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DISSERTATION

EFFECT OF BIOSOLIDS APPLICATION AND ROLE OF DISSOLVED ORGANIC MATTER ON THE MOVEMENT OF HEAVY METALS IN SOILS

Submitted by
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In partial fulfillment of the requirements
For the Degree of Doctor of Philosophy
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WE HEREBY RECOMMENDED THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY MOHAMMAD I. AL-WABEL ENTITLED EFFECT OF BIOSOLIDS APPLICATION AND ROLE OF DISSOLVED ORGANIC MATTER ON THE MOVEMENT OF HEAVY METALS IN SOILS BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

Committee on Graduate Work

Co-advisor

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ABSTRACT OF DISSERTATION

EFFECT OF BIOSOLIDS APPLICATION AND ROLE OF DISSOLVED ORGANIC MATTER ON THE MOVEMENT OF HEAVY METALS IN SOILS

The use of biosolids as a soil fertilizer has been shown to be an agronomicaly beneficial practice. Biosolids supply nutrients and organic matter to semi-arid soils. However, biosolids contain heavy metals. Long-term use may result in the accumulation of heavy metals in soils. The movement of heavy metals in the soil profile is an important environmental concern and not well understood by scientists This research was conducted on two soils that received long-term biosolids application from different biosolid sources. One was a dryland soil (Fine, smectitic, mesic Aridic Argiustoll) that had received semi-annual application from 1982 to 1992, and another was an irrigated soil (Loamy, mixed, mesic Arenic Ustollic Haplargid) that had received six applications from 1988 to 1997. Two different sources of biosolids were applied at a rate of 26.8 and 28 Mg ha^{-1} yr^{-1}, respectively. Soil profiles were collected from these two locations to depth of 100-cm. Electrical conductivity (EC), pH, organic matter (O.M.) and NO_3-N, total and AB-DTPA extractable Cu, Zn, and Pb contents of the samples were measured. A column study was also conducted to determine the effect of dissolved organic carbon (DOC) and EC of the leaching water on the movement of heavy metals through the soil profile.

The results for the dryland soil profile indicated that the concentration of Cu, Zn and Pb increased in the topsoil and that Zn and Cu moved below the treated layer while Pb did not. Also, we found a positive correlation between O.M. and Cu, Zn and Pb, while

their correlation was negative with EC and pH. In the irrigated soil, the treated and untreated soils were found to be originally different. This made the determination of the effect of biosolids addition on soil properties difficult. The results of the column study did show that DOC was significantly increased immediately after the addition of biosolids and had decreased to near background levels after ten leaching cycles. The addition also increased both DOC and Cu in the column effluents resulting in a positive correlation between Cu and DOC across application treatments for both soils. Zn mobility was positively correlated with EC. From the anodic stripping voltammetry (ASV) analysis, the results showed that more than 99% of Cu and Zn and at least 90% of Pb complexed with either DOC or mineral colloids and only a very small percentage of the total dissolved metals concentrations existed as free ions or inorganic complexes. Moreover the results also showed the highest concentration of the DOC and the heavy metals in the leaching effluent were observed immediately after biosolids addition.

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DEDICATION

I dedicate this dissertation to my beloved parents who encouraged me to complete my study and who left this world before I finished this work. They were the lights of hope to me, and I will not ever return what they did for me except in praying for them. I also dedicate this work to my family, my wife Haifa and my sons Ibrahiem, Abdulrahman, and Abdullah, to whom I owe more than I can possibly express. Without their patience, support, smiles and prayers this work would have not been possible.

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CHAPTER I

GENERAL INTRODUCTION AND LITERATURE REVIEW

INTRODUCTION

Facts and beneficial uses of biosolids:

The application of organic wastes (agricultural, municipal, and industrial) to soils has increased in the last century. The land application of biosolids to agricultural land is a natural way of recycling these materials. Application methods may include spreading, spraying, injecting, or incorporating the biosolids into the soil. The process results in either a surface application, which is then tilled into the soil, or the biosolids can be injected directly into the soil. Due to the content of heavy metals or other pathogenic materials in biosolids, there are laws and regulations controlling the loading rates of heavy metals. In the US, the Environmental Protection Agency (EPA) promulgated regulation No. 40 in the Code of Federal Regulations (CFR) part 503 to control the handling and application of biosolids materials with the objective of ensuring there will be no adverse affect on human health or the environment (U.S. Environmental Protection Agency, 1994). This need for land application has been driven by several potential benefits, such as avoiding the accumulation of waste in the environment and the addition of nutrients to soils and the improvement of soil characteristics that may result from adding organic matter to low organic soils.

