

THE DISTRIBUTION AND FATE OF
Cu AND Zn IN
TREATED MUNICIPAL SEWAGE SLUDGE

by

Jessica Audette

A thesis
submitted to the University of Manitoba
in partial fulfillment of the
requirements for the degree of
Master of Science
in the
Department of Soil Science

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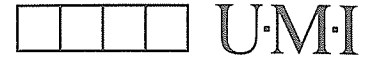
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A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of

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ABSTRACT

The City of Winnipeg sewage sludge disposal program usually involves the application of dewatered sludge to agricultural land. When this is not feasible, sewage sludge is disposed of in landfills. Crop nutrient benefits are derived from the sludge. However, there are concerns associated with the fate of metals added with the sewage sludge. A better understanding of the chemistry of the release of metals from sewage sludge is necessary to predict the potential for the contamination of the food chain by sludge-borne metals.

Sewage sludge from the City of Winnipeg's Northend Water Treatment Facility was subjected to chemical fractionation to study the distribution of sludge-borne Cu and Zn. Sequential chemical fractionation indicated that Cu and Zn were distributed between the oxide and organomineral fraction (that released after treatment with acidified ammonium oxalate) and the organic fraction (that released by peroxidation), and that very little of the total Cu and Zn were either water-soluble or exchangeable.

The acidity of the organic functional groups and the organic carbon content of the sewage sludge was also determined. Total acidity due to the organic functional groups was 245 cmol kg^{-1} , with 224 cmol kg^{-1} due to phenolic OH groups and only 21 cmol kg^{-1} due to carboxylic groups.

groups.

A second study was initiated to determine the effect of ionic strength of the extracting solution on the amount of Cu and Zn released from the sewage sludge. Solutions of CaCl_2 and KCl were used as extractors at various ionic strengths ranging from 0.001 M and 3.0 M. At ionic strengths < 1.0 M, the extracting solution had little effect on the amount of Cu and Zn released. When the ionic strengths of the extracting solutions > 1.0 M, increasing amounts of Cu and Zn were released, possibly due to dissolution of the solid phases of the sludge matrix. For both extractants, CaCl_2 and KCl , it was found that much greater amounts of Cu than Zn were released. This was attributed to the difference in electron configurations between Cu and Zn which would result in different bonding mechanisms.

A final experiment examined the fate of sludge-borne Cu and Zn upon addition to the soil. This was carried out as an incubation experiment for 16 weeks using sewage sludge and two soils which varied in texture, a heavy clay and a clay loam. Chemical fractionation of the sludge-soil mixtures was carried out at specific time intervals to determine if any changes in the metal distribution had occurred. There did not appear to be an increase in soluble or exchangeable Cu and Zn even though there was a concurrent loss in organic carbon content. Plant available fractions

(DTPA extractable) of Cu and Zn increased during the first week of the incubation period but declined thereafter. Organically bound Cu and Zn remained fairly constant throughout the time period investigated and the Cu and Zn associated with the organomineral fraction increased.

The results of this investigation revealed that the risk of crop toxicities resulting from Cu and Zn added to the soil as a sewage sludge amendment is low. In fact, the data showed that Cu and Zn reverted to stable inorganic forms upon addition to soil.

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Sincerely,

Jessica

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I. INTRODUCTION

The disposal of sewage sludge on agricultural land is by no means a new concept and has been incorporated by many urban centers. Crop producers have recognized the agronomic benefits associated with the application of sludge, mainly due to the supply of nutrients such as N, P, K, and S, and trace elements such as Cu and Zn. Sewage sludge is carbon-rich, it contains nutrients but is contaminated with pollutants when added to the soil. In terms of persistence, experience has shown that the physical presence of the sludge material following application of dewatered sewage sludge to agricultural land around Winnipeg usually did not exceed two growing seasons. Therefore, it is expected that most of the chemical changes occur rather rapidly following its disposal on land. Since contamination and pollution of soils by heavy metals as well as trace metals are real possibilities, the study of the chemical transformations and fate of organic and inorganic constituents of sludge is judicious. Results obtained in the short term may provide information on the long-term effects of sludge application on soil, water and food quality.

The speciation of the elements is important in the consideration of bioavailability and mobility of the elements in a sludge-soil system (Silviera and Sommers 1977; Bell *et al.* 1991). Also, the soil factors such as pH, Eh,

organic matter content and the mineralogy may affect the dynamics of the metals (Lindsay 1979; McBride 1981; Mott 1981; Dudley *et al.* 1986). Many examples of methods of metal fractionation into the various components of the sewage sludge were found in the literature (Stover *et al.* 1976; Emmerich *et al.* 1982; Steinhilber and Boswell 1983). The metal fractionation results were variable depending on the method used, the metals under investigation and the source of the sludge material. Thus, there is a need for a reliable speciation scheme. The difficulty, however, lies with the complex and variable nature of the sludge material.

Another approach that has been used to determine the stability of the metals within sewage sludge is the examination of the organic functional groups. Upon the addition of sewage sludge to soil, microbial processes act on the material, resulting in changes in metal complexing functional groups in the sludge organic fraction. Therefore, one may expect changes in binding mechanisms between the metals and the sludge, possibly transforming the metals to more hazardous forms.

This project was undertaken to characterize the sewage sludge with respect to the organic functional groups and the metal distribution (specifically Cu and Zn) within the sludge matrix. A second study was initiated to determine the feasibility of the metal removal from the sludge under conditions of varying ionic strength. The third objective

was to examine the sludge and soil over time to determine if any changes occurred in (i) the organic fraction, and (ii) the metal distribution pattern.

II. LITERATURE REVIEW

2.1 The production of sewage sludge

Sewage sludge is a waste product resulting from the concentration of domestic sewage, urban runoff, and industrial wastes through a waste treatment system. Most large communities process the sewage sludge before returning the waste water and sludge to the environment. Treatment processes of waste water can vary from simple settling lagoons to full scale operations involving many steps to ensure environmentally sound waste water disposal.

Sewage lagoons are often used in municipal areas where the majority of wastes are domestic or on individual farms involving concentrated animal operations. Waste water is pumped into the lagoon and the solids are allowed to settle. The water is removed from the top by pumping or simply allowing it to drain into a drainage system and periodically, the solids are disposed of onto land.

A waste water treatment plant is much more complex. In general, the process involves a primary treatment, a secondary treatment and an activation process. The primary treatment is a sedimentation process that allows particulate matter to settle. According to Sterritt and Lester (1983), insoluble forms of heavy metals are removed in this process. However, the fraction of metals removed varied from 20 to 95% (Lester 1987).

A secondary treatment is intended to speed up the breakdown of remaining organic solids. This is accomplished by passing the waste water through an oxygen reactor tank to encourage the natural bacterial population. With this process, soluble metals are removed from the waste water by uptake into the microbial biomass. Again, the fraction of total soluble metals removed can vary immensely (Sterritt and Lester 1983).

The addition of microorganisms to the waste water constitutes an activation process. Sludge digestion is allowed to proceed either aerobically or anaerobically. Digestion of the sludge produces a stabilized sludge which can be applied to agricultural land, as well as waste water that is sufficiently purified to allow disposal into the river system.

The composition of sewage sludge is extremely variable. It depends largely on the source of the original material and the treatment process. Sewage sludge is a highly carbonaceous material. Organic carbon contents may range from 20 to 37% (Riffaldi *et al.* 1983). Ashing the sludge sample at 450°C has been used to estimate the inorganic fraction. Using this method, Miller *et al.* (1986) reported approximately one third of a manure sludge represents inorganic material. In sewage sludge, a greater inorganic fraction could be expected due to additions from urban runoff and industrial wastes. It has been suggested that

the inorganic fraction may include oxides, hydroxides, carbonates, sulfides and phosphates (Dudley *et al.* 1986; Miller *et al.* 1986; Lake *et al.* 1984).

The disposal of sewage sludge has become a major concern from many standpoints. Economic constraints exist which limit the distance of transport and the types of treatment processes which ensure a safe product for disposal. For instance, land application of sewage sludge is governed by the level of pollutants which become concentrated in the sludge during treatment. Also, the costs of additional treatment required for sludge which is to be applied to agricultural land has increased due to increasing energy costs. Landfill is no longer a feasible alternative as costs have risen and the availability of sites has decreased. Incineration practices may result in harmful emissions and marine disposal may have an impact on water quality and sediment contamination. Disposal of sludge on agricultural land is an alternative that is being considered by large urban centres where cropping is a mainstream economic activity.

2.1.1 Beneficial properties of sewage sludge.

The disposal of sewage sludge on agricultural land can be beneficial to soil quality with respect to the physical condition and plant growth requirements, mainly nutrients.

Sewage sludge affects the physical condition of the soil. Metzger and Yaron (1987) reviewed the subject and

have attributed these effects to the persistence of sludge organic carbon in the soil medium. The addition of sludge organic material enhanced the soil's water holding capacity. This was due to structural modifications, particularly increases in total porosity which, in turn, resulted in a lower bulk density. Increased aggregate stability was another result of sludge amendments. Experimental work showed that the microbial activity was responsible for the aggregation processes. The combined effects of increased porosity and aggregation resulted in an improvement in both the initial infiltration rate and the steady state infiltration rate. The authors concluded that long-lasting improvement of the soil physical status can be obtained by successive and moderate (yearly rate of 7-25 tonnes ha⁻¹) applications of sludge.

Sewage sludge provides major nutrients such as nitrogen, phosphorus and potassium as well as many of the trace elements required by plants. Coker (1966) demonstrated that sludge used as a fertilizer resulted in the same yield increase in barley as that produced by equivalent amounts of inorganic fertilizer including N, P, and K. Milne and Graveland (1972) confirmed that increases in grain yield were obtained with increasing amounts of sludge added to several Alberta soils, varying from clay to sandy loam. Cunningham *et al.* (1975a) tested sludge from various sources for yield response. They found

significant crop yield increases for sludge application rates up to 125 tonnes ha⁻¹ and using regression analysis, found a direct correlation between yield increases and the amount of N, P, and K supplied by the sludge. However, at higher rates of sludge application (251 and 502 tonnes ha⁻¹, based on oven-dry solids), toxicity effects were recognized as yields were decreased. These yield reductions were found to be correlated to the increasing supply of metals, specifically Cu, Zn, and Ni.

The application of sludge to soil enhances microbial numbers and consequently, microbial activity (Goda *et al.* 1986). The result of the enhanced microbial activity is quicker nutrient cycling and thus greater plant availability of nutrients.

2.1.2 Potentially Harmful Effects

As regulations covering stream pollution became stricter, the supply of sewage sludge for land disposal increased. The philosophy governing the use of sewage sludge for agricultural purposes is the benefits derived from N, P, K, and micronutrients. In counter balance, whenever N, P, K, and micronutrients are in excess, potentially harmful effects must be considered.

Initially, the amount of sewage sludge applied to the land was determined by the rate of nitrogen that one wanted to supply (Coker 1966). Later, however, it was realized that some sludge resulted in yield decreases even though the

optimum rate of nitrogen was supplied. It was then suggested that the sewage sludge application rates should be limited by the concentration of metals which they contain (Cunningham *et al.* 1975a).

It has been difficult to establish general loading limits for agricultural application of sewage sludge because the metal concentrations vary immensely (Cunningham *et al.* 1975a; Wollan and Beckett 1979; Hue 1988). In Germany, Kloke *et al.* (1984) have reported threshold values of certain heavy metals in sewage sludge and soil based on total content but have recognized the need to speciate the metals as different chemical forms influence their availability to plants. The forms of metal which exists depends on many interacting factors. These include soil characteristics such as cation exchange capacity, pH, clay and organic matter content, as well as time of sludge application relative to cropping, treatment processes to which the sludge had been subjected and also the type of crop to be grown on the sludge-amended soil. Researchers from Germany have used results from long term field experiments to reassess the heavy metal content for sewage sludge and soils that could limit sludge application to land (Sauerbeck and Styperek 1987). These authors also stressed the importance of "plant available" metals rather than total metal concentrations. To establish safe limits, the soil-plant transfer factor was considered. This value provides a

ratio of heavy metal content in soil to that found in the plant. Thus, phytotoxic levels of heavy metals were used to determine the upper limits for heavy metal concentrations in the soil. It is important to note that these soil-plant transfer factors varied with the crop species, the soil type and pH.

In a series of experiments using several different sludges, Cunningham *et al.* (1975a,b,c) found that low rates of sludge application (63-125 T ha⁻¹ based on oven dry solids) resulted in significant yield increases, but yield decreases resulted at higher rates. These effects did not persist since the yield of subsequent crops showed that the toxic or beneficial effects due to sludge had largely disappeared. The authors suggested that the results indicated a conversion of the metals to less plant available forms over time. It was also demonstrated that metals associated with the sludge were not as toxic (i.e. resulted in lower yield reductions and lower tissue concentrations) as metals supplied to the plant as an inorganic salt. Evidence of increased soil pH after incubation with limed sludge may account for some of the reductions in metal availability over time (Goda *et al.* 1986).

The application of sludge containing high concentrations of heavy metals has sometimes resulted in toxic effects on native microbial populations. Vedy *et al.* (1986) conducted incubation experiments to study the effect

of metal-enriched sludge on microbial activity. This was accomplished by measuring CO₂ evolution. As well, adenosine triphosphate (ATP) concentrations were measured to obtain estimates of total biomass. It was found that CO₂ production from the metal enriched samples was always less than the control and that the severity of the toxicity varied with the nature of the metal. ATP biomass was reduced for all metal-enriched samples.

Goda *et al.* (1986) have summarized the results of an investigation of sludge application to agricultural land in Japan. They also found yield reductions after repeated applications of sludge. It was suggested that the unbalanced composition of elements in the sludge (less K relative to N and P) and the high soil pH, which limits micronutrient availability, caused the reductions in yield. However, analysis of the plant tissue showed neither deficient nor excessive concentrations of any elements. The investigators later showed that toxicities which inhibited root elongation arose from synthetic cationic polymers which were added to the sludge as coagulants.

Weerasinghe *et al.* (1985) have examined the presence of polychlorinated dibenzodioxins and polychlorinated dibenzofurans in sewage sludge. Several congeners were detected, but the authors were not able to report any definite hazards associated with these compounds. The possible sources of contamination were suspected to be wood

processing operations, service stations, dry cleaning, pesticide and printing operations as well as commercial and academic laboratories.

Nitrate leaching can be a problem associated with sludge-amended soil. Furrer and Stauffer (1986) have investigated the potential for groundwater contamination by nitrate after additions of pig slurry and sewage sludge. Their results showed that nitrate leaching depended mainly on the type of plant cover. Permanent grass cover resulted in very little leaching while fallow resulted in large losses of nitrate due to leaching. The researchers also studied the influence of increasing N-application rates on nitrate losses and found that the losses on the grass cover plots did not increase with increasing N-application. Thus, it was concluded that the practice of fallow was more important than N-application rates when considering nitrate losses.

2.2 Fate of sewage sludge in sludge-amended soil

Land disposal of organic wastes carries associated risks of contamination and pollution by heavy metals. The addition of such material to the soil system results in a variety of chemical and physicochemical reactions as well as microbiological processes, which, in turn, result in the transformation of the sludge to new organic substances and mineralization products. The hazard associated with trace

elements is most likely related to changes in the metal-complexing functional groups in the sludge organic fractions which are altered mainly by microbial activity (Schaumberg *et al.* 1980). Therefore, the persistence of the organic fraction of the added sludge is an important consideration in the study of sludge effects on the soil medium.

In a review by Metzger and Yaron (1987), sludge organic carbon mineralization rates were found to be highly variable and affected by the type of treatment to which the sludge was subjected before application. For anaerobically digested sludge, 20-40% of the organic carbon was degraded within four months of incubation with soil, while undigested sludge had much higher amounts of mineralizable organic carbon. It has been suggested that a proportion of the organic fraction in sludge was either resistant to microbial degradation or was immediately converted to more stable humic forms. An investigation by Hohla *et al.* (1978) provided conclusive evidence of the persistent nature of sludge organic carbon. The study involved repeated applications of sewage sludge over six years. This resulted in an increase in organic carbon content of the surface horizon of the soil. Their data showed that 60% of the sludge organic carbon was lost during this period. A study by Akinremi *et al.* (1991) using the Century Model to simulate organic matter levels in soil following sewage sludge application to land showed that there was little

increase in stable soil organic matter two years after sludge application. This, however, does not preclude any short-term benefits to soil structure and benefits from the release of plant available N.

The mineralization of organic nitrogen has also been used as an indicator for the decomposition of sludge. The nitrogen in liquid sludge exists mainly as NH_4^+ -N and organic-N. Although plants can utilize NH_4^+ -N, substantial losses due to volatilization can occur in certain conditions. Organic-N must first be mineralized to NO_3^- or NH_4^+ for it to be available to the plant. In an effort to determine which factors affect the mineralization of nitrogen, Barbarika *et al.* (1985) examined five published incubation studies involving sewage sludge from eleven different sources. Statistical analyses showed that the nitrogen mineralization rate was effected by the total N content, the temperature at which the incubation was carried out, the duration of the incubation, and the C/N ratio of both the sludge and the soil. This is consistent with the results of a recent incubation study which also found that temperature and the total N content were important factors in the control of the N-mineralization rates (Cerrato *et al.* 1990). These authors examined three rates of sewage sludge incubated with soil for 40 weeks. The data showed that high rates of N were mineralized early in the experiment, suggesting that a labile organic fraction had rapidly

decomposed. After four weeks, the rate of N mineralization decreased and became constant as a less labile organic fraction decomposed. In total, approximately 30% of the N added was mineralized in the samples incubated at 25°C. Magdoff and Amadon (1980) estimated 55% of the organic-N was mineralized in the first year of a field experiment in which sludge was added to corn and hay crops.

2.3 Fate of sludge-borne metals

2.3.1 Bonding mechanisms

The importance of soil organic matter in metal retention has long been recognized. Thus, many scientists have attempted to define its chemistry to aid in the understanding of the metal complexing characteristics. Since sewage sludge is a highly organic material, many of the processes involving metal complexation would be expected to be the same as for soil organic matter.

