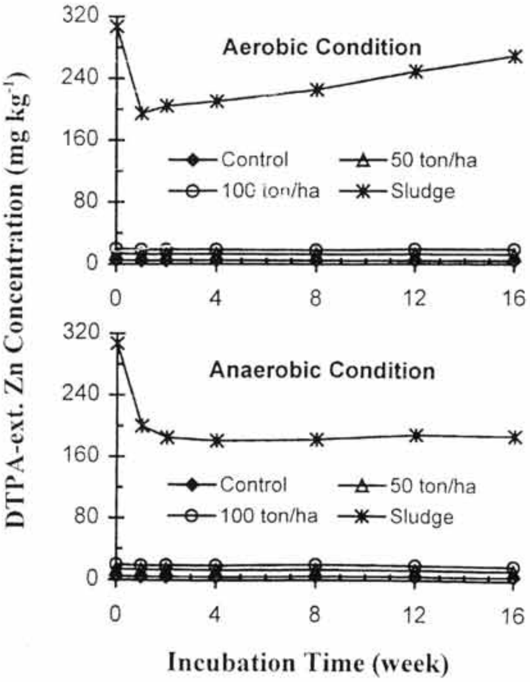

Fig. 4. Changes in DTPA-extractable Zn during incubations.

solution.15) Unfortunately, however, atomic absorption measures total heavy metal concentration in soil solution, and thus, it was not known how much heavy metal was present as the free inorganic or chelated forms. Chanmugathas and Bollag reported that, in a short-term exposure, metals added to soil was immobilized as a result of both microbial activity and soil sorption.16) In the long-term, however, metal immobilization was followed by its release into solution under aerobic conditions, whereas no metal mobilization occurred under anaerobic conditions. In addition, the redox potential of the soil can influence the oxidation state in which heavy metals exist and thus can influence their availability to plants. The decreases in redox potential may result in the formation of sulfides of Cd, Cu and Zn. Sulfides of heavy metals are quite insoluble thereby metal availability to plants is reduced.17)

On the other hand, in "Sludge" treatment, the DTPA-extractable Cd, Cu and Zn concentrations ranged 2.1-4.5, 25-95 and 181-307 mg kg^{-1}, respectively. The DTPA-extractable concen-trations were greater than the values in "Control" and "Soil-Sludge mixtures" treatments. The DTPA-extractable Zn was much greater than the DTPA-extractable Cu. The DTPA-extractable Cd, Cu and Zn concentrations decreased dramatically during the first week of incubation under both conditions, and then the values slightly increased under aerobic condition, but remained consistent under anaerobic condition there-after. The DTPA-extractable Cd, Cu and Zn concentrations under aerobic condition were higher than the values under an-aerobic condition because the decomposition rate of organic matter is faster under aerobic than under anaero-bic condition. The sewage sludge contained 251.3 g kg^{-1} organic carbon and the organic carbon content is an important factor as this would be the most likely source of metals released. Since no measure of sludge decom-position was made (i.e., loss of carbon), this explanation is only speculative. Schauer et al. reported that there was a general increase in the DTPA extractable heavy metals with time, which appeared to be related to the decom-position of the sludge.18) Metzger and Yaron found that, for anaerobically digested sludge, 20-40% of the organic carbon was degraded within 16 weeks of aerobic incubation.13)

Total amounts of chelating ion and anionic forms of Cd, Cu and Zn. For all of the treatments, the total amounts of Cd in chelating ion and anionic forms were too little to be measured under both aerobic and anaerobic conditions. Direct observations of sludge-Cd chemistry are impossible at this study because of the great complexity of sludge mineral and low sludge-Cd concentration. However, theoretical considerations and indirect methods (chemical extraction) suggest that sludge-Cd may exist as a combination of organically complexed metal, adsorbed forms and coprecipitates with Fe, Al and Ca solid phases.19) The soil factors such as pH, Eh, organic carbon content and the mineralogy may affect the dynamics of the metals. The pH of the soil has a dominant effect on solution concentration of metals, by influencing the distribution of metals between the soil and the solution.20) At high pH (above neutral pH), soluble Cd might be precipitated as cadmium phosphates, carbonates, or hydroxides.21) Street et al. stated that above pH 7.2, there was approximately a hundredfold decrease in Cd^{2+} activity for each unit increase in pH.22)

Table 2. Total amounts of Cu and Zn in membranes after the 16 weeks of incubation in the sludge only sample.

Incubation Condition	Chelating Ion Exchange		Anion Exchange	
	Cu	Zn	Cu	Zn
	(μg)			
Aerobi	80	65	45	18
Anaerobic	17	8	16	6