Advantages of biosolids application:

The addition of biosolids to agricultural land also improves the soils physical properties. For instance, on biosolids amended dryland soils, the retention of moisture increases even in drought conditions; additionally, such additions help the soil to build

good structure, thereby reducing wind erosion. On irrigated soils, the addition of biosolids increases the water-holding capacity, and may lead to stress reduction on the plants between irrigation cycles. The fine-textured soils, the addition of biosolids causes the soil to be more friable and increases the number of pore voids; this helps improve the movement of water and air through the soil, and results in more space for root growth. Furthermore, the addition of biosolids to some soils increases aggregate stability, increases the volumetric moisture content, and decreases in soil bulk density. Both soil porosity and water hydraulic conductivity are also increased, which in turn increases the infiltration rate.

The addition of biosolids to agricultural lands also increases the content of organic matter, which improves the soil tilth and provides an improved seedbed. It also improves seed germination and root penetration. Addition of organic matter reduces soil compaction, and increases the carbon level in soil; the increased amount of organic matter will retain nutrients and also help plants withstand drought. Storm-water runoff and erosion are also reduced by the addition of biosolids.

Disadvantages of biosolids application:

On the other hand, biosolids application can have some disadvantages as well. One major disadvantage is the increase of heavy elements in the soil, especially from waste that comes from industrial sources. Heavy metals continue to be of major concern because of their potential toxicity to the environment. This is because the concentrations of heavy metals in biosolids are greater than what is normally found in soils. Consequently, it is possible for these metals to accumulate in the topsoil and possibly contaminate ground

water if leaching occurs or contaminate surface water if runoff occurs. These heavy metals typically occur in small concentrations in the soil and are usually harmless to plants. While some of them, such as Cu and Zn, are necessary for plant growth, others, if found in high amounts, can become toxic to plants, thereby reducing their yield and providing a potential pathway for heavy metals to enter into the food chain.

Distribution of heavy metals in the soil profile:

One environmental problem caused by heavy metals stems from their movement from the treated layer to subsurface soil. The heavy metals found in the soil are distributed between a solid and a solution phase. Some factors affecting this are the complexation of heavy metals with inorganic or organic molecules. In many early experiments, scientists looked at profile distributions of total metal concentrations and concluded there was no movement and that these elements are therefore immobile. However, some recent experiments have shown that heavy metals can display mobility and move below the treated layers, but this movement may not be significant.

In some studies, researchers were unable to recover the mass balance between the amount of heavy metals that had been added to the topsoil with the amount found in the soil profile and removed in the plant material. Additionally, other researchers found some traces of heavy metals in shallow waters below the treated layers.

Effect of some soil factors on the mobility of heavy metals:

Heavy metals found in soils can be found in different forms. These forms are distinguished as: 1) water soluble, 2) exchangeable, 3) sorbed, 4) organic, 5) oxide, and

6) carbonate and sulfide, plus residual forms. The most mobile forms are the water soluble and the exchangeable form, which have been found to be the most bioavailable forms of the total metal content.

Soil reaction (pH):

Soil reaction is one of the important factors that can affect the mobility of metals by the transformation of metals between the different chemical forms, and may be the best indicator of the chemical characteristics of the soil. An element's mobility increases when the soil pH decreases. Mobility of heavy metals in soil is related to pH-dependent charges on the surface of the clay or other soil components. This effect can be described by the hydrolysis reactions and the changes in the OH groups on the organic matter, oxides, and minerals. However, when the pH increases >7 the retention of metals in the soil particles increases.

Dissolved organic matter:

The migration of heavy metals could be enhanced by their complexation with some fraction of the organic matter. In addition to humic-like substances, composting biosolids produces a water-soluble organic matter known as dissolved organic carbon (DOC), which can pass through a 0.45μm filter. This DOC has a low molecular weight and is a mixture of polymeric materials containing a number of polar and non-polar sites.

Understanding the effect of DOC on the movement of heavy metals in the soil profile is necessary. Despite the role of adsorption in removing heavy metals from the soil solution, the interaction between heavy metals and DOC, and the behavior of DOC

after it complexes with heavy metals and their migration through the soil profile is very important. The addition of biosolids may increase the binding of heavy metals to the solid phase, which in turn may decrease the mobility of these metals through the soil profile. Adding biosolids may also affect the distribution of metals in various soil chemical fractions.

With respect to the effect of DOC on the migration of heavy metals from topsoil to sub-surface soil in biosolid-treated soils, there is a lack of information regarding the mechanism of movement and the complexation of heavy metals by DOC. Understanding the rate of complexation between DOC and heavy metals, adsorption, desorption, the form of the element that migrates, and how these processes depend on soil properties will help scientists to understand the movement of heavy metals in biosolid-treated soils. For this reason, this study was undertaken with the following objectives.

Objectives:

The objectives of this project were twofold:

1) To investigate the distribution and mobility of Zn, Cu, and Pb in the profiles of two different soils that had received long-term application of biosolids.