The definition of soil organic matter refers to fresh or partially decomposed material as well as those organic compounds which do not occur in the form of fresh or partially decayed plants and animals (Stevenson 1982). According to Schnitzer and Kodama (1977), organic matter can be simplified by dividing it into non-humic and humic substances. Non-humic substances are defined as those which still possess recognizable physical and chemical characteristics such as carbohydrates, proteins, peptides,

amino acids, fats, waxes, and low molecular weight organic acids. These compounds can be readily attacked by microorganisms to form new breakdown products. Humic substances are chemically more complex and resistant to microbial breakdown. Humic substances can be partitioned into three major fractions: humic acid, fulvic acid, and humin. These fractions were differentiated based on their chemical characteristics. It was found (Stevenson 1982) that FA was less polymerized, had a lower molecular weight, but possessed greater exchangeable acidity than did HA. Further analysis revealed that both HA and FA had a high content of oxygen-containing functional groups but total acidity and carboxyl acidity of FA was approximately twice that of HA and the ratio of carboxyl groups to phenolic OH groups was greater for FA than for HA (Schnitzer and Kodama 1977). These properties result in significant differences with respect to metal complexation reactions. It has been suggested that metals bound to the humic acid fraction occur as insoluble complexes while those associated with fulvic acid tend to be water soluble (Stevenson and Ardakani 1972).

Miller and Ohlrogge (1958) have confirmed the presence of water soluble chelating agents in organic materials. Since the 1950's, it was observed that manure could relieve some nutrient deficiency symptoms in the soil. The researchers used different organic materials including fresh dairy manure, dried alfalfa, and animal faeces. Extracts of

the organic materials were prepared and the pH was adjusted. To test the chelating ability of the organic extract, soils which were labelled with ^{65}Zn were mixed with the solutions and equilibrated. The amount of Zn removed from the soil was determined from the activity of Zn in the extract solution. The presence of complex formation was established by comparison of the removal of Zn by a cation exchange resin from the organic extract and from ionic solutions of Zn. The results indicated that Zn was indeed chelated in the extract as very little Zn was removed (0-24%) by the resin whereas 90-100% of the Zn was removed from the ionic solutions. The authors were also able to demonstrate the importance of the degree of decomposition of the organic material with respect to its ability to complex inorganic constituents. It was found that decomposition greatly reduced the ability of the extract to remove Zn from the soil. This suggested that decomposition of the soluble organic material involved the loss of metal-complexing sites either by oxidation to CO_2 (Dudley *et al.* 1986) or by the formation of polymerization products (Steinhilber and Boswell 1983).

Schnitzer *et al.* (1969) have conducted an extensive investigation of the chemical structure and properties of soil humic substances. The Bh horizon of a Podzolic soil was used in the study. The extracted organic matter was classified as fulvic acid (FA) as it was soluble in both

dilute alkali and acid. Using chemical, spectroscopic, thermographic and x-ray methods, the researchers were able to characterize the functional groups with respect to the amount and type. Schnitzer and Gupta (1965) developed simple titration methods for the quantification of functional groups in soil organic matter. Carboxyl groups were determined by ion exchange with $\text{Ca}(\text{CH}_3\text{COO})_2$ and "total acidity" was determined by equilibration with $\text{Ba}(\text{OH})_2$. The results indicated that all of the functional groups of this particular FA were oxygen containing functional groups and the greatest proportion were carboxyl groups. This information was used in conjunction with further studies involving metal-FA complexes to determine the mechanism of the interactions. By selectively blocking alcoholic OH, phenolic OH, and carboxyl groups, it was found that alcoholic OH groups were not involved in metal-FA interactions but two reactions were identified in which phenolic OH and carboxyl groups participated. The first involved both acidic COOH and phenolic OH groups simultaneously, while the second reaction was relatively minor and involved only less acidic COOH groups. As more fulvic acid ionization data became available, Gamble et al (1970) were able to confirm the existence of a bidentate chelate which complexed Cu^{2+} with COO^- and phenolic OH groups of the fulvic acid. The stability constants of water soluble metal-FA complexes increased with an increase in pH

from 3.5 to 5 (Schnitzer 1969). It was suggested that this was due to the increased ionization of the functional groups. The use of infrared spectroscopy confirmed the conversion of COOH to COO⁻ groups, providing the means for the bonding of metal ions by electrovalent linkages. Similar experiments were carried out by Tan *et al.* (1971) using extracts of poultry litter. They obtained stability constants for Cu-complexes which were in agreement with those reported by the previous authors, but obtained higher values for the Zn-complexes. Infrared analysis indicated an increase in carboxyl stretching vibration for the metal treated extracts over the non treated extracts. As well, Tan *et al.* (1971) observed a shift in the OH or NH bands, possibly indicating the formation of metal chelates with OH and NH₂ groups. Earlier studies had not been able to prove this conclusively.

Riffaldi *et al.* (1983) provided further evidence of metal complexation with the acidic carboxyl and phenolic OH groups of FA extracted from sewage sludge. Significant positive correlations were found between Cd adsorption data and the FA carbon content, carboxyl and phenolic OH groups.

Sposito *et al.* (1977) studied the acidic nature of fulvic acid extracted from a sewage sludge-soil mixture. The first study was initiated to obtain a better understanding of the change in the chemistry of the soil solution upon addition of sewage sludge to agricultural land

(Sposito and Holtzclaw 1977). The behaviour of fulvic acid in solution was assumed to be similar to that of polyacidic organic molecules. However, the chemical composition, molecular weight, and acidity of its functional groups varied considerably resulting in complex solution chemistry. The titration of FA at various concentrations with either KOH or HCl provided data which suggested that the FA contained functional groups ranging in acidity from very strong (ionized at $\text{pH} < 2$) to very weak (ionized at $\text{pH} > 10$). The strongly acidic groups were thought to be sulfonic acid groups, and the more weakly acidic groups were thought to be the carboxyl, N-containing groups, phenolic OH and SH groups. The titration curve was found to be strongly dependent on the concentration of FA in solution, indicating inter- and intramolecular associations between the FA molecules. Thus, the geometric configuration of the FA and the acidity of the functional groups could change remarkably with a change in solution properties. This was confirmed in a subsequent study where it was found that the number of titratable protons decreased with both an increase in FA concentration and in ionic strength due to hydrogen bonding among FA molecules (Sposito *et al.* 1977). The change in conformation of the organic polymer has implications for its metal binding capacity as well as for the release of metals under various extraction conditions (Silberberg 1968; Theng 1979; Gamble *et al.* 1985; Sojo *et al.* 1989; Wang *et al.* 1992).

The inorganic soil fraction also has the ability to adsorb and complex metals. The surface charge of clay minerals provide binding sites for metal ions. Thus, the amount and type of clay minerals present in the soil can significantly affect metal sorption. As well, any factor that can affect the charge of the clay surface, such as pH, can affect the sorption process.

Hydrous oxides in the soil also play a significant role in the retention of metals (Mott 1981). Oxides have large active surface areas consisting of hydroxyl and aquo-groups. Two mechanisms of adsorption for iron oxides have been described. Specific adsorption, as described by Kalbasi *et al* (1978), is a covalent bonding between the divalent cation and the hydroxyl or aquo- group. Two H⁺ ions are released for every divalent cation adsorbed. The researchers suggested the formation of an olation bridge and ring structure. Cations held in this manner are bound more strongly than those adsorbed non-specifically. Non-specifically adsorbed ions can be replaced by cations in neutral salt solution. The micronutrient cations in soil, such as Cu and Zn, would be expected to be held by both types of bonding mechanisms, giving them a range in plant availability (Goh *et al.* 1988). Again, adsorption of metals is highly pH dependent. McBride (1981) observed that an increase in pH caused the adsorbed ion to become much less exchangeable (i.e. the ratio of specific to non-

specific bonds increased).

2.3.2 Distribution of metals in the sludge and sludge-soil system

Metals released into the soil system are subject to many different reaction processes. Depending on the properties of the soil medium and the soil solution, metals can be adsorbed onto the matrices described above, precipitated as insoluble compounds, occluded within newly formed material or remain in the solution as individual ions or soluble organic complexes where they may ultimately be taken up by the plant (Adriano 1986).

Sewage sludge incorporation into agricultural soils is a source of heavy metals to the sludge-soil system. Waste treatment facilities remove metals from the waste water stream by concentrating them in the sludge through precipitation, adsorption or uptake reactions (Sterritt and Lester 1983). Thus, these metals may already be complexed with organic ligands of the sludge and not available to the soil solution. However, as the sludge organic matter is decomposed, the metals may be released. It is therefore imperative to understand how the sludge influences the soil system with respect to its capacity to retain metals.

Since the 1970's, many studies have been initiated to fractionate sewage sludge and sludge-amended soils to determine the distribution and speciation of metals (Lagerwerff *et al.* 1976; Steinhilber and Boswell 1983; Hue

et al. 1988; Bell *et al.* 1991). Lagerwerff *et al.* (1976) noted a remarkable difference in the extractability of Cd, Cu, Pb, and Zn from two sludges; one from Baltimore, MD, the other from Washington, D.C. They attributed this difference to the pH of the sludge. The lower pH of the Baltimore sludge resulted in greater extractability of the metals especially Zn and Cd over that extracted from the Washington sludge. It was suspected that the Washington sludge had been limed as part of the treatment process. The authors simulated weathering using 30% H₂O₂ and again measured extractable metals. The data showed a 6-7 fold increase in extractable Cu compared to only 1.5-2 fold increase in extractable Cd and Zn after oxidation. The prevalence of easily oxidizable organocopper complexes relative to such species of Cd and Zn was evident from the data obtained.

A fractionation scheme for metals in sewage sludge was devised by Stover *et al.* (1976). They modified existing methods for the fractionation of metals in soils and tested the procedure using pure metal precipitates. Twelve different sludges were subjected to a sequential extraction procedure starting with KNO₃ which displaced metals bound by exchange sites on sludge inorganic and organic components. The second extractant used in the fractionation procedure was KF which removed metals through the formation of soluble fluoride complexes with minimal solubilization of organically-bound metals. Metals chelated or complexed by

the organic matter of the sludge were extracted with $\text{Na}_4\text{P}_2\text{O}_7$. Following this, EDTA reagent was used for the dissolution of metal carbonates. The last step involved the use of HNO_3 which dissolved nearly all metal sulfides and other metal species not extracted previously. The results from this study revealed a considerable variation in the percentage of total metals extracted among the sludge used in the experiment and variation among the metals under investigation. The authors stressed the importance of the chemical properties of the sludge as well as the nature of the metals in determining the retention mechanisms of the metals in sludge. In general, it was found that a low percentage of the metals were exchangeable, less than 2% for Zn and 1-27% for Cu and Ni and 0% for Cd and Pb. According to this extraction procedure, the greatest proportion of the metals existed mainly as carbonates and sulfides, with the exception of Zn which was found to exist predominantly as organic complexes. Thus, the conversion of the metals to water soluble, exchangeable or sorbed forms by chemical or microbial processes would be necessary for plant uptake to occur.

Lake et al. (1984) reviewed recent methods of sequentially extracting metals from soils and sludge-amended soils. In general, the metals most easily removed were extracted first and stronger reagents were used in sequence to remove the more stable forms of metals. All of the

extraction techniques employed to fractionate metals used a reagent with a displacing cation to define exchangeable metals. To distinguish adsorbed and organically bound metals, acetic acid, and either sodium or potassium pyrophosphate or sodium hydroxide were used as extractants. Some authors defined "available" metals with the use of the complexing agent diethylenetriamine pentaacetic acid (DTPA). Ammonium oxalate has been used by several researchers to extract occluded or oxide bound metals (McKeague and Day 1966; Steinhilber and Boswell 1983; Miller *et al.* 1986). A strong acid was used as the final extractant to release residual metals. The authors have recognized the fact that the extraction procedures represent only arbitrary divisions between different metal forms, since reagents were not completely selective for one particular form.

Emmerich and his associates (1982) used an extraction procedure similar to Stover *et al.* (1976) to fractionate Cd, Cu, Ni, and Zn in 3 soils; a fine sandy loam, a coarse sandy loam, and a coarse loamy sand, as well as in sewage sludge, and soil-sludge mixtures. The data for the sludge fractionation corresponded closely to that reported by Stover *et al.* (1976). Metal recovery data from the soils indicated that most of the metals were extracted mainly by HNO_3 , which was defined as a residual fraction, a small proportion of the metals were extracted by EDTA, and in all cases less than 1% of the total metals were either

exchangeable or adsorbed. Of the metals investigated, only Cu was significantly associated with the organic fraction of the soil. After sludge treatment, the soil was again fractionated. The results obtained for the percentage of metals extracted were compared with calculated results based on the fraction of metals supplied by the soil and the sludge alone assuming that the chemical form of the metals had not changed during the study. From this comparison, it was shown that the speciation of Cu did not change significantly, with the added metal remaining in the organically bound form. Nickel and Zn percentages both indicated a change from organically bound and carbonate forms to the residual form. Analyses of the soils below the sludge-soil mixture revealed little or no change from the original soil extracts indicating that the metals in the soil were in stable forms. Thus, the authors concluded sewage sludge was controlling the chemical forms of the metals in the sludge-soil mixture as the percentages of metals extracted varied less than 10% between the three soils. A more recent study by Hue *et al.* (1988) examined the heavy metal availability to plants from three mineralogically different soils amended with sewage sludge. The results showed significant differences in the amounts of heavy metals accumulated in the test crop among the three soils. It was suggested that the differences in the adsorption capacity of the soils with respect to their

ability to retain heavy metals caused these effects. This contradiction to the previous study may be due to the markedly different soils used in the study compared with the relatively similar soils used by Emmerich *et al.* (1982).

2.3.3 Time-dependent changes in metal distribution from sludge-amended soils

Many researchers have fractionated sewage sludge to determine the distribution of heavy metals and their plant availability. Incubation studies involving soils amended with sewage sludge suggested changes in the chemical form of the metals in question, and possibly changes in the availability of metals to plants. Silviera and Sommers (1977) investigated the metal distribution in two different soils incubated with sewage sludge from three sources. The samples were sequentially extracted at 0, 7, 14 and 28 days. Water-soluble and 1 M KNO_3 extractable metals comprised less than 2% of the total concentration and did not show a significant change over the time period studied. Several researchers found that very small proportions of the total metals in sewage sludge or sludge-amended soils exist as soluble or exchangeable forms (Lagerwerff *et al.* 1976; Sposito *et al.* 1983; Steinhilber and Boswell 1983). Copper extracted with DTPA increased with time for all sludge in both soils whereas Zn and Cd only increased in 2 of the sludges (Silviera and Sommers 1977). Thus, the authors suggested that the potential for plant uptake of the metals

(assuming DTPA extractable metals represents plant available metals) varied with the sludge applied and the time after application.

Lagerwerff *et al.* (1976) used a different approach to determine the effect of degradation of the organic matter in the sewage sludge on the metal distribution. This was accomplished by oxidizing the sewage sludge in dilute H_2O_2 to simulate weathering. Subsequent extractions using H_2O and 0.01 M HCl revealed an increase in the extractability of Cd, Zn, and especially Cu in comparison to that extracted before the oxidation treatment.

A long-term field study of sludge amended soils was initiated in 1979 to compare the solid-phase forms of Cu, Zn, Ni, Cd, and Pb (Sposito *et al.* 1983). Results from the sequential fractionation of the samples revealed a trend to increasing percentages of metals in the EDTA fraction (that which is assumed to be associated with carbonates) and the HNO_3 fraction over the four years of the study. It was suggested that the gradual mineralization of the organic matter in the applied sewage sludge caused a shift toward precipitated inorganic forms of the metals in the sludge-amended soils. Similar results were reported previously by Wollan and Beckett (1979). Steinhilber and Boswell (1983) have reported metal fractionation results from two different sewage sludges aged for a two year period. Their findings were inconclusive which indicated that sludges may be

affected very differently by weathering.

An incubation study using sewage sludge and two soils, one acidic and one near neutral pH, produced results which showed a correlation between the amounts of metals extracted by 0.01 M CaCl₂ and the pH of the mixture (Dudley et al. 1986). During the first two weeks of incubation, the pH increased into the alkaline range. Soluble Zn declined and soluble Cu increased. This was attributed to the concurrent increase in soluble C resulting in organic complex formation with Cu. Beyond 4 weeks of incubation, the pH declined and soluble Zn increased again. Soluble Cu, however, decreased during this period, likely due to losses of soluble organic materials via oxidation.

A comparison of heavy metal extractability from sludge-amended and metal salt-amended soil was conducted by Bell et al. (1991). Sewage sludge or Cd salt was added to field plots at rates calculated to supply the same amount of Cd. Nine years later, soil samples were taken and fractionated using 4 extractants. The percentages of Cd released in each fraction indicated the largest proportion existed as exchangeable Cd. This was true for both the Cd salt and sludge treatments. Zinc and Mn were in contrast to the results for Cd, as they were extracted mainly as associations with oxides with very little of the total existing as exchangeable metals. Cadmium was more labile than Mn and Zn in this soil and thus would have a greater

potential for contamination of the soil and food chain. A comparison of the Cd salt treatment and the sewage sludge treatment demonstrated that the proportion of Cd, Zn and Mn associated with the oxide pool was always greater for the sewage sludge treatment than for the Cd salt treatment. The difference between the sewage sludge and salt treatments was attributed to the greater quantity of paracrystalline Fe oxides which existed in the sludge-amended soil. The authors maintained that the sludge addition enhanced the retention of metals in an Fe oxide pool relative to the soluble and exchangeable forms.

2.4 Factors affecting the plant availability of heavy metals

Considerable effort has been expended to define "available" metals in terms of plant uptake. In general, it has been accepted that soluble and exchangeable metals are available to the plant. As well, some organically complexed metals have been found to be plant-available (Norvell 1972; Hue 1988; Petruzzelli 1989). The determination of soluble and exchangeable metals from the soil can be relatively simple. Aqueous extractions are usually used to determine water-soluble metals while a cation-exchanger can be used as an extractant for exchangeable metals in the soil. DTPA is a chelating agent which is believed to extract plant available metals. Soluble complexes would be formed with

free metal ions in solution thus reducing their activities. In response, metal ions desorb from soil surfaces or dissolve from solid phases to replenish the free metal ions in solution. Lindsay and Norvell (1978) have tested the effectiveness of the DTPA soil test in estimating micronutrient levels corresponding to crop responses in near-neutral and calcareous soils. They found very good correlations between DTPA extractable Zn, Fe, Mn, and Cu and crop responses. Thus, it was concluded that DTPA extractable micronutrients were representative of plant available micronutrients. The same conclusion resulted from an experiment several years later using sludge-amended soils (LeClaire *et al.* 1984). Other attempts to correlate plant available metals to a particular soil fraction using other extractants have met with limited success (Bloomfield and Pruden 1975; Cunningham *et al.* 1975a; Sims and Kline 1991).