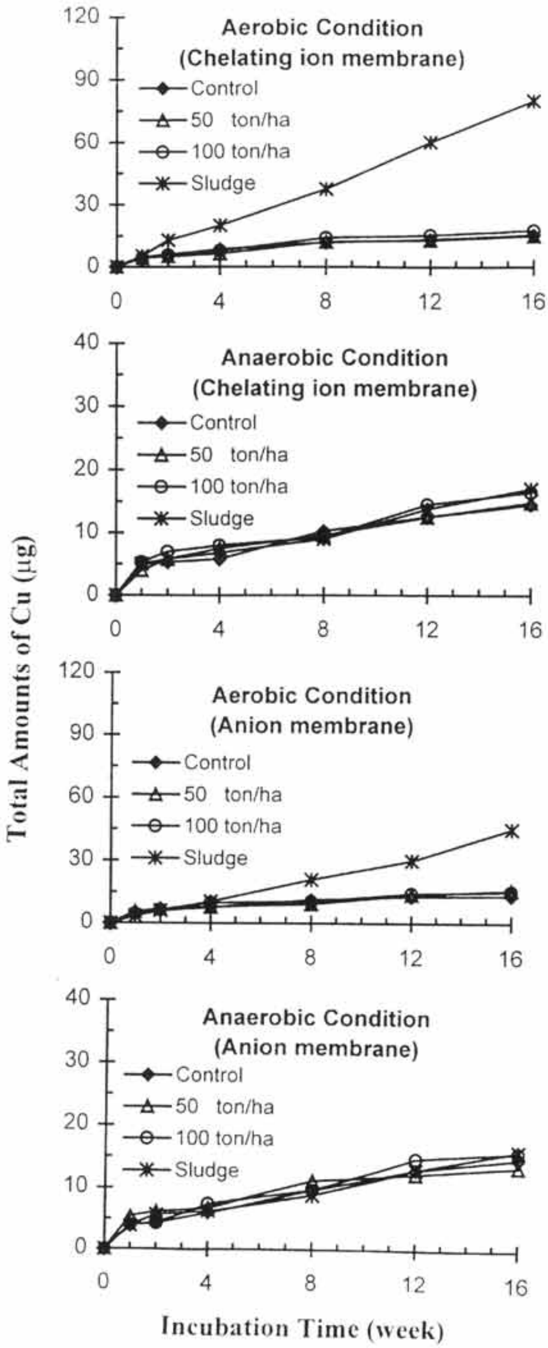

Fig. 6. Changes in total amounts of chelating ion and anionic forms of Zn during incubations.

Fig. 5 and 6 show the changes in the total amounts of Cu and Zn in anion and chelating ion exchange membrane during the aerobic and anaerobic incubation. For all of the treatments, the total amounts of Cu and Zn in chelating ion and anionic forms slightly increased throughout the incubation period under both incubation conditions. The trend might be expected since increasing incubation time would permit more decomposition of sludge and release available Cu and Zn from the organic source.

In "Control" and "Soil-Sludge mixtures" treatments, the mean values of total amounts of Cu and Zn in anion and chelating ion exchange membrane after the 16 weeks of aerobic and anaerobic incubations were about 16 g for Cu and 7 g for Zn. The total amounts of Cu and Zn in chelating ion exchange membrane differed little from the values in anion exchange membrane. Despite the high organic carbon content, very little of the Cu and Zn were chelated or anionic forms. It is probably because the pH of sludge-treated soils was high both under aerobic (up to 7.1) and anaerobic condition (up to 8.0). Especially in calcareous soil, free metal ions are rapidly adsorbed or precipitated in the solid phase and the solution concentration remains low.[22)]

In "Sludge" treatment, the total amounts of Cu and Zn in chelating ion exchange membrane after 16 weeks of incubation were about 80 g for Cu and 65 g for Zn under aerobic condition; 17 g for Cu and 8 g for Zn under anaerobic condition. The total amounts of Cu and Zn in anion exchange membrane after 16 weeks of incubation were about 45 g for Cu and 18 g for Zn under aerobic condition; 16 g for Cu and 6 g for Zn under anaerobic condition (Table 2). The total amounts of chelated or anionic forms of Cu were greater than those of Zn under both incubation conditions. The total amounts of Cu and Zn in anion and chelating ion exchange membrane were greater under aerobic condition than under anaerobic condition. The total amounts of Cu and Zn in chelating ion exchange membrane were greater than the values in anion exchange membrane under both incubation conditions. The results show that the decomposition of sludge is a source of kinetically labile forms of heavy metals, with more metals available under the aerobic condition. Sludge constituents can lower metal activity in soil solutions via complexing by soluble ligands or colloidal surfaces. Heavy metals are chelated by organic ligands and may endager adjacent water bodies. The chelated metal is usually considered to be in a more available form for plants.[23)] Avnimeleth and Raveh reported that decomposition of chelates in the anaerobic systems was very slow and insignificant,[24)] but decomposition in aerobic systems was relatively fast, leading to residual chelation capacity of only 0.1~1% of the initial value after a 74 day incubation. Butterworth and Alloway found that a considerable amount of Cd in the sludge-amended soil solution occurred in the cationic (Cd^{2+}) form, while soluble Cu was largely present as stable complexes, and Zn was distributed between these forms.[25)]

Conclusions

The chelated or anionic forms of Cd, Cu and Zn in the soils, treated with sludge at the rate of 50 or 100 dry Mg ha^{-1}, were not different from those of untreated soil during the 16 weeks of incubation in this study. However, the sludge alone, when incubated under the same condition resulted in rapid rise in chelated and anionic forms of Cu and Zn with incubation time under aerobic condition only. The concentrations of chelated forms were 2-5 times higher than anionic form throughout the incubation period. Thus, it is speculated that the released Cu and Zn due to decomposition of sludge, when mixed with soil, could have been rendered insoluble by the interaction with inorganic soil constituents.

The results obtained from this study suggest that the risk of contamination by Cd, Cu and Zn added with this sewage sludge at rates of 50 and 100 dry Mg ha^{-1} to agricultural land may be negligible. It should be noted that the results from this investigation show the short-term effects of sewage sludge application on the speciation of heavy metals. The long-term effects of sewage sludge on the speciation of heavy metals in soil and the verification of individual species of chelated or anionic forms need further study.

Acknowledgments. The authors gratefully acknowledge the financial sup-port for this research by the City of Winnipeg.

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