There are many factors affecting the solubility or availability of metals to plants. They include soil pH, redox conditions, and the presence of soil components which are able to adsorb or retain metal ions. For example, organic ligands may form soluble complexes with metal ions and larger organic molecules may be responsible for occluding metals, and clay minerals and oxides may bind metals through exchange sites or may incorporate them into their structure (Theng 1979; Mott 1981; Gamble *et al.* 1985).

The effect of soil pH on the availability of

micronutrients to crops has been well documented. Schnitzer (1969) measured the stability constants of complexes formed between water soluble fulvic acid and divalent metal ions at pH 5.0 and 3.5. It was shown that stability constants were higher for all metals at pH 5 than at pH 3.5. The author suggested the increased ionization of the functional groups with the increase in pH caused the stability constants to increase. The pH dependency of the surface charge of clay minerals and oxides results in similar effects with respect to metal adsorption (Mott 1981). Thus, in general, an increase in pH results in greater metal retention by soil constituents and causes reduced plant availability. A comparison of composted and uncomposted sludge on the effect of Cd, Cu and Zn availability to lettuce and oat crops showed that addition of compost resulted in an increase in pH (Simeoni *et al.* 1984). The increase in pH was correlated to decreasing Cd and Zn availability to the plants. Similar results were reported by Dudley *et al.* (1986) for Zn and Ni. However, they found the opposite to be true for Cu. This was attributed to the greater affinity of Cu for organic acids in the soil solution, thus resulting in more soluble Cu at the higher pH. Hue (1988) proposed a similar mechanism for Mn which was found to be phytotoxic although the sludge applied contained relatively low quantities of Mn. Soil-solution Mn increased significantly with increased sludge rates. Thereafter, soil-solution Mn increased 100

fold in all sludge treatments between the time the lettuce crop was transplanted to the time it was harvested (about four weeks later). The pH of the soil solution at harvest was essentially the same for all treatments (pH 5.0). The extent of Mn complexation by the organic acids was determined by comparison of HPLC chromatograms of the untreated soil-solution to that treated with DTPA one hour prior to analysis. This method indicated 76-99% of the soluble Mn was organically complexed.

When a contaminated sandy soil was mixed with a selective cation exchanger, a heavy clay soil, peat or lime, before planting, significant yield increases were observed in all treatments (Kiekins and Cottenie 1984). This experiment demonstrated the possibility of reducing the plant availability of heavy metals by active processes, thereby confirming the importance of precipitation, complexation and adsorption mechanisms with regard to immobilization of heavy metals. In a study comparing sludge amendments to three different soils, Hue *et al.* (1988) found that the soil with the highest adsorption capacity could tolerate the highest sludge loading rate without any phytotoxic effects on lettuce crops. The importance of iron oxides in lowering the solution activity of heavy metals was noted by Bell *et al.* (1991). The fact that heavy metals readily form hydroxy species while the more prevalent cations such as Ca and Mg do not, permits the selective

adsorption of heavy metals to the oxygen and hydroxyl surface groups of iron oxides (Lindsay 1979).

The redox potential of the soil can influence the oxidation state in which heavy metals exist and thus can influence their availability to plants. For example, a decrease in redox potential may result in initial increases in the concentration of available metals owing to the dissolution of oxides (Petruzzelli 1989). Further decreases in redox potential may result in the formation of sulfides of Cd, Zn, Ni, Co, Cu, and Pb (Adriano 1986). Sulfides of these elements are quite insoluble thereby metal availability to plants is reduced. In contrast, Fe and Mn are more soluble under reducing conditions since different oxidation states possess different solubility characteristics.

III. CHARACTERIZATION OF THE PROPERTIES OF SEWAGE SLUDGE IN RELATION TO METAL RETENTION

3.1 Introduction

The growing awareness of environmental contamination caused by waste disposal has directed research in the area of environmental chemistry. In terms of sewage sludge disposal, it is prudent to examine the possibility of heavy metal contamination of the soil and the ground water. Furthermore, plant uptake of heavy metals must be considered as this would provide a pathway for heavy metals to enter the food chain. The difficulty associated with making generalizations regarding sewage sludge is their extreme variability in both physical and chemical properties. The variability stems from the source of the sewage sludge and the treatment processes to which it has been subjected.

Not until the middle of the 1970's was the importance of metal speciation in sewage sludge recognized as a factor in determining metal mobility (Lagerwerff *et al.* 1976, Stover *et al.* 1976, Silveira and Sommers 1977). Previously, sewage sludge studies involved mainly plant tissue analysis of a crop grown on a sludge-amended soil as an indication of plant availability of heavy metals from sewage sludge. As well, total concentrations of metals in sewage sludge were used to define maximum sludge loading limits on land rather than "available" metal concentrations (Kloke *et al.* 1984).

More research is needed to establish pertinent sludge characteristics which can be related to the availability of metals and their distribution within the sludge-soil system.

This study was conducted to define various properties of the sewage sludge obtained from the City of Winnipeg. The information will be used to relate results from subsequent experiments involving factors which can affect the release of metals from the sludge. The sewage sludge was obtained from the waste water treatment facilities in Winnipeg and analyzed for organic carbon content, total nitrogen, cation exchange capacity (CEC), pH, and organic functional groups. Also, the metal distribution was determined in the sewage sludge using a chemical fractionation procedure.

3.2 Materials and Methods

3.2.1 Sewage Sludge

The sewage sludge was obtained from the City of Winnipeg's North End Water Pollution Control Centre. The waste water that enters the treatment plant undergoes primary and secondary treatments to remove suspended solids. These solids, known as sludge, are then diverted to digestion tanks to allow anaerobic digestion to proceed. It is this stabilized sludge which is applied to agricultural land, and which was used for this study.

All sewage sludge used in this experiment and the

following two experiments was lyophilized on a Lab Con Co. Freeze Dry 5 freeze drier (Fisher Scientific Co., Winnipeg, Mb) at -68°C to -75°C and a pressure of 0.5 to 1 Pa for at least 96 h. This step ensured a constant moisture content (8-10%) and produced a powdery product which when sieved (<2 mm), was much easier to handle and store than the original material.

3.2.2 Analytical Procedures

Chemical properties of the sewage sludge were determined according to the procedures outlined below. All analyses were performed in duplicate.

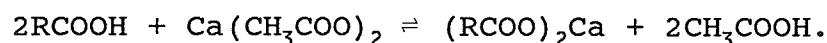
A. Organic Carbon Content

The organic carbon content was determined by oxidation with potassium dichromate according to the modified Mebius procedure (Yeomans and Bremner 1988). Heating the soil sample for 30 min at 170°C with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 resulted in a more complete oxidation of soil organic C to CO_2 and thus does not require the use of a correction factor as does the Walkley-Black method. Also, the method used digestion tubes in 40-tube block digesters rather than reflux apparatus needed for the original method. This allowed for a more rapid and precise determination of organic carbon. The equipment used for the analysis included a 40-tube Kjeldahl block digester, from Tecator Inc. Titration of the excess potassium dichromate was performed with the use of a Metrohm 686 titroprocessor.

B. Functional Group Acidity

The methods of Schnitzer and Gupta (1965) were employed in the determination of acidic functional groups in the sewage sludge. However, the organic fraction of the sewage sludge was not pre-purified in this study.

(i) Carboxylic Acids: Both aromatic and aliphatic carboxylic acids were determined by shaking a 0.5 g sample with an excess of calcium acetate solution and determining the amount of acetic acid liberated according to the equation



The resulting filtrate was titrated with standard 0.1 N NaOH solution to pH 9.8. The following equation was used:

$$\frac{(\text{Titre for sample} - \text{titre for blank}) * \text{N base} * 1000}{\text{weight of sample, mg}}$$

$$= \text{meq COOH groups / g of sludge.}$$

The result was then multiplied by 100 to give values with units of cmol kg^{-1} .

(ii) "Total Acidity": The determination was made by equilibrating the sample with $\text{Ba}(\text{OH})_2$. The hydroxide is used to dissociate the protons from functional groups. Titration of the excess $\text{Ba}(\text{OH})_2$ with standard 0.5 N HCl solution to pH 8.4 allows for the calculation of total acidity using the following equation:

$$\frac{(\text{Titre for blank} - \text{titre for sample}) * \text{N acid} * 1000}{\text{weight of sample, mg}}$$

$$= \text{meq total acidity / g of sludge.}$$

The results were multiplied by 100 to give values in units of cmol kg^{-1} .

(iii) Phenolic OH groups: were calculated from the difference between "Total Acidity" and carboxyl acidity.

C. Cation Exchange Capacity

The cation exchange capacity of the sewage sludge was determined according to the procedure of Alexiades and Jackson (1965). The sludge samples were saturated with Ca^{2+} using 0.5M CaCl_2 , and then exchanged with Mg^{2+} using 0.5M MgCl_2 . The exchangeable Ca in the extract was determined by atomic absorption spectrophotometry and expressed on an oven-dry basis (105°C).

D. pH

The pH of the sludge was determined after diluting sludge with either water (1:2) or 0.01 mol L^{-1} CaCl_2 (1:2) using a standard glass combination electrode. The method was modified from McLean (1982).

E. Total Nitrogen

Total nitrogen was determined by the Kjeldahl method modified by Bremner and Mulvaney (1982).

F. Metal Distribution

The distribution of Cu and Zn in the sewage sludge was estimated following sequential extractions with deionized water, 0.5 mol L^{-1} CaCl_2 , 30% hydrogen peroxide, and 0.2 mol L^{-1} acidified ammonium oxalate. The deionized water and CaCl_2 released soluble and exchangeable metals,

respectively. The hydrogen peroxide solution was used to oxidize organic matter and release occluded metals. Acidified ammonium oxalate, when used in the dark, extracts poorly crystalline Fe oxides (Schwertmann and Taylor 1989). It has also been shown that ammonium oxalate can dissolve organo-oxide complexes (McKeague and Day 1966). Smith and Mitchell (1984) found that organic colloids were closely associated with Fe and Al oxides. The greater the disorder of the oxides, the greater is the surface available for interaction with organic molecules (Oades 1989). Thus, the acidified ammonium oxalate procedure will also release any metals associated with poorly ordered oxides and organo-oxide complexes. The sequential extraction was carried out using the following extractors:

1. Deionized Water

Two grams of sludge (oven dry equivalent) were shaken with 20 mL of deionized water for 1 h, and then centrifuged for 15 minutes at 20 000 g. The supernatant was collected for analysis and the weight of the sample and centrifuge tube was recorded. In lieu of washing between extract steps, each sample was corrected for carryover from the previous step based on the Zn or Cu concentration in the previous extracting solution and the mass of the solution carried over.

2. 0.5 mol L⁻¹ CaCl₂

Seventeen mL of 0.5 mol L⁻¹ CaCl₂ was added to the

residue from step 1 and shaken for 1 h. Deionized water was added dropwise to balance the samples for centrifugation as in step 1. Again, the supernatant was collected.

3. Hydrogen Peroxide

The method of Lavkulich and Wiens (1970) was modified as follows. Ten mL of deionized water and 3 mL of 30% H₂O₂ were added to the residue from step 2. The reaction was allowed to proceed at room temperature and then in a water bath set at 60 to 70°C until the reaction had subsided. The sample was centrifuged for 15 minutes at 20 000 g and the supernatant collected in a 100 mL volumetric flask. This treatment was repeated three times. The sample was then washed three times with water and supernatants were combined. The residue was dried, its weight was recorded and it was saved for use in the acid ammonium oxalate extraction.

4. Acidified Ammonium Oxalate

The acidified ammonium oxalate extraction procedure is described by McKeague and Day (1966). The solution of 0.2 mol L⁻¹ ammonium oxalate was acidified to pH 3. Ten mL of this solution was added to 250 mg of residue obtained from the previous step. The samples were placed in a box and shaken for 2 h in the dark to avoid photoreduction, centrifuged and the supernatants collected.

G. Total Metals

The total concentration of metals in the sewage sludge was determined using a modified acid digestion procedure with a 3:1 ratio of nitric/perchloric acid (Isaac and Kerber 1971). All the supernatants collected were analyzed for Cu, Zn, Fe and Al by atomic absorption spectroscopy.

3.3 Results and Discussion

3.3.1 Properties of the Sewage Sludge

Table 3.1 displays the values for the chemical properties of the sewage sludge. The organic carbon content accounted for 19% of the dry weight of the sludge. This value is within the range of organic carbon contents reported for various sludges (Cunningham *et al.* 1975a; Riffaldi *et al.* 1983). After ignition at 450°C, the sludge contained 543 g kg⁻¹ ash, indicating the material is roughly 50% organic and 50% inorganic materials. Total nitrogen is 2.45% of the sludge weight; this results in a C/N ratio of 8:1. The pH of the sludge paste was neutral to slightly alkaline reflecting the addition of lime in the treatment process or high carbonate content of the soil in the area. The total acidic charge due to the functional groups in the sludge was found to be 245 cmol kg⁻¹. However, the CEC of the sludge only accounted for 60 cmol kg⁻¹. The difference can be explained by the pH at which the analyses were conducted. Total acidity was determined by back titration down to pH 8.4, while the CEC represents the unbuffered

charge. The determination for total carboxylic groups resulted in 21 cmol of charge kg^{-1} and therefore, 224 cmol of charge kg^{-1} of sludge resulted from the phenolic OH groups as calculated by the difference between the total acidity and the carboxylic acidity.

Table 3.1 Selected chemical properties of the sewage sludge.

Organic Carbon	193 g kg^{-1} *
Total Nitrogen	24.5 g kg^{-1}
pH water	8.0
0.01 M CaCl_2	7.9
Cation Exchange Capacity	60 cmol kg^{-1}
Total Acidic Groups	245 cmol kg^{-1}
Total Carboxylic Groups	21 cmol kg^{-1}
Phenolic OH Groups	224 cmol kg^{-1}

* calculated per the dry weight of the sludge.

3.3.2 The Distribution of Metals in Sewage Sludge

The results of the metal analyses are reported in Table 3.2. The four extractants; water, CaCl_2 , H_2O_2 , and acidified ammonium oxalate, were used in sequence and the total metal content was determined by acid digest on a separate sample. The sum of the individual fractions for all four of the metals analyzed was very close to the "total" values obtained by acid digestion of the sludge. Therefore, it was

assumed that the extractants used were successful in removing the metals held by a specific sludge fraction or in a specific form.

Table 3.2 Distribution of metals in the sewage sludge.

Extractant	Cu ^A mg kg ⁻¹	Zn mg kg ⁻¹	Fe mg kg ⁻¹	Al mg kg ⁻¹
Deionized water	3.3	0.62	ND ^B	ND
0.5 M CaCl ₂	1.3	3.7	ND	ND
30% H ₂ O ₂	230	69	130	110
Ammonium oxalate	410	690	9500	9400
Total (acid digest)	610	790	9600	13000

A- metal content expressed as mg per kg dry sludge.

B- values were not determined.

The large amounts of Fe and Al extracted from the sewage sludge by ammonium oxalate indicate that the extractant does indeed dissolve oxides and hydroxides as reported by Schwertmann and Taylor (1989). Beckett (1989) summarized the results of several experiments conducted to determine the types of oxides dissolved by acid ammonium oxalate in the dark. It was found that x-ray amorphous iron oxides or hydroxides, amorphous "aged" and "gel" hydrous oxides, fulvic iron complexes, poorly crystallized oxyhydroxides and amorphous aluminum were dissolved by acid ammonium oxalate when used in the dark. Approximately 10% of the total Fe and Al was released by the H₂O₂ treatment.

The 25% loss in weight of the sample after extraction with H_2O_2 indicated that not all of the organic matter had been oxidized since the original sludge material contained 19% organic carbon or approximately 50% organic material. These results suggested that an easily oxidizable organic fraction existed along with an organic fraction which was protected, possibly through complexation with the mineral fraction (Sequi *et al.* 1975; Smith and Mitchell 1984; Stevenson 1982).

The amounts of Cu and Zn released in deionized water and $CaCl_2$ represented less than 1% of the total Cu and Zn found in the sludge. The low concentration of trace elements found in both the soluble fraction and deemed exchangeable further suggested a specific adsorption mechanism whereby the surfaces of oxides (Kalbasi *et al.* 1978) or organic functional groups (Schnitzer *et al.* 1969) were involved. Discrete and insoluble organomineral complexes could also be responsible for specific adsorption of Cu and Zn. However, less surface area and fewer functional groups would be available for adsorption.

It has been suggested that the process of drying the sample prior to analysis would affect the forms of metals within the material (Bartlett and James 1980). Miller *et al.* (1986) demonstrated an increase in soluble Cu in swine manure from 2% in the original slurry to 8% in the freeze-dried material. This result was attributed to the effect of

drying on fragmentation and dissolution of organics (Bartlett and James 1980). As the sewage sludge under investigation was subjected to freeze-drying, one might expect the value for soluble Cu and Zn to be an overestimation of the amount in the original material.

Approximately one third of the Cu and less than one tenth of the Zn was extracted by the H_2O_2 , while the remaining fractions were removed by the acid ammonium oxalate. Considering the Fe and Al data, one can assume that a large proportion of the solid phase of the sludge material exists as a complex between the organic matter and amorphous Fe and Al oxides (Bell *et al.* 1991). The Cu and Zn associated with this organomineral complex was extracted by the acid ammonium oxalate reagent.

The results showed a substantial difference in the proportions of Cu and Zn extracted by the hydrogen peroxide and the acid ammonium oxalate reagents. Lagerwerff *et al.* (1976) have also presented evidence which suggests the prevalence of easily oxidizable organocopper complexes relative to such species of Zn. The electron configuration of Cu gives it the unique ability to form inner-sphere complexes over a wide pH range (McBride 1981). Copper, in the II oxidation state has an unfilled *d* shell, whereas Zn has a filled *d* shell. This difference in electron configuration allows Cu^{2+} to form a greater number of

hybridized orbitals and thus, a greater variety of complexing reactions than does the Zn^{2+} ion (Cotton and Wilkinson 1988).

IV. THE EFFECT OF IONIC STRENGTH ON Cu AND Zn EXTRACTED FROM SEWAGE SLUDGE

4.1 Introduction

The disposal of digested and dewatered municipal sewage sludge on agricultural land carries associated risks of contamination of the soil by heavy metals. Knowledge of the chemistry and mobility of Cu and Zn in the sludge - soil system is crucial to the understanding of the potential uptake of these metals by crops.

From the first experiment, it was found that despite the high organic C content and acidity of the sewage sludge, very little of the total Cu and Zn was exchangeable, suggesting that plant uptake and mobility would be low. Results from a Cd adsorption study conducted using the same sludge showed that the sludge had the ability to remove Cd from solution (Fitzgerald *et al.* 1992). However, over time, slight increases of Cd in solution were observed, suggesting that Cd was released. Possibly transformations within the sludge resulted in fewer binding sites or caused an alteration in Cd speciation. Similar changes to the Cu and Zn fractions may affect their ultimate fate.

The activities of dissolved ions will be affected by the ionic strength of the soil solution. The significance of the ionic strength of the soil solution with respect to mineral equilibria has been well documented (Adams 1971;

Nakayama 1971; Barrow and Shaw 1982; Black and Campbell 1982). The ionic strength of an electrolytic solution is a measure of the intensity of the electrical field in the solution. To determine the ionic strength of a solution, it is necessary to know the concentration and valence of all the ions in the solution according to the equation

$$\mu = \frac{1}{2} \sum (C_i Z_i^2).$$

One reason for its importance is the effect that ionic strength has on the variable charge of soil colloids, as the availability of cations and nitrate is largely dependent on the surface charges carried by the soil colloids (Black and Campbell 1982). Another reason for the significance of ionic strength is its contribution to the determination of the activity of individual ions in solution. Thus, a change in ionic strength results in a change in ion activity and therefore, a shift in the equilibrium of the solution (Adams 1971). Nakayama (1971) has shown increased solubility of gypsum in the presence of increasing salt concentrations. The dissolution of solids and subsequent release of ions into the soil solution may interfere with exchange processes, displacing cations from exchange sites. In the field situation, the ionic strength of the soil solution will vary over the growing season, due to environmental conditions especially the moisture status. Fertilizer additions, either chemical or organic, as well as mineral dissolution will also affect the ionic strength of the soil

solution.

Three precepts provide the rationale for this study: (1) if the ionic strength of the soil solution increases, dissolution of solid forms of Cu and Zn may occur; (2) an increase in ionic strength of the soil solution may result in a greater displacement of exchangeable Cu and Zn; (3) the ionic strength can affect the variable charge on the colloids and thereby the number of available exchange sites. The purpose of this study was to determine the effect of increasing ionic strength on the extractability of Cu and Zn from sewage sludge.

4.2 Materials and Methods

Two extracting solutions at various ionic strengths were used to determine the effect of ionic strength on the amounts of metals released from the sludge. The monovalent KCl salt and the divalent CaCl_2 salt were chosen and solutions were prepared at ionic strengths ranging from 0.001 to 3.0 mol L^{-1} . Twenty mL of extracting solution was added to duplicate 2 g samples of lyophilized sludge, the suspension was shaken for 6 h, and centrifuged for 15 min at 20 000 g. The resulting supernatants were analyzed for Cu and Zn by atomic absorption spectrophotometry.

In addition, the effect of the valency of the cations of the extracting solution on the amounts of Cu and Zn released was determined. This was accomplished by comparing

the extractability of Cu and Zn using CaCl_2 and KCl solutions at the same ionic strengths. The ionic strengths chosen were 1.0 and 0.001 mol L^{-1} . The extraction procedure was the same as that described above.

4.3 Results and Discussion

The concentrations of Cu and Zn extracted from the sewage sludge by CaCl_2 and KCl are presented in Table 4.1 and Table 4.2 respectively. The extraction data is also given as a percentage of the total acid extractable Cu and Zn present in the sludge.

Despite the high organic C content and acidity of the sewage sludge, very little of the Cu and Zn were exchangeable with neutral salts, indicating strong complexation (most likely chelation) and/or inorganic forms. For both extractants used, approximately 10% of the total Cu and less than 3% of the total Zn was released in all cases. The differences are likely due to the differences in the forms of Cu and Zn (i.e. organic (H_2O_2 reactive) vs inorganic (acid ammonium oxalate reactive)), as discussed in Chapter 3.

Extraction with CaCl_2 and KCl showed that at comparable ionic strengths, KCl extracted more Cu than did CaCl_2 whereas the amount of Zn extracted was not affected by the type of extractant. For example, CaCl_2 at 0.03 M extracted 40.4 mg Cu kg^{-1} , KCl at 0.04 M extracted 55.7 μg Cu g^{-1} ,

Table 4.1. The concentration of Cu and Zn extracted from sewage sludge by CaCl₂ (mean ± S.E.).*

μ (M)	pH	Cu		Zn	
		(mg kg ⁻¹)	% of total	(mg kg ⁻¹)	% of total
0	7.2	56.7	9.3 ± 0.2	1.52	0.19 ± .01
0.003	7.5	55.6	9.1 ± 0.1	1.43	0.18 ± .01
0.015	7.4	45.6	7.5 ± 0.1	1.12	0.14 ± .01
0.03	7.4	40.4	6.6 ± 0.1	0.83	0.11 ± 0.0
0.15	7.1	37.1	6.1 ± 0.2	2.13	0.27 ± 0.0
0.3	7.2	38.1	6.3 ± 0.1	3.63	0.46 ± .03
1.5	6.5	44.0	7.2 ± 0.6	8.88	1.10 ± .01
3.0	6.3	47.9	7.9 ± 0.2	16.73	2.10 ± .08

*average of two replicates

Table 4.2. The concentration of Cu and Zn extracted from sewage sludge by KCl (means ± S.E.).*

μ (M)	pH	Cu		Zn	
		(mg kg ⁻¹)	% of total	(mg kg ⁻¹)	% of total
0.001	7.8	56.4	9.3 ± 0.1	1.5	0.18 ± .04
0.004	7.7	58.8	9.7 ± 0.1	1.5	0.20 ± .04
0.02	7.3	57.0	9.4 ± 0.1	1.4	0.18 ± 0.0
0.04	7.2	55.7	9.2 ± 0.1	1.2	0.15 ± .01
0.2	7.2	57.3	9.4 ± 0.4	1.2	0.15 ± .01
0.4	7.2	59.8	9.8 ± 0.1	1.3	0.16 ± 0.0
1.0	7.1	65.4	10.7 ± .1	1.8	0.23 ± .01
2.0	7.2	68.9	11.3 ± .1	2.4	0.31 ± 0.0

*average of two replicates

while the amount of Zn extracted remained fairly consistent for both KCl and CaCl₂ over the range of ionic strengths used. Increasing the ionic strength of the extracting solution did not result in greater solution Cu and Zn except, however, when the concentration of the extracting solution was greater than 1 M. This concentration would not normally be encountered in the soil solution.

The data in Table 4.1 indicate that increasing the ionic strength of the CaCl₂ extracting solution to approximately 0.2 M resulted in decreased amounts of Cu and Zn released. That is, Cu and Zn became less available as ionic strength of the extracting solution increased up to approximately 0.1 M, beyond which the amount extracted increased again. These results were contrary to what was expected considering the effect of increasing ionic strength on exchange reactions. Instead, the data showed evidence of metal occlusion within the sludge matrix. To explain this phenomenon, one must consider the effect of solution ionic strength on the conformation of the organic polymers within the sludge. It has been well documented that the ionic strength of the solution is inversely related to the thickness of the electrical double layer around charged particles (Hayes and Swift 1978; Theng 1979). Therefore, the repulsive forces between organic polymers and segments of polymers are reduced, allowing the segments to come closer. The consequences, according to Silberberg (1968)

are twofold: (i) within a polymer, neighbouring sections of the chain could form chemical bonds which would result in loops and coiling; and (ii) between polymers, Van der Waals forces could result in further coagulation. Hayes and Swift (1978) suggested that the coagulation of the organic macromolecule would also result in slowing down the ion exchange process. In this situation, tortuosity and general frictional forces within the molecule will be greatly increased and the passage of ions through the macromolecule will be restricted. The end result in the sludge system is organic matter containing Cu and Zn which is less accessible and thus less extractable in a solution of intermediate ionic strength.

A second theory could explain the observation of less Cu and Zn extracted with increasing ionic strengths of CaCl_2 . The increasing salt concentration may result in structural reorganization of the ligand due to replacement of water molecules surrounding the adsorbent and the adsorbate (Theng 1979). Thus, the frequency and strength of metal-ligand interactions increases.

Extracting solutions of very high ionic strengths (greater than 0.2 M) resulted in increasing amounts of Cu and Zn released from the sludge. This is possibly due to dissolution of solid phases rather than increased exchange reactions (Goh *et al.* 1988). The pH of the extracting solution decreased with increasing ionic strength, in the

CaCl₂ system, lending further support to the possibility of dissolution reactions. Therefore, it is proposed that increasing the ionic strength of the extracting solution results in two opposing effects with respect to the release of metals: (i) a chemical effect of increased exchange reactions and increased solubility of solids; and (ii) a physical effect of ionic strength on polymer conformation. The evidence supported by the data suggest that at a solution ionic strength greater than 0.2 M the chemical effects of ionic strength will outweigh the physical effects. However, the Cu extracted by 3.0 M CaCl₂ was still much less than that extracted by the very low ionic strength solutions. Again, the explanation can be attributed to the strong association of Cu with the organic fraction whereas Zn was found to be associated with the inorganic fraction. The organic fraction would be more susceptible to the physical coiling effect resulting in the occlusion of a large fraction of the Cu.

The effect of the KCl extractant differed from that of the CaCl₂ extractant in that the decrease in the amount of Cu and Zn released with increasing ionic strength was not as pronounced (Table 4.2). The difference can be attributed to the valency of the cation of the extractant. Divalent ions are able to form bridge complexes between organic macromolecules causing aggregation (Gamble *et al.* 1985; Ghosh and Schnitzer 1981). The fact that Cu-containing

colloidal particles experience greater coiling and aggregation in divalent electrolytes is not conclusive evidence that the Cu is always less extractable. In fact, given time, the difference in extractability of Cu and Zn may be non-existent at comparable ionic strengths. Swift (1992, p.c. First ISSS Working Group MO Meeting, Edmonton) pointed out that if a macromolecule is strongly coiled (i.e. Ca system), the diffusion kinetics is much slower than in an uncoiled or disperse system (i.e. K or Na as electrolyte). In our study, we do not know if equilibrium had been reached within the 6 h reaction period. If equilibrium had not been reached, then, at that stage, there may be very little effect of coiling on the extractability of Cu in both CaCl₂ and KCl.

A comparison of the amounts of Cu and Zn extracted by salts of different cation valence but the same ionic strength is given in Table 4.3.

Table 4.3. Effect of cation valence on Cu and Zn extractability.

	CaCl ₂		KCl	
μ (M)	1.0	0.001	1.0	0.001
mg Cu kg ⁻¹	44	56	65	56
mg Zn kg ⁻¹	9	1	2	1

As in Table 4.1, less Cu was extracted with the high ionic strength CaCl₂ solution than with the low ionic

strength solution. For Zn, the opposite was true for the CaCl_2 extractant. The explanation for these differences was discussed previously. Comparisons across Table 4.3 show that relatively equal amounts of Cu were extracted by both CaCl_2 and KCl at both ionic strengths indicating dissolution reactions. The amount of Zn extracted by the 1.0 M KCl was much less than that extracted by the 1.0 M CaCl_2 . These data further support the previous conclusion that Zn is specifically adsorbed by singly coordinated hydroxyls on the short-range ordered oxides, which may be purely inorganic or commonly organomineral in nature. Thus, the doubly charged Ca cation can displace the Zn with greater ease than can the monovalent K cation. The difference in behaviour between Zn^{2+} and Cu^{2+} with short-range ordered compounds arises from the fact that Zn^{2+} does not have partially filled *d* orbitals. Thus, Zn^{2+} reacts strongly with hydroxyls only, whereas Cu^{2+} can also be specifically bound by organic functional groups (Kalbasi *et al.* 1978; Cavallaro and McBride 1980; Goh *et al.* 1986).

From this study, it can be concluded that the availability of Cu from sewage sludge from the City of Winnipeg is greater than that of Zn, however, the extractability of both metals is low even in solutions of high ionic strengths. It should be noted that soil solution ionic strengths are normally in the range of 0.01-0.05 M (Ponnamperuma *et al.* 1966; Black and Campbell 1982) and

higher concentrations are rarely encountered in the soil.

The results from this study provide evidence of a physical effect of solution ionic strength on the conformation of the organic macromolecules which render the metals less available within a certain range of ionic strength.

V. CHANGES IN FRACTIONATION OF
Cu AND Zn DURING MINERALIZATION OF TREATED
MUNICIPAL SEWAGE SLUDGE IN SOIL

5.1 Introduction

As the purpose of this research was to determine the potential for soil contamination by metals released from sewage sludge, one first endeavoured to determine the fractions in which the metals were bound in the sewage sludge. This was accomplished in the first study which indicated that a large proportion of the Cu and Zn in the sewage sludge was associated with the organomineral fraction and that less was associated with the purely organic fraction. The second study determined that very little of the Cu and Zn was exchangeable and increasing the ionic strength within the normal range found in the soil solution had very little effect on the release of metals. Once sewage sludge is applied to agricultural land, it is subject to decomposition and mineralization. It is imperative to understand how these sludge transformations may affect the speciation, and subsequent mobility of the metals present.

The stability of metals within the sludge-soil matrix has been studied by several researchers employing chemical fractionation techniques (Lagerwerff *et al.* 1976; Steinhilber and Boswell 1983; Bell *et al.* 1991). These

methods provided a comparison of the relative stability of the metals. The metals released by a stronger extractant suggest greater stability than those released with a weaker extractant. Conversely, metals released by weak extractants are deemed to be more mobile and plant available, hence are of greater concern.

The organic fraction of sewage sludge has undergone extensive examination. For example, functional group characterization of sludge has been used to explain metal binding characteristics (Riffaldi *et al.* 1983; Hernandez *et al.* 1988; Steinhilber and Boswell 1983). This study made use of both of these techniques to determine if and what changes occur to metal binding sites during the mineralization of sewage sludge, and how these changes affect the mobility of the metals.

5.2. Materials and Methods

5.2.1. Soils

The soils chosen for the incubation study comprised the top 0-15 cm of the A horizon of a Lakeland series soil and the top 0-15 cm of the A horizon of a Glenlea series soil. The Lakeland series, a clay loam of the Black Suborder, was selected because it is one of the soils presently used for sludge disposal by the City of Winnipeg and the Glenlea series was selected for its heavy clay texture. The soils were collected in June of 1990. In each case, the soils

were passed through a 2 mm sieve and stored at 4°C in the field moist condition. The soils were thoroughly mixed before use. The moisture contents of the soils were determined by oven drying at 105° C to allow for the calculation of the mass of the oven dry equivalents.

5.2.2. Sewage Sludge

A fresh sample of sewage sludge was collected for this experiment and prepared as described previously in Chapter 3. The chemical properties and the metal distribution of the sewage sludge are given in Tables 3.1 and 3.2.

5.2.3. Experimental Design and Procedures

To determine the effect of mineralization of sewage sludge in soil on the fractionation of metals, an incubation study was conducted. The experiment consisted of treatments of sludge, soil, and sludge-soil mixtures which were incubated individually in bottles for periods up to 16 weeks. The duration was chosen to simulate one growing season. The controls in the study were the "sludge only" and the "soil only" treatments. The mixtures of sludge and soil were prepared in 1:1 and 1:4 ratios. These ratios are much higher than one would expect in any sludge disposal program where sludge application rates typically vary from 25 to 100 tonnes ha⁻¹ on a dry weight basis. This would result in sludge-soil ratios of 1:80 to 1:20 assuming the mass of a hectare furrow slice is 2 million kg. However, depending on the method of sludge application, large clods

of sludge may be left on the surface resulting in poor and non-uniform incorporation into the surface layer of the soil.

Bulk sludge and soil samples were passed through a 2 mm sieve and uniformly mixed. Triplicate 15 gm samples (oven dry equivalent) were added to four-ounce French square bottles. The treatments "sludge only", sludge-soil at a 1:1 ratio, sludge-soil at a 1:4 ratio, and "soil only" were wetted to moisture contents of 150, 100, 70, and 40% (w/w) respectively. The bottles were then capped with sponge caps to allow for aeration and incubated for periods of 0, 1, 4, 8, and 16 weeks at a constant temperature of $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$ in an incubator. Periodically, the samples were weighed and deionized water was added to maintain the moisture content. After the required duration, the entire sample was freeze dried, sieved and stored for further analyses.

5.2.4. Analyses

After incubation all of the samples were analyzed for organic carbon content, functional group acidity, and also subjected to the sequential extraction procedure described in Chapter 3. The supernatants collected were analyzed for Cu and Zn using atomic absorption spectroscopy.

The DTPA soil test by Lindsay and Norvell (1978) was used to estimate plant available Cu and Zn. This determination was not part of the sequential extraction procedure but was performed on a separate subsample of each

treatment. The extractant consists of 0.005M DTPA (diethylene triamine pentaacetic acid), 0.1M triethanolamine, and 0.01M CaCl₂, with a pH of 7.3. DTPA is a chelating agent which can effectively complex Cu and Zn. The CaCl₂ was included in the reagent to avoid excessive dissolution of CaCO₃, which would release occluded micronutrients not normally available to the plant. Triethanolamine was selected as a buffer, again to prevent the dissolution of inorganic constituents which would release micronutrients.

5.3. Results and discussion

Changes in the organic fraction are an important consideration in this study as this would be the most likely source of metals released. Table 5.1 gives organic carbon content and the functional group acidity measured after the five incubation periods for the four treatments.

The organic carbon content of the sewage sludge declined dramatically, from 25% to 16% after sixteen weeks of incubation. The loss of organic carbon occurred mainly after the four week period. Dudley *et al.* (1986) noted in a similar experiment that the pH increased into the alkaline range during the first two weeks of the incubation and attributed this to the production of high amounts of ammonium and nitrate. Perhaps the growth of the microbial population was retarded due to the pH or the microbes first acted to break down the sludge organic matter into smaller

organic fragments before finally oxidizing it to CO_2 . The values for "total acidity" ranged from 213 to 258 cmol kg^{-1} over the 16 week period but there is no trend. Carboxyl acidity and phenolic OH acidity also varied erratically over the incubation period. However, the acidity values suggested that the organic fraction had been undergoing extreme changes during the incubation period.

The organic carbon content of both soils changed very little over the 16 week incubation period, likely because the soil organic matter was fairly stable. The total acidity was similar for each soil. The values were less than half that of the sewage sludge. The difference in total acidity values between the sludge and the soil samples was to be expected as the soils had organic carbon contents in the range of 4 to 6%, while the sewage sludge contained 25% organic carbon. For the Lakeland series soil, the total acidity was 113 cmol kg^{-1} initially and declined to almost half by the eighth week of incubation. The total acidity of the Glenlea series soil remained fairly constant over the entire incubation period, with values ranging from 87 to 118 cmol kg^{-1} . In both soils, the acidity appeared to be mainly due to the phenolic OH groups.

For the mixtures of sludge and soil, at both the 1:1 and 1:4 ratios, the organic carbon contents ranged proportionally according to the ratios of sludge to soil. The values for the organic carbon contents showed the same

Table 5.1 Changes in organic carbon and functional group acidity over the 16 week incubation period*.

Time weeks	Organic carbon %	Total acidity cmol kg ⁻¹	Carboxyl acidity cmol kg ⁻¹	Phenolic OH cmol kg ⁻¹
Sewage sludge				
0	24.8	245.0	21.0	224.0
1	21.5	213.0	27.0	186.0
4	23.2	228.0	9.0	219.0
8	16.7	258.0	19.0	239.0
16	15.9	224.0	24.0	200.0
Lakeland Series soil				
0	4.81	113.0	2.0	111.0
1	4.95	87.3	3.7	83.6
4	6.15	66.1	3.7	62.4
8	4.02	65.4	2.7	62.7
16	4.23	75.0	1.3	73.7
Glenlea soil				
0	6.65	105.0	5.0	100.0
1	6.68	87.3	8.3	79.0
4	7.25	91.1	3.5	87.6
8	5.64	94.1	4.0	90.1
16	5.57	118.0	5.0	113.0
Lakeland soil and sludge (1:1 mixture)				
0	13.7	203.0	12.0	191.0
1	13.8	170.0	20.0	150.0
4	13.5	149.0	5.0	144.0
8	10.0	149.0	8.0	141.0
16	9.96	125.0	6.0	119.0
Lakeland soil and sludge (4:1 mixture)				
0	8.10	139.0	7.0	132.0
1	7.75	116.0	16.0	100.0
4	8.52	84.2	1.2	83.4
8	6.39	95.4	6.3	89.1
16	6.53	111.0	5.0	106.0
Glenlea soil and sludge (1:1 mixture)				
0	14.1	195.0	13.0	183.0
1	13.8	194.0	20.0	174.0
4	14.2	156.0	5.0	151.0
8	11.0	195.0	11.0	184.0
16	10.5	160.0	11.0	149.0
Glenlea soil and sludge (4:1 mixture)				
0	9.74	162.0	10.0	152.0
1	9.83	123.0	21.0	102.0
4	9.96	122.0	3.0	119.0
8	7.54	131.0	6.0	125.0
16	7.43	149.0	6.0	143.0

* values represent averages of three replications.

trend for all mixtures. That is, the values remained fairly consistent from 0 to 4 weeks then dropped significantly by the eighth week of incubation and showed little change thereafter. Total acidity values declined overall but the changes did not adequately reflect the changes in the organic carbon content. This suggested that although organic matter had decomposed, functional groups were not lost at the same rate. One could expect, however, that new functional groups would be present on the simpler degradation products.

In Table 5.2, the values for water-soluble and 0.5 mol L⁻¹ CaCl₂-exchangeable Cu and Zn are reported for the sewage sludge, the soils and the sludge and soil mixtures. Overall, the results showed that very little of the total Cu and Zn was exchangeable and even less was soluble. The sewage sludge did not exhibit any change in the amount of soluble Cu or Zn released over the duration of the incubation to the extent that their release would pose serious environmental concerns. Only 1 to 4 mg Cu kg⁻¹ sludge was released by extraction with water and less than 1 mg Zn kg⁻¹ was released at any time during the incubation. The values for exchangeable Cu differed little from the values for soluble Cu. The exchangeable Zn in the sewage sludge was slightly greater than the soluble Zn values, but still there was no obvious change in exchangeable Cu or Zn over the incubation period.

The soils also released very little Cu and Zn when extracted with water and CaCl_2 . Less than 1 mg kg^{-1} of either Cu or Zn was soluble at any time during the incubation, while only 1 to 4 mg kg^{-1} was exchangeable. Again, there was no obvious change in the amounts of Cu and Zn released by either extractant within sixteen weeks.

As the amounts of Cu and Zn released by the sewage sludge and the soils were very low, there was little expectation of differences within the mixtures of sludge and soil. Soluble Cu in the sludge-soil mixtures ranged from 1 to 6 mg kg^{-1} and soluble Zn remained consistently lower, less than 1 mg kg^{-1} . Exchangeable Cu and Zn values were slightly higher than the values for soluble Cu and Zn and also remained fairly constant.

Due to the decrease in organic carbon content over time in all of the treatments containing sewage sludge, it was expected that soluble and exchangeable Cu and Zn would increase. However, as shown in Table 5.1, the functional group acidity remained fairly high such that any metals released through decomposition were immediately taken up by other groups. Similar results regarding the low solubility and exchangeability of metals from sewage sludge and sludge-soil mixtures were found in the literature (Stover *et al.* 1976; Silviera and Sommers 1977; Emmerich *et al.* 1982; Sposito *et al.* 1983). Emmerich *et al.* (1982) suggested that the metals had reverted to a more residual form.

Table 5.2 The concentration of soluble and exchangeable Cu and Zn extracted during the incubation period¹.

Time weeks	Soluble		Exchangeable	
	Cu	Zn	Cu	Zn
-----mg kg ⁻¹ -----				
Sewage sludge				
0	3.30	0.56	1.33	3.68
1	4.16	0.91	1.91	4.95
4	1.15	0.76	4.09	6.80
8	4.25	0.72	1.92	6.21
16	1.46	0.73	2.03	4.43
Lakeland soil				
0	0.27	0.10	1.72	2.45
1	0.30	0.13	2.10	3.01
4	0.40	0.07	2.94	3.87
8	0.23	0.27	2.06	2.81
16	0.10	0.10	2.11	2.89
Glenlea soil				
0	0.36	0.36	1.71	2.29
1	0.27	0.23	1.84	2.51
4	0.40	0.30	2.50	3.51
8	0.17	0.36	2.18	2.75
16	0.10	0.30	1.91	2.68
Lakeland soil and sludge (1:1 mixture)				
0	0.60	0.17	1.90	2.58
1	3.64	0.30	4.62	5.18
4	1.29	0.26	3.45	6.67
8	1.58	0.26	2.56	4.18
16	1.13	0.33	2.37	4.08
Lakeland soil and sludge (4:1 mixture)				
0	0.53	0.10	1.85	2.21
1	0.76	0.10	1.86	2.77
4	0.56	0.10	3.06	3.94
8	0.40	0.20	2.26	3.09
16	0.33	0.20	2.24	2.26
Glenlea soil and sludge (1:1 mixture)				
0	1.52	0.23	2.16	3.44
1	6.47	0.40	1.18	4.26
4	1.58	0.17	2.76	6.01
8	1.79	0.40	2.53	6.09
16	1.46	0.40	2.01	4.91
Glenlea soil and sludge (4:1 mixture)				
0	0.43	0.30	1.54	2.22
1	0.96	0.26	2.80	3.89
4	1.03	0.13	2.65	4.60
8	0.63	0.20	2.28	3.45
16	0.57	0.27	1.90	2.68

* values represent average of three replicates.

Figures 5.1 to 5.7 show the changes in the fractionation of Cu and Zn during the incubation period for each treatment. For the sewage sludge samples, the largest fraction of metals existed as inorganic or organomineral complexes (that is, metals extracted by acidified ammonium oxalate and designated "AO", Figure 5.1). This fraction decreased in the first four weeks of incubation and then increased again to approximately their initial levels. A greater amount of Zn existed in this fraction than Cu. After treatment with H_2O_2 , greater concentrations of Cu than Zn were released, further evidence of the lack of organo-Zn complexes. The DTPA extractable Cu and Zn, considered to be an indication of plant available Cu and Zn, demonstrated a slight increase in the first week of incubation and thereafter declined to less than 10 mg kg^{-1} sludge. Plant available metals reached a maximum of 300 mg Zn and only 100 mg Cu per kg of sludge. Organically bound (H_2O_2 oxidizable) Cu was greater than Zn and appeared to increase initially and then decline to the initial concentrations by the eighth week of incubation.

The fractionation of Cu and Zn varied within the two soils. In the Lakeland series soil, the curves for Cu and Zn were similar with the largest proportion of Cu and Zn existing in the AO fraction (Figure 5.2). Less than five mg Cu or Zn per kg soil was extracted at any time by the DTPA and the H_2O_2 . The Cu concentration curves for the Glenlea

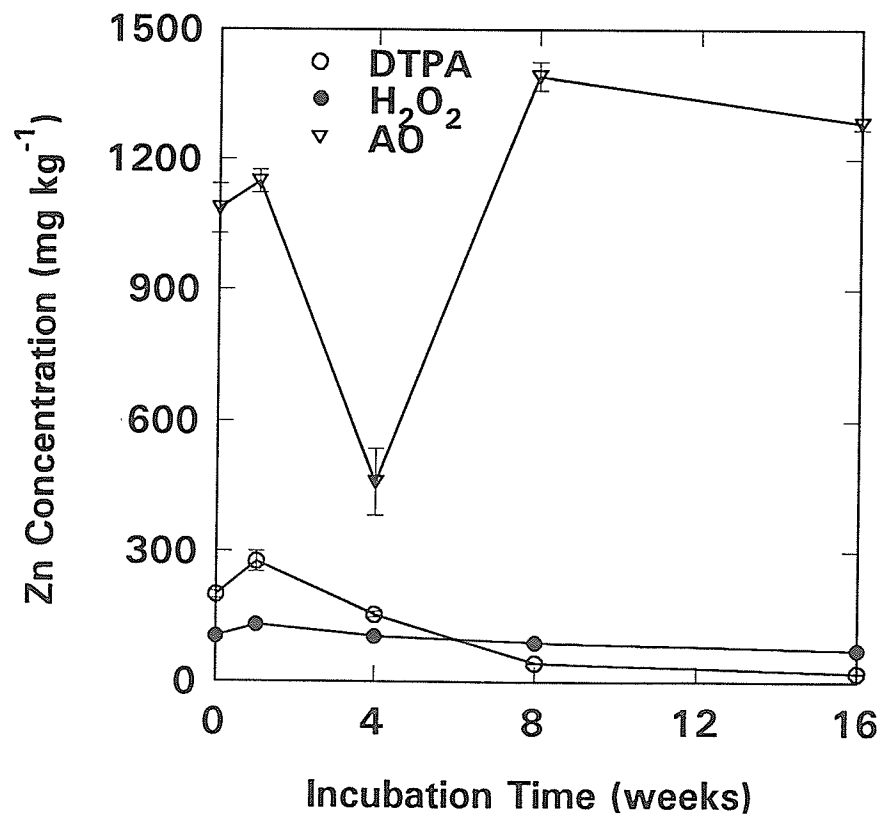
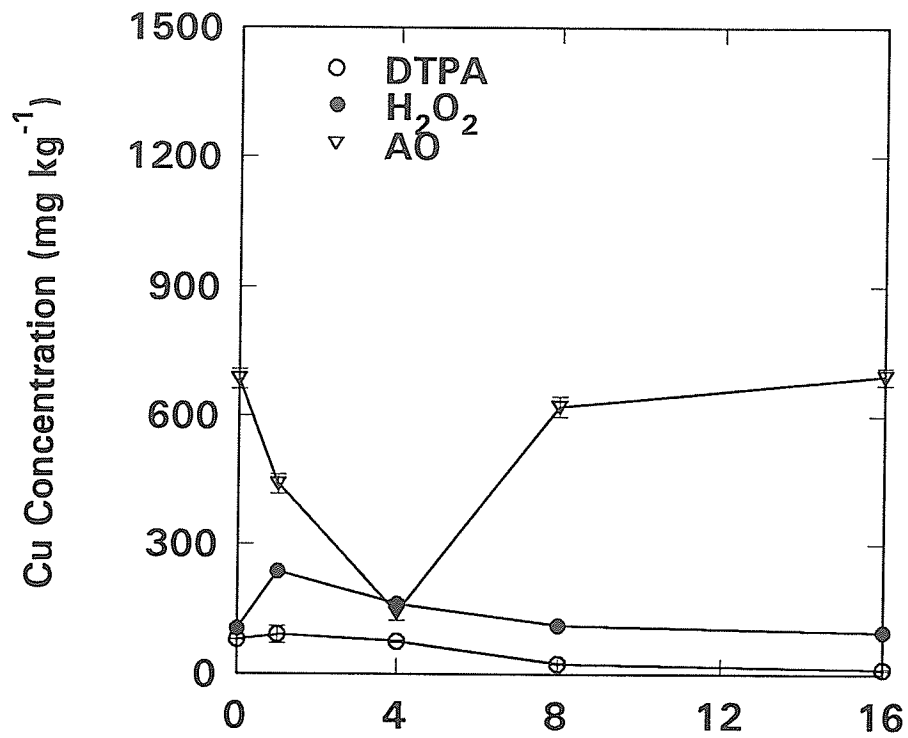


Figure 5.1 The fractionation of Cu and Zn in sewage sludge.

soil (Figure 5.3) was similar to that for the Lakeland soil, in that the largest proportion of Cu was extracted in the AO fraction. However, within the Glenlea series soil, the fractionation of Zn differed from Cu as the AO fraction of Zn declined and the H₂O₂ fraction increased continuously over the incubation period. These same trends were not observed for the AO- and H₂O₂-fractions of Cu. For both soils, the DTPA extractable Cu and Zn was negligible.

All curves for the Cu and Zn concentrations for the sludge-soil mixtures are very similar. In general, the concentration of the DTPA extractable Cu and Zn increase in the first week of incubation and then gradually decrease to less than 10 mg Cu or Zn per kg of sample by the eighth week of incubation. Thus, one would expect a low potential for plant uptake. The H₂O₂ fraction appeared to be least affected by incubation time. Only a slight decrease occurred initially but by the sixteenth week, the values for both Cu and Zn approached the initial values. The AO extractable fraction generally showed an increase over the duration of the incubation. Also, the amount of Zn extracted in this fraction was always greater than the amount of Cu extracted.

The fractionation data for the 16 week incubation period indicated very low levels of soluble and exchangeable Cu and Zn throughout the duration of the study. DTPA extractable fractions of Cu and Zn were initially quite high

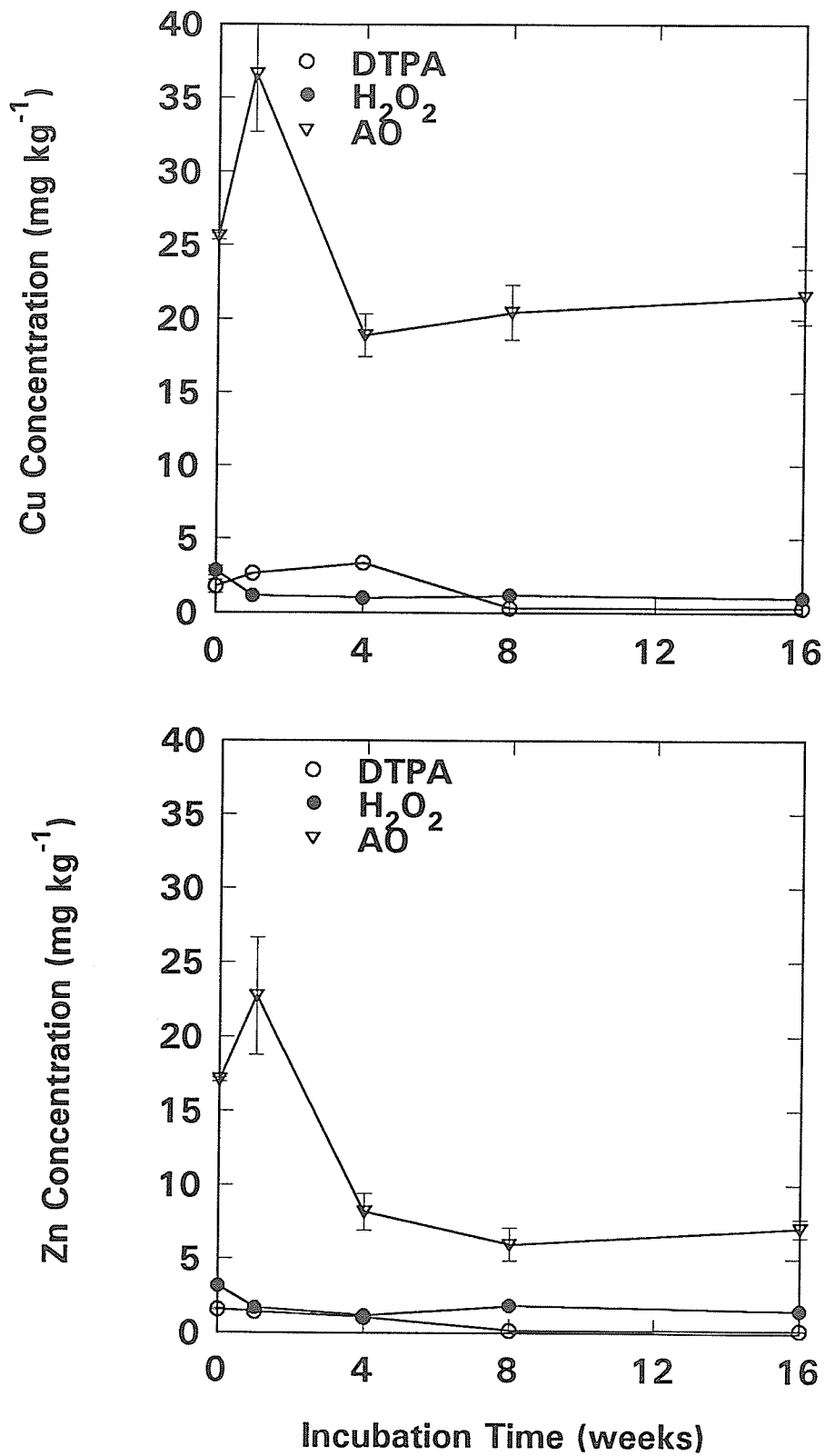


Figure 5.2 The fractionation of Cu and Zn in the Lakeland soil.

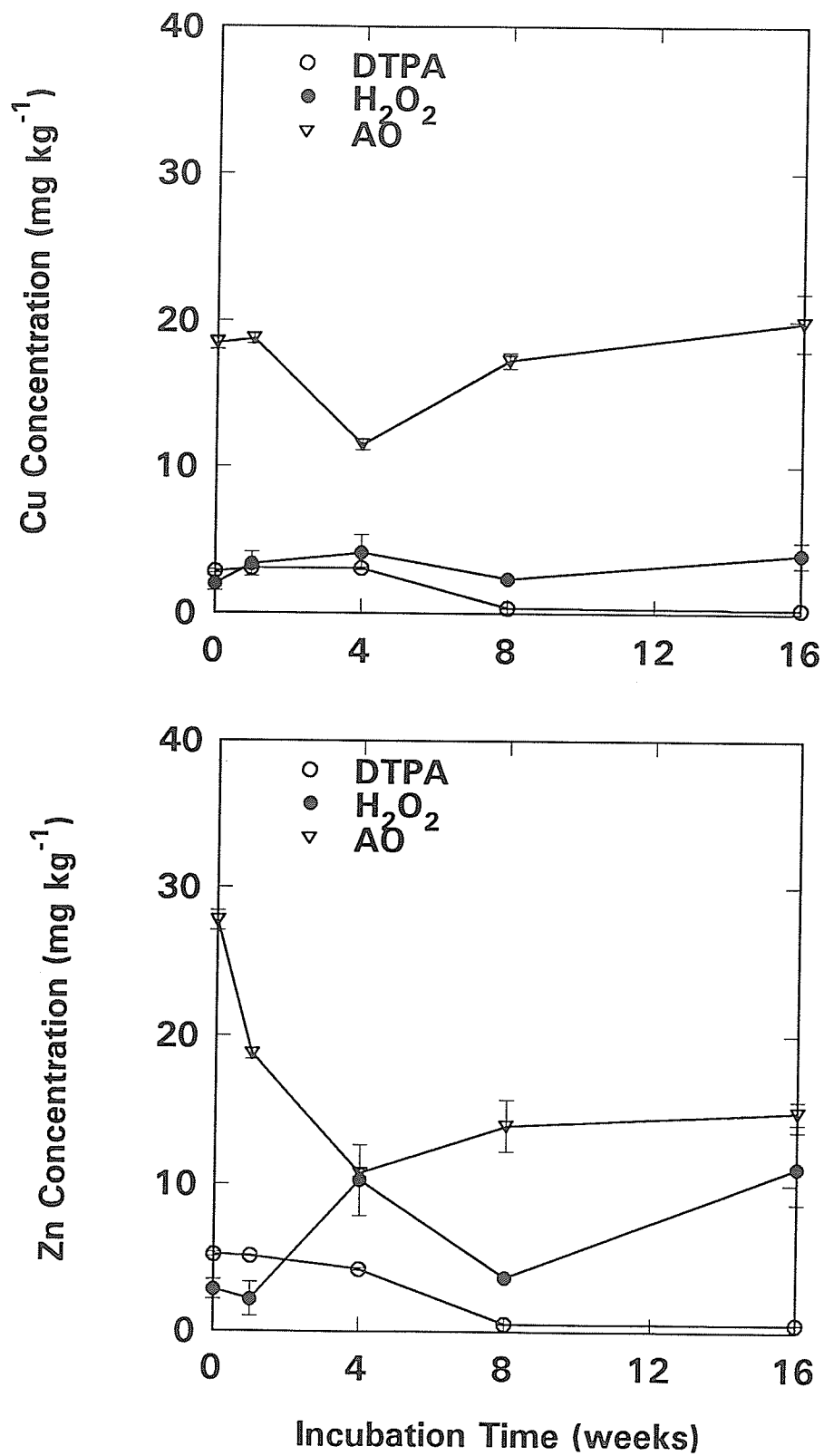


Figure 5.3 The fractionation of Cu and Zn in the Glenlea soil.

in the sludge-soil mixtures (50-200 mg kg⁻¹) but rapidly declined to negligible levels. The proportion of organically bound metals remained fairly constant and the only fraction that appeared to increase was the AO fraction or the inorganic fraction. From the previous study, it was concluded that this fraction was fairly stable and would therefore not be a likely source of metals released to the soil system.

The redistribution of the Cu and Zn to more recalcitrant forms has been noted by other researchers (Emmerich *et al.* 1982; Bell *et al.* 1991). Bell *et al.* (1991) demonstrated that an increase in paracrystalline iron oxides occurred in soils treated with sewage sludge. These results appeared to be related to the quantities of iron oxide found in the sewage sludge itself and in the sludge-amended soil. The fractionation techniques used by Bell *et al.* (1991) indicated that the largest percentage of Zn was associated with the paracrystalline iron oxides.

In an attempt to determine the cause of the variation in the DTPA extractable fractions, concentrations of organic carbon and total acidity were determined (Figures 5.8 and 5.9). Figure 5.8 depicts the concentrations of Cu and Zn relative to the organic matter contents for the sewage sludge treatment and the sludge-amended soils at the 1:1 ratio. The measurements taken at one week showed a dramatic increase in Cu and Zn extracted by DTPA, but only the sewage

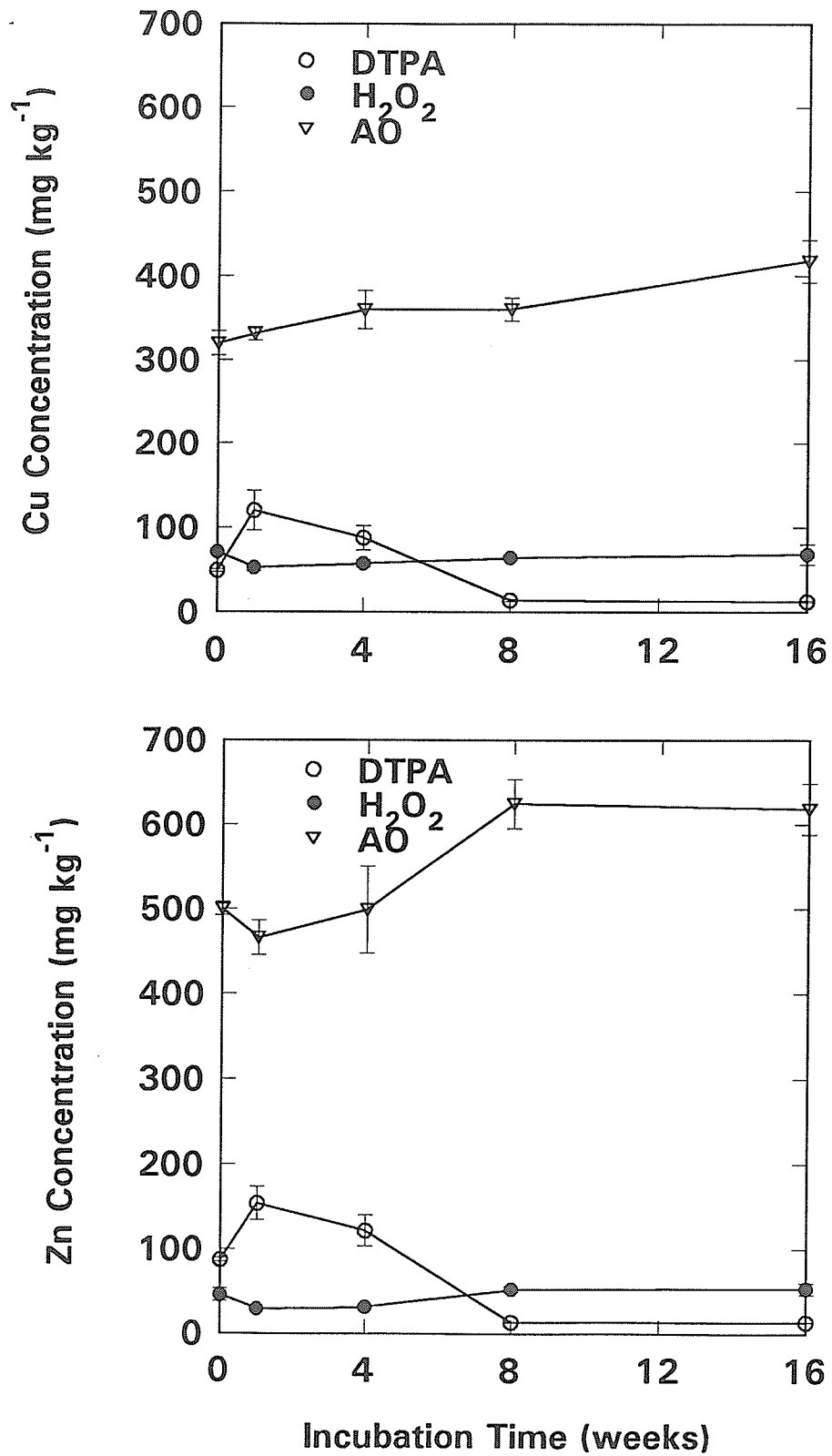


Figure 5.4 The fractionation of Cu and Zn in the Lakeland soil and sludge mixture (1:1 ratio).

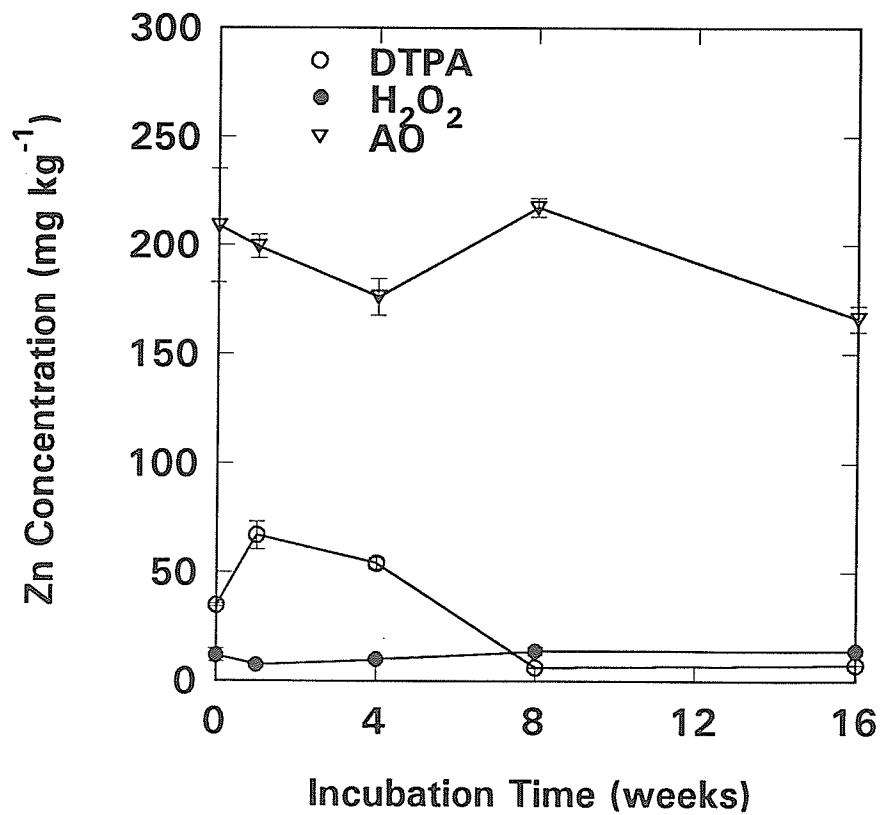
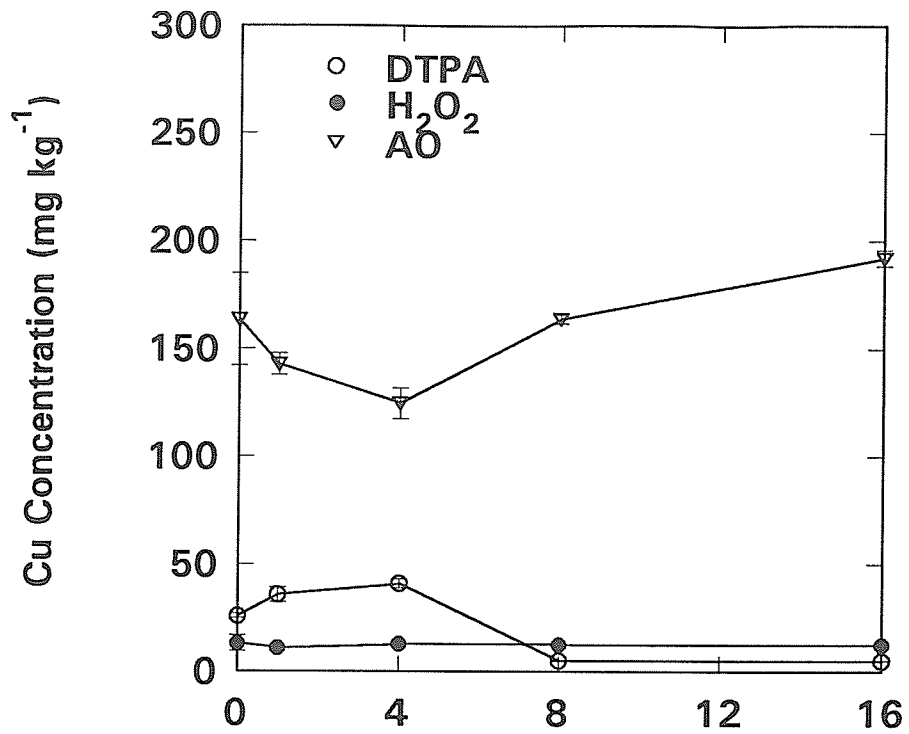


Figure 5.5 The fractionation of Cu and Zn in the Lakeland soil and sludge mixture (4:1 ratio)

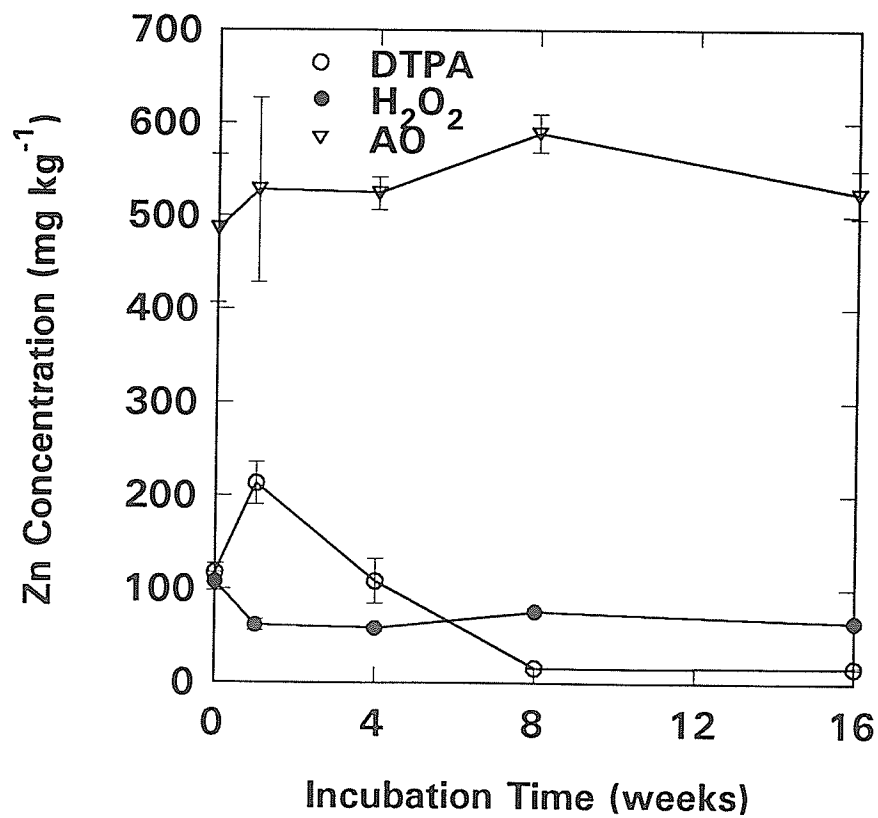
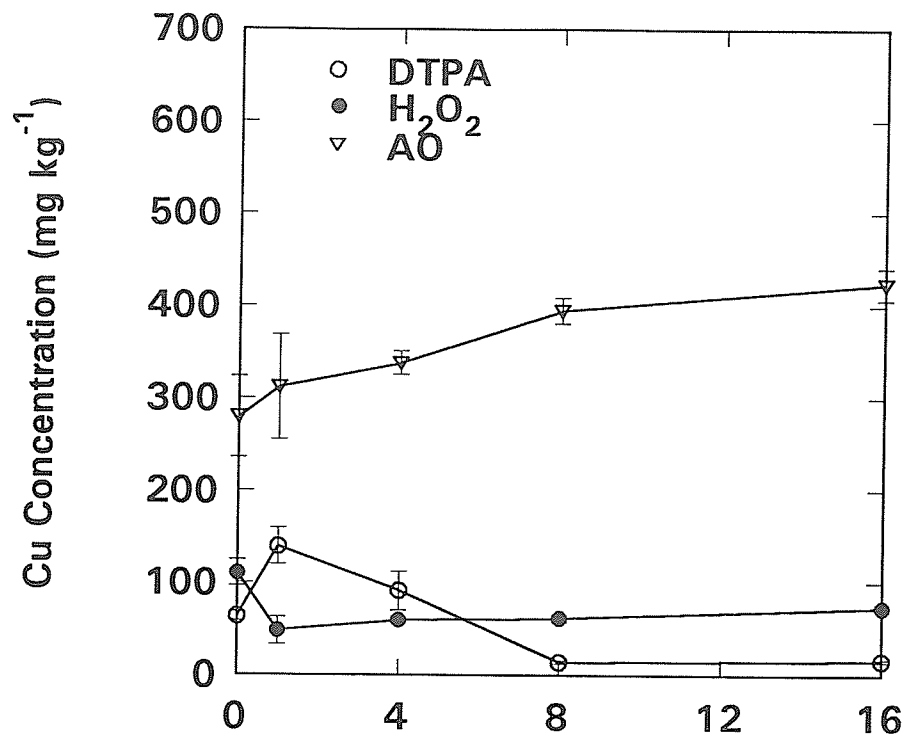


Figure 5.6 The fractionation of Cu and Zn in the Glenlea soil and sludge mixture (1:1 ratio).

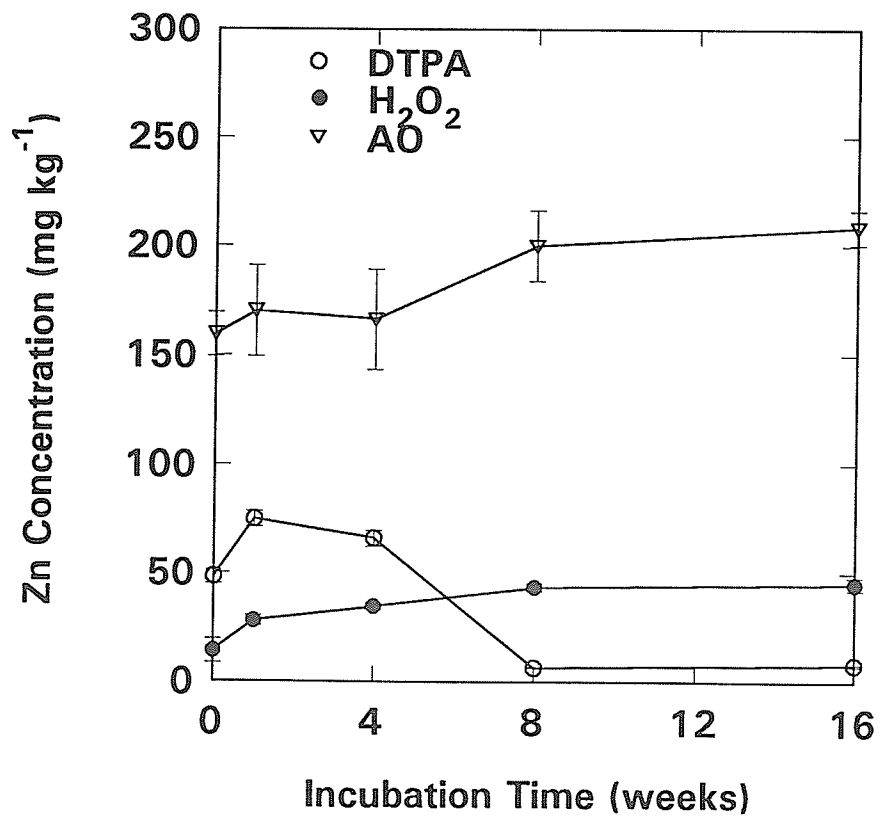
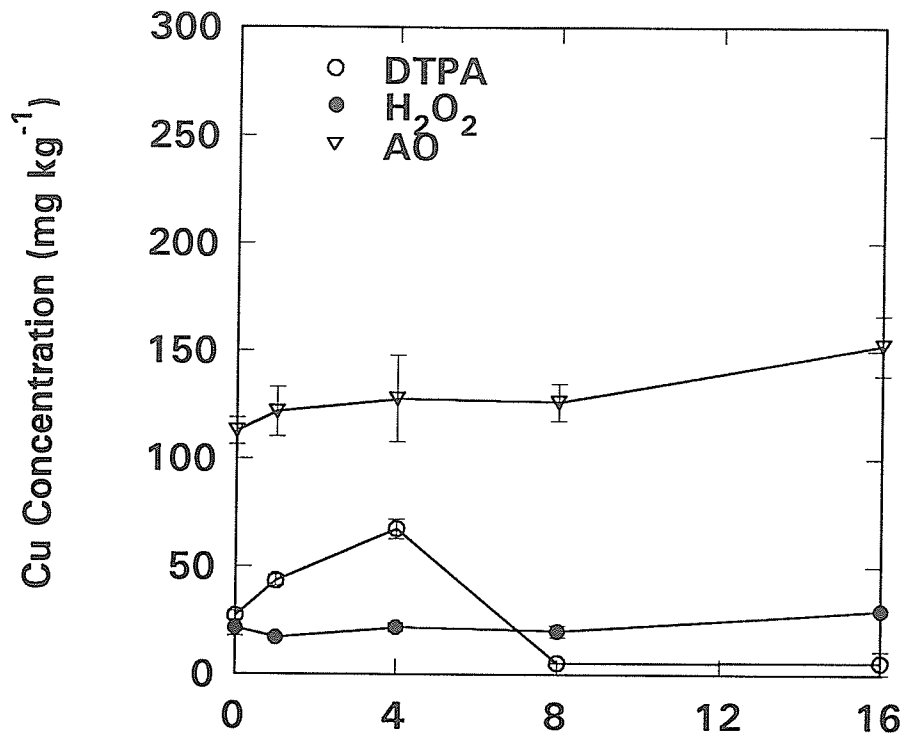


Figure 5.7 The fractionation of Cu and Zn in the Glenlea soil and sludge mixture (4:1 ratio)

sludge treatment showed an obvious reduction in organic carbon content that would account for the concurrent release of metals. Figure 5.9 shows the concentrations of Cu and Zn extracted by DTPA relative to the total acidity measured for the same time period. An initial decrease in total acidity corresponded to an initial increase in the DTPA extractable metals, suggesting that the loss of functional groups was responsible for the release of Cu and Zn. However, the DTPA fractions continued to decline from the fourth to the eighth week whereas the total acidity values increased up to the initial values over the same time period for the sewage sludge and Glenlea soil + sludge treatments and decreased slightly for the Lakeland soil + sludge treatment. It is likely that microbial activity was responsible for the decline in the concentrations of Cu and Zn extracted by DTPA over time.

The differences in the soil types appeared to have little effect on the metal distribution over the incubation period studied. This is not surprising as the soils possessed similar properties except for the amount of clay present. The textural classification of the Lakeland soil is clay loam and the Glenlea soil is classified as a heavy clay. Emmerich et al. (1982) reported on the contribution of the soil to the fractionation results study using several different soils treated with sewage sludge. The authors also concluded that the sewage sludge played a greater role

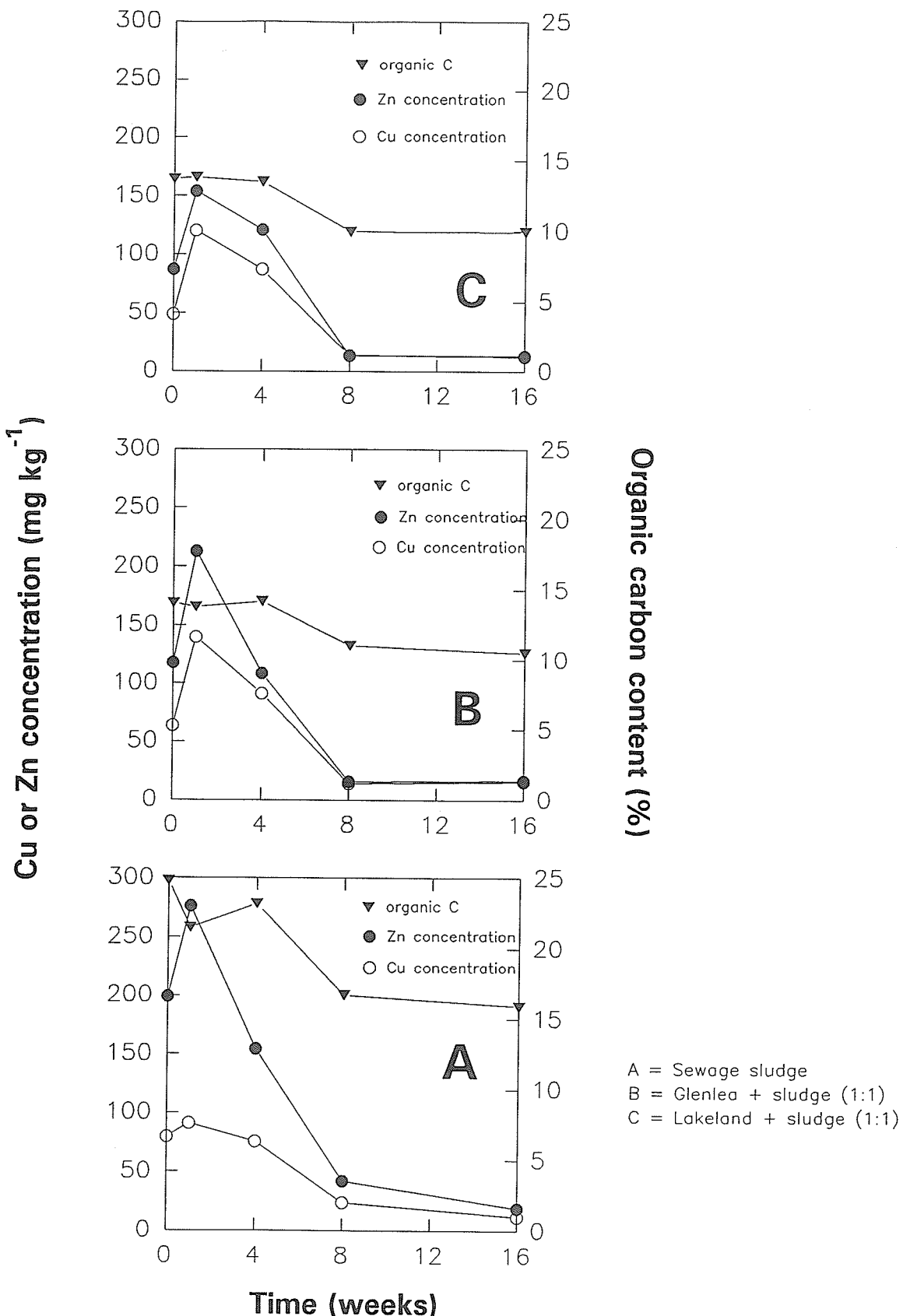


Figure 5.8 The relationship of DTPA extractable Cu and Zn to organic carbon during sewage sludge incubation.

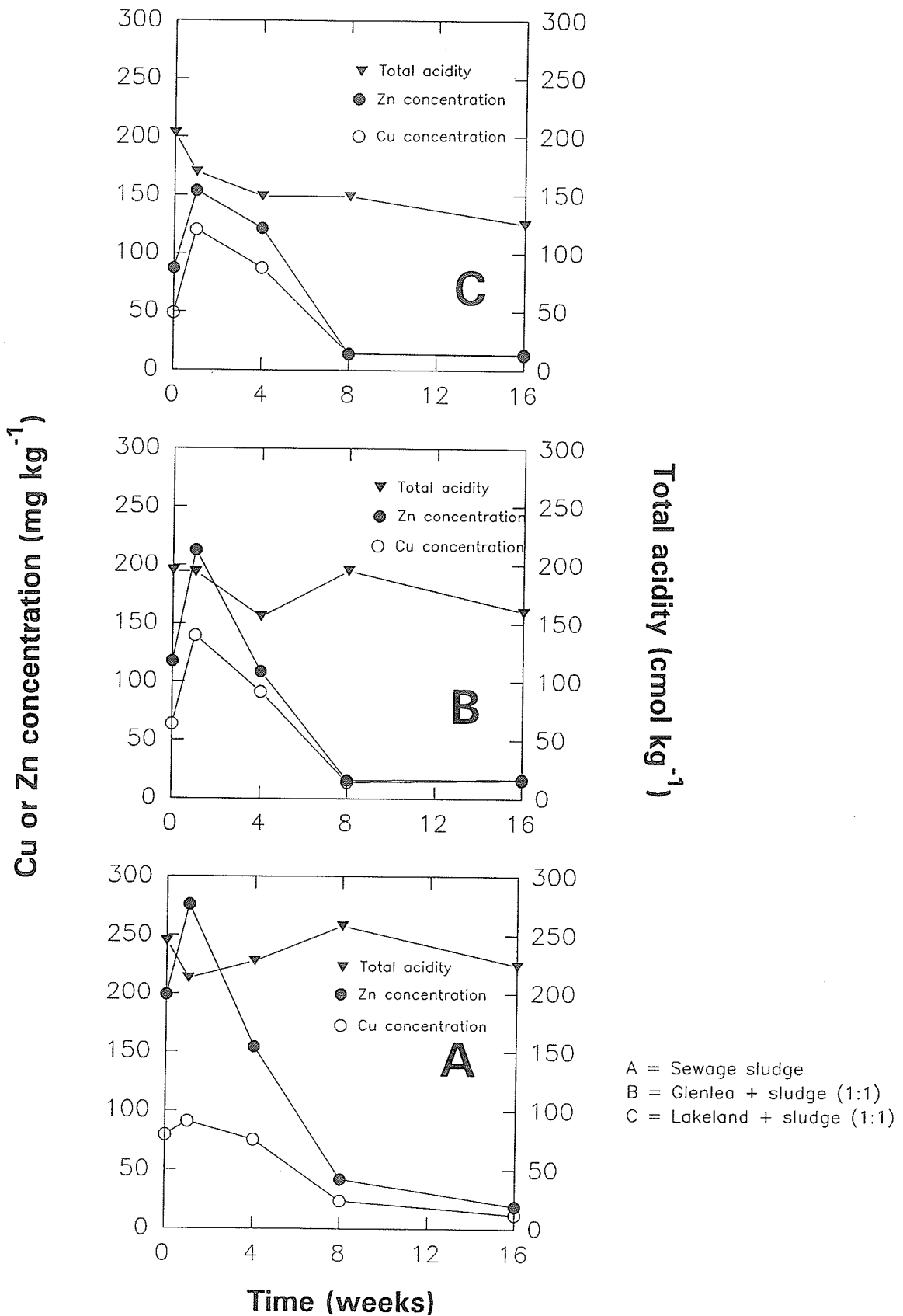


Figure 5.9 The relationship of DTPA extractable Cu and Zn to total acidity during sewage sludge incubation.

in determining the forms of metals that resulted after the soil had been incubated with sludge.

The fluctuations in the concentrations of extractable metals suggest that more than one process controlled the distribution of Cu and Zn in sewage sludge-amended soil. In the complex system of sewage sludge and soil, the metals may interact with the system in any combination of processes. In this experiment, it appeared that initially (i.e. the first four weeks of incubation) plant availability of Cu and Zn increased due to the degradation of organic matter and the loss of acidic functional groups. Thereafter, the formation of new products, whether a more stable organic fraction, new inorganic material such as amorphous oxides or a combination of both, resulted in very low concentrations of plant available Cu and Zn and an increase in ammonium oxalate extractable Cu and Zn.

VI. SUMMARY AND CONCLUSIONS

This study was undertaken in response to the concern for the potential for contamination of soil by heavy metals through the disposal of sewage sludge. The first part of the study involved the chemical characterization of the sewage sludge. It was necessary to define the various components of the sewage sludge in order to determine the metal distribution within the sludge matrix. The second part of the study was to determine the effect of ionic strength on the availability of the Cu and Zn from the sewage sludge. Ionic strength was considered an important variable with respect to metal availability due to its constant variation in the soil solution. Finally, the change in the metal distribution was investigated upon the mineralization of sewage sludge in soil.

The sewage sludge consisted of approximately 20% organic carbon and possessed a large inorganic fraction which was evident in the high concentrations of iron and aluminum found in the sludge. The results from the metal fractionation study showed that a higher proportion of Cu was associated with the organic fraction than Zn, and that most of the Cu and Zn was released after treatment with acidified ammonium oxalate. Despite the high organic carbon content and acidity of the sewage sludge, very little of the Cu and Zn were exchangeable with neutral salts, indicating

chelation or inorganic forms.

Extractions at comparable ionic strengths showed that KCl extracted more Cu than did CaCl₂ and that both extractants released much more Cu than Zn, approximately 10% and 1% respectively. The extraction results supported the evidence obtained from the metal fractionation which demonstrated a difference in the forms with which Cu and Zn were complexed. Increasing the ionic strength of the extracting solution within the normal soil range did not result in increasing amounts of Cu and Zn released from the sewage sludge samples. The extracting solutions of ionic strengths greater than 1 M did result in an increase in Cu and Zn released. The data suggested the presence of a physical effect of ionic strength on the organic polymer conformation, which resulted in the occlusion of metals within the polymer. At the high ionic strength, chemical reactions such as the increase in exchange reactions and increased dissolution of solid phases appeared to dominate resulting in greater amounts of Cu and Zn released.

When sludge was added to soil, there was an initial rapid organic matter decomposition and a decrease in acidic functional groups. However, there did not appear to be an increase in soluble or exchangeable Cu and Zn. At soil-sludge ratios of 1:1 and 4:1, the concentration of Cu and Zn extracted with DTPA would indicate the possibility of plant toxicity early after sludge application but the risk could

be eliminated by separating sludge application and cropping by an appropriate time interval. However, the rates of sewage sludge application rates investigated were high compared to the maximum loading limits presently used by the City of Winnipeg. The significant decline in organic carbon content did not result in corresponding decreases in organically bound Cu and Zn. The increase in Cu and Zn associated with the oxide and organomineral fraction suggested that any metals released from the decomposing organic matter were immediately complexed with the new organic products formed or with the inorganic and organomineral fraction in soil. The data strongly suggest a rapid transfer of these metals from sewage sludge to soil components. The author concedes that some of these soil components are new products formed upon reaction between sewage sludge and soil. However, the preponderance of evidence suggests that the two soils used in this study are effective sinks for sludge-borne Cu and Zn.

In general, the results obtained from this work suggest that the risk of contamination by Cu and Zn added with sewage sludge to agricultural land is negligible. Copper and Zn were found to exist mainly as associations with oxides or organomineral materials in the sewage sludge. These metal complexes appeared to be stable as neither increasing solution ionic strength, nor mineralization of the sewage sludge resulted in increased concentrations of

soluble, exchangeable or DTPA extractable Cu and Zn. Therefore, plant availability and mobility of Cu and Zn from this sewage sludge is low. Thus, one would not expect detrimental environmental effects such as food chain contamination, ground water contamination or crop toxicity to occur due to sludge-borne Cu or Zn supplied from the City of Winnipeg.

LITERATURE CITED

- Adams, F. 1971. Ionic concentrations and activities in soil solutions. *Soil Sci. Soc. Amer. Proc.* 35:420-426.
- Akinremi, O.O., T.B. Goh, E.G. Gregorich, and C.A. Monreal. 1991. Validation of the Century Model for the simulation of C and N dynamics using short- and long-term data generated in Manitoba. Report submitted to Agriculture Canada on Soil Quality Evaluation Project #7. 21 pages.
- Alexiades, C.A. and M.L. Jackson. 1965. Quantitative determination of vermiculite in soils. *Soil Sci. Soc. Amer. Proc.* 29:522-527.
- Barbarika, A. Jr., L.J. Sikora, and D. Colacicco. 1985. Factors affecting the mineralization of nitrogen in sewage sludge applied to soils. *Soil Sci. Soc. Amer. J.* 49:1403-1406.
- Barrow, N.J. and T.C. Shaw. 1982. Effects of ionic strength and nature of the cation on the desorption of fluoride from soil. *J. Soil Sci.* 33:219-231.
- Bartlett, R. and B. James. 1980. Studying dried, stored soil samples-some pitfalls. *Soil Sci. Soc. Am. J.* 44:721-724.
- Beckett, P.H.T. 1989. The use of extractants in studies on trace metals in soils, sewage sludges, and sludge-treated soils. In B.A. Stewart (ed.). Advances in Soil Science, Volume 9. pp. 143-172. Springer-Verlag New York, Inc.
- Black, A.S. and A.S. Campbell. 1982. Ionic strength of soil solution and its effect on charge properties of some New Zealand soils. *J. Soil Sci.* 33:249-262.
- Bloomfield, C. and G. Pruden. 1975. The effects of aerobic and anaerobic incubation on the extractabilities of heavy metals in digested sewage sludge. *Environ. Pollut.* 8:217-232.
- Bremner, J.M. and C.S. Mulvaney. 1982. Nitrogen-Total. In A.L. Page, R.H. Miller, and D.R. Keeney (eds.). Methods of soil analysis Part 2- Chemical and microbiological properties. Second Edition. pp. 595-625. American Society of Agronomy, Inc. and Soil Science Society of America, Inc. Madison, Wis.

- Cavallaro, N. and M.B. McBride. 1980. Activities of Cu^{2+} and Cd^{2+} in soil solutions as affected by pH. *Soil Sci. Soc. Am. J.* 44:729-732.
- Cerrato, M.E., T.B. Goh, and G.J. Racz. 1990. Mineralization of nitrogen in sewage sludge amended soil in southern Manitoba. *Agronomy Abstracts.* p. 265.
- Coker, E.G. 1966. The value of liquid digested sewage sludge. III. The results of an experiment on barley. *J. Agric. Sci.* 67:105-107.
- Cotton, F.A. and G. Wilkinson. 1988. Advanced inorganic chemistry. Fifth Edition. Chapters 16 and 18. Wiley Interscience Publ., New York. 1455p.
- Cunningham, J.D., D.R. Keeney, and J.A. Ryan. 1975a. Yield and metal composition of corn and rye grown on sewage sludge-amended soil. *J. Environ. Qual.* 4:448-454.
- Cunningham, J.D., J.A. Ryan, and D.R. Keeney. 1975b. Phytotoxicity in and metal uptake from soil treated with metal-amended sewage sludge. *J. Environ. Qual.* 4:455-460.
- Cunningham, J.D., J.A. Ryan, and D.R. Keeney. 1975c. Phytotoxicity and uptake of metals added to soils as inorganic salts or in sewage sludge. *J. Environ. Qual.* 4:460-462.
- Dudley, L.M., B.L. McNeal, and J.E. Baham. 1986. Time-dependent changes in soluble organics, copper, nickel, and zinc from sludge amended soils. *J. Environ. Qual.* 15:188-192.
- Emmerich, W.E., L.J. Lund, A.L. Page, and A.C. Chang. 1982. Solid phase forms of heavy metals in sewage sludge-treated soils. *J. Environ. Qual.* 11:178-181.
- Fitzgerald, M., T.B. Goh, V. Huzel, J. Audette, and A.B. Hastie. 1992. Retention of cadmium by treated municipal sewage sludge. In Proceedings of the 35th Annual Manitoba Society of Soil Science Meetings. Winnipeg, Manitoba. pp. 186-196.
- Furrer, O.J. and W. Stauffer. 1986. Influence of sewage sludge and slurry application on nutrient leaching losses. In: A.D. Kofoed et al. (eds.). Efficient land use of sludge manure. pp. 108-115. Elsevier Applied Science Publishers Ltd., New York.

- Gamble, D.S., C.H. Langford, and A.W. Underdown. 1985. Light scattering measurements of Cu(II)-fulvic acid complexing: The interdependence of apparent complexing capacity and aggregation. *Org. Geochem.* 8:35-39.
- Gamble, D.S., M. Schnitzer, and . Hoffmann. 1970. Cu²⁺-fulvic acid chelation equilibrium in 0.1 M KCl at 25°C. *Can. J. Chem.* 48:3197-3204.
- Ghosh, K. and M. Schnitzer. 1981. Fluorescence excitation spectra and viscosity behaviour of a fulvic acid and its copper and iron complexes. *Soil Sci. Soc. Am. J.* 45:25-29.
- Goda, T., T. Kuboi, and K. Fujii. 1986. Environmental impacts of sewage sludge applied to cropland. *Intern. J. Environmental Studies.* 27:239-253.
- Goh, T.B., A. Violante, and P.M. Huang. 1986. Influence of tannic acid on retention of copper and zinc by aluminum precipitation products. *Soil Sci. Soc. Am. J.* 50:820-825.
- Goh, T.B., J. Koenig, and G.J. Racz. 1988. The availability and uptake of copper and zinc adsorbed on iron oxides. In Proceedings of the 31st Annual Meetings of the Manitoba Society of Soil Science. Winnipeg, Manitoba. pp. 128-136.
- Hayes, M.H.B. and R.S. Swift. 1978. The chemistry of soil organic colloids. In D.J. Greenland and M.H.B. Hayes (eds.). The chemistry of soil constituents. pp. 179-320. Wiley Interscience Publ., New York.
- Hernandez, T., J.I. Moreno, and F. Costa. 1988. Characterization of sewage sludge humic substances. *Biological Wastes.* 26:167-174.
- Hohla, G.N., R.L. Jones, and T.D. Hinesly. 1978. The effect of anaerobically digested sewage sludge on organic fractions of Bount silt loam. *J. Environ. Qual.* 7:559-563.
- Hue, N.V., J.A. Silva, and R. Arafin. 1988. Sewage sludge-soil interactions as measured by plant and soil chemical composition. *J. Environ. Qual.* 17:384-390.
- Hue, N.V. 1988. A possible mechanism for manganese phytotoxicity in Hawaii soils amended with a low-manganese sewage sludge. *J. Environ. Qual.* 17:473-479.

- Isaac, R.A. and J.D. Kerber. 1971. Atomic absorption and flame photometry: Technique and uses in soil, plant, and water analysis. In L.M. Walsh (ed.). Instrumental methods for analysis of soils and plant tissue. pp.17-39. Soil Science Society of America, Inc. Madison, Wis.
- Kalbasi, M., G.J. Racz, and L.A. Loewen-Rudgers. 1978. Mechanism of zinc adsorption by iron and aluminum oxides. *Soil Sci.* 125:146-150.
- Kiekins, L. and A. Cottenie. 1982. Possibilities of reducing plant availability of heavy metals in a contaminated soil. In R.D. Davis et al. (eds.) Environmental effects of organic and inorganic contaminants in sewage sludge. pp. 215-226. Proc. of a workshop held at Stevenage. D. Riedel Publishing Co. Dordrecht, Holland.
- Kloke, A., D.R. Sauerbeck, and H. Vetter. 1984. The contamination of plants and soils with heavy metals in terrestrial food chains. In: J.O. Nriagu (ed.). Changing metal cycles and human health. pp. 113-141. Springer-Verlag, Berlin.
- Lagerwerff, J.V., G.T. Biersdorf, and D.L. Bower. 1976. Retention of metals in sewage sludge I: Constituent heavy metals. *J. Environ. Qual.* 5:19-23.
- Lake, D.L., P.W.W. Kirk, and J.N. Lester. 1984. Fractionation, characterization, and speciation of heavy metals in sewage sludge and sludge-amended soils: A review. *J. Environ. Qual.* 13:175-183.
- Lavkulich, L.M. and J.H. Wiens. 1970. Comparison of organic matter destruction by hydrogen peroxide and sodium hypochlorite and its effects on selected mineral constituents. *Soil Sci. Soc. Amer. Proc.* 34:755-758.
- Lester, J.N. 1987. Biological treatment. In J.N. Lester (ed.). Heavy metals in wastewater and sludge treatment processes. Volume 2 Treatment and disposal. pp. 15-40. CRC Press Inc. Boca Ratan, Florida.
- LeClaire, J.P., A. C. Chang. C.S. LeVesque, and G. Sposito. 1984. Trace metal chemistry in arid-zone field soils amended with sewage sludge: IV. Correlations between zinc uptake and extracted soil zinc fractions. *Soil Sci. Soc. Am. J.* 48:509-513.
- Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley and Sons, Inc. New York. 449p.

- Lindsay, W.L., and W.A. Norvell. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Sci. Soc. Am. J.* 42:421-428.
- Magdoff, F.R., and F.F. Amadon. 1980. Nitrogen availability from sewage sludge. *J. Environ. Qual.* 9:451-455.
- McBride, M.B. 1981. Forms and distribution of copper in solid and solution phases of soil. In J.F. Loneragan, A.D. Robson, and D.R. Graham (eds.). Copper in soils and plants. pp. 25-45. Academic Press. Australia.
- McKeague, J.A. and J.H. Day. 1966. Dithionite- and Oxalate- extractable Fe and Al as aids in differentiating various classes of soils. *Can. J. Soil Sci.* 46:13-22.
- McLean, E.O. 1982. Soil pH and lime requirement. In A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis Part 2-Chemical and microbiological properties. Second Edition. pp. 199-224. American Society of Agronomy, Inc. and Soil Science Society of America, Inc. Madison, Wis.
- Metzger, L. and B. Yaron. 1987. Influence of sludge organic matter on soil physical properties. In Advances in Soil Science. Volume 7. pp. 141-163. Springer-Verlag New York Inc. New York.
- Miller, M.H. and O.J. Ohlrogge. 1958. Water soluble chelating agents in organic materials: I. Characterization of chelating agents and their reactions with trace metals in soils. *Soil Sci. Soc. Amer. Proc.* 22:225-228.
- Miller, W.P., D.C. Martens, L.W. Zelazny, and E.T. Kornegay. 1986. Forms of solid phase copper in copper-enriched swine manure. *J. Environ. Qual.* 15:69-72.
- Milne, R.A. and D.N. Graveland. 1972. Sewage sludge as a fertilizer. *Can. J. Soil Sci.* 52:270-273.
- Mott, C.J.B. 1981. Anion and ligand exchange. In D.J. Greenland and M.H.B. Hayes (eds.). The chemistry of soil processes. pp. 179-220. Wiley, Chichester and New York.
- Nakayama, F.S. 1971. Problems associated with the determination and application of the solubility product constant. *Soil Sci. Soc. Amer. Proc.* 35:442-445.

- Norvell, W.A. 1972. Equilibria of metal chelates in soil solution. In J.J. Mortvedt (ed.) Micronutrients in Agriculture. pp. 115-136. Am. Soc. Agron. Madison, Wis.
- Oades, J.M. 1989. An introduction to organic matter in mineral soils. In J.B. Dixon and S.B. Weed (eds.). Minerals in the soil environment. Second Edition. pp. 89-161. Soil Science Society of America, Inc. Madison, Wisconsin.
- Petruzzelli, G. 1989. Recycling wastes in agriculture: Heavy metal bioavailability. Agric. Ecosystems Environ. 27:493-503.
- Ponnamperuma, F.N., E.M. Tianco, and T.A. Loy. 1966. Ionic strengths of the solutions of flooded soils and other natural aqueous solutions from specific conductance. Soil Science. 102:408-413.
- Riffaldi, R., R. Levi-Minzi, A. Saviozzi, and M. Tropea. 1983. Sorption and release of cadmium by some sewage sludges. J. Environ. Qual. 12:253-256.
- Sauerbeck, D. and P. Styperek. 1987. Heavy metals in soils and plants of 25 long-term field experiments treated with sewage sludge. In E. Welte and I. Szaboles (eds.). Proceedings of the 4th International CIEC Symposium. Braunschweig. pp. 439-451.
- Schaumberg, G.D., C.S. LeVesque-Madore, G. Sposito, and L.J. Lund. 1980. Infrared spectroscopic study of the water-soluble fraction of sewage sludge-soil mixtures during incubation. J. Environ. Qual. 9:297-303.
- Schnitzer, M. 1969. Reactions between fulvic acid, a soil humic compound and inorganic soil constituents. Soil Sci. Soc. Amer. Proc. 33:75-81.
- Schnitzer, M. and U.C. Gupta. 1965. Determination of acidity in soil organic matter. Soil Sci. Soc. Amer. Proc. 29:274-277.
- Schnitzer, M. and H. Kodama. 1977. Reactions of minerals with soil humic substances. In J.B. Dixon and S.B. Weed (eds.). Minerals in Soil Environments. pp. 741-770. Soil Science Society of America, Inc. Madison, Wisconsin.

- Schwertmann, U., and R.M. Taylor. 1989. Iron oxides. In J.B. Dixon and S.B. Weed (eds.). Minerals in the soil environment. Second Edition. pp. 370-439. Soil Science Society of America, Inc. Madison, Wisconsin.
- Sequi, P., G. Guidi, and G. Petruzzelli. 1975. Influence of metals on solubility of soil organic matter. *Geoderma*. 13:153-161.
- Silberberg, A. 1968. Adsorption of flexible macromolecules. IV. Effect of solute-solvent interactions, solute concentration, and molecular weight. *J. Chem. Phys.* 48:2835-2851.
- Silviera, D.J. and L.E. Sommers. 1977. Extractability of copper, zinc, cadmium, and lead in soils incubated with sewage sludge. *J. Environ. Qual.* 6:47-52.
- Simeoni, L.A., K.A. Barbarick, and B.R. Sabey. 1984. Effect of small-scale composting of sewage sludge on heavy metal availability to plants. *J. Environ. Qual.* 13:264-268.
- Sims, J.T. and J.S. Kline. 1991. Chemical fractionation and plant uptake of heavy metals in soils amended with co-composted sewage sludge. *J. Environ. Qual.* 20:387-395.
- Smith, B.F.L. and B.D. Mitchell. 1984. Characterization of x-ray amorphous material in a Scottish soil by some selective chemical techniques. *Clay Miner.* 19:737-744.
- Sojo, L.E., D.S. Gamble, C.H. Langford, and R.H. Zienius. 1989. The reactions of paraquat and divalent metal ions with humic acid: Factors influencing stoichiometry. *J. Environ. Sci. Health.* B24:619-646.
- Sposito, G., C.S. LeVesque, J.P. LeClaire, and A.C. Chang. 1983. Trace metal chemistry in arid-zone field soils amended with sewage sludge: III. Effect of time on the extraction of trace metals. *Soil Sci. Soc. Am. J.* 47:898-902.
- Sposito, G. and K.M. Holtzclaw. 1977. Titration studies on the polynuclear, polyacidic nature of fulvic acid extracted from sewage sludge-soil mixtures. *Soil Sci. Soc. Am. J.* 41:330-336.
- Sposito, G., K.M. Holtzclaw, and D.A. Keech. 1977. Proton binding in fulvic acid extracted from sewage sludge-soil mixtures. *Soil Sci. Soc. Am. J.* 41:1119-1125.

- Stevenson, F.J. 1982. Humus chemistry. Chapter 2. Extraction, fractionation, and general chemical composition of soil organic matter. John Wiley and Sons, Toronto. pp. 26-54.
- Stevenson, F.J. and M.S. Ardakani. 1972. Organic matter reactions involving micronutrients in soil. In J.J. Mortvedt, P.M. Giordano, and W.L. Lindsay (eds.) Micronutrients in Agriculture. pp. 79-114. Soil Science Society of America. Madison, Wisconsin.
- Sterritt, R.M. and J.N. Lester. 1983. Mechanisms of heavy metal concentration into sewage sludge. In P. L'Hermite and H. Ott (eds.). Proc. Int. Conf. Processing and use of sewage sludge. pp. 172-175. D. Reidel Publishing Co., Dordrecht, Boston and Lancaster.
- Stover, R.C., L.E. Sommers, and D.J. Silviera. 1976. Evaluation of metals in waste water sludge. J. Water Pollut. Control Fed. 48:2165-2175.
- Tan, K.H., L.D. King, and H.D. Morris. 1971. Complex reactions of Zn with organic matter extracted from sewage sludge. Soil Sci. Soc. Amer. Proc. 35:748-751.
- Tan, K.H., R.A. Leonard, A.R. Bertrand, and S.R. Wilkinson. 1971. The metal complexing capacity and the nature of the chelating ligands of water extract of poultry litter. Soil Sci. Soc. Amer. Proc. 35:265-269.
- Theng, B.K.G. 1979. Formation and properties of clay-polymer complexes. Developments in Soil Science Volume 9. Chapter 2. Elsevier Publishing Co. Amsterdam. 362p.
- Vedy, J.C., T. Dellis, and A.C.M. Bourg. 1986. Biototoxicity of trace metals and composted sludge / Mineral substrate interactions. Toxicological and Environmental Chemistry. 12:237-254.
- Wang, Z., D.S. Gamble, and C.H. Langford. 1992. Interaction of atrazine with Laurentian soil. Environ. Sci. Technol. 26:560-565.
- Weerasinghe, N.C.A., M.L. Gross, and D.J. Lisk. 1985. Polychlorinated dibenzodioxins and polychlorinated dibenzofurans in sewage sludges. Chemosphere. 14:557-564.
- Wollan, E. and P.H.T. Beckett. 1979. Changes in the extractability of heavy metals on the interaction of sewage sludge with soil. Environ. Pollut. 13:215-230.

Yeomans, J.C. and J.M. Bremner. 1988. A rapid and precise method for routine determination of organic carbon in soil. Commun. in Soil Sci. Plant Anal. 19(13):1467-1476.