(2) To study the effects of DOC, electrical conductivity of leaching water(EC), and soil pH on mechanisms of migration of heavy metals from the treated soil layers in two different soils that had received long-term biosolids application.

LITERATURE REVIEW

General facts about biosolids:

The application of biosolids to agricultural lands has become a common practice because of its advantages in supplying the soil with some of its needs in an economical way. This technique has raised some environmental issues about the toxicity of the heavy metals that are commonly found in the biosolids.

Mobility and bioavailability of heavy metals depend on their chemical forms in the soil solution. Mobility is a term used to estimate the movement and risk of contaminants in soil. In this work, we define the mobility as the ability of certain elements to move or migrate in a soil profile by physical-chemical processes. The concept of mobility of heavy metals has long been studied by many researchers (Gerritse et. al., 1982; Domergue and Vedy, 1992; McBride et. al., 1997a).

High amounts of biosolids can supply high levels of heavy metals, such as Cu, Zn, and Pb to soils. These applications usually result in small accumulations of heavy metals that are not toxic to plants. Some of these metals, such as Zn and Cu, are essential for plant growth. Others, such as Pb and Ni, can be toxic to plants if they build up in excessive amounts. This can affect the productivity of the soil and these heavy metals may enter the food chain or contaminate surface or ground water sources.

Movement of heavy metals in the soil profile:

Heavy metals have generally been thought to be immobile in soils, as they tend to accumulate in the top layer where they are applied. Although some researchers have found that there is no significant movement of some heavy metals from the treated layer to subsoil layers, mass balance studies have brought these conclusions into question. Baveye et al. (1999), in studies of mass balance and distribution of trace elements in a silt loam soil following long-term application of biosolids, not only found increasing concentrations of Cu, Pb and Zn in the top layer but also found that total Zn level increased to a 45 cm depth, while the levels of Cu and Pb did not increase significantly with depth. Baveye et al. (1999) also found through soil profile mass balance calculations that a relatively high proportion of the heavy metals applied could not be accounted for in the soil profile. Following long-term applications of biosolids McBride et al. (1997a) found that they were unable to account for all the heavy metals applied in the top surface layer. At one site that had received one heavy application of biosolids 15 years earlier, they found that about 40% of the total Cu and Zn had been lost from the top layer. They concluded that a large fraction of certain heavy metals that had been applied had been redistributed to a deeper depth by physical, chemical, or biological processes.

Dowdy et al. (1991) in their study of a soil that received 765 Mg ha^{-1} as a cumulative amount of biosolids, found small amounts of Zn and Cd moved out of the incorporated zone. They found less than 50% of the total added amounts of Zn and Cd in the topsoil.

Alloway and Jackson (1991) found in their review of biosolids application and its effect on supplying heavy metals to soils, that most of the heavy metals were retained in

the topsoil and their bioavailability remained constant during the residual period of biosolids in the soil.

Some researchers believe that complexation of heavy metals with some ligands may assist in the migration of heavy metals. Barriuso et al. (1992), and Dunnivant et al. (1992) reported that the subsurface transport of inorganic and organic contaminants might be related to the movement of endogenous and/or exogenous dissolved organic matter (DOM) through the soil profile.

As we can learn from the literature, many questions still exist as to the fate of heavy metals in soils that have received biosolids. Mass balance studies generally cannot account for all of the heavy metals applied to the soil system.

Factors affecting heavy metals movement:

Soil reaction:

Soil reaction plays a major role in the solubility and availability of heavy metals. Application of biosolids to alkaline soils may decrease soil pH, which then can increase the metal solubility. Bevacqua and Mellano (1994), in their study of sandy loam soil that had been treated with 74 Mg ha^{-1} of composted biosolids, found that the treated plot had a lowered pH compared to that of the control plot. The same conclusion was reported by Tester (1990) in loamy sand soil that received biosolids to about 240 Mg ha^{-1}. He found the addition of biosolids compost reduced the pH with soil depth. The same conclusion was reported by Narwal et al. (1983); and delCastilho et al. (1993). Neilsen et al. (1986) reported that Zn availability shifted from a less available to a more plant available form after soil pH decreased. Brown et al. (1997) in their study of four different types of biosolids (high metal biosolids, limed undigested, limed-digested, and limed composted

biosolids) effect on metal movement, found the pH of the 1-meter profile was affected significantly. The soil pH was above 7 in the soil that been treated with limed-undigested biosolids in a rate of 224 Mg ha^{-1}. The same conclusion has been found by other researchers (Sloan and Basta, 1995; Dixon et al., 1995; Merrington and Madden, 2000).

Electrical conductivity:

It has been found that the application of biosolids to agricultural soils causes an increase in soil salinity. Work by delCatilho et al. (1993) on an acidic loamy-sand soil that had been amended with cattle manure slurry in a rate of 25 Mg ha^{-1} for about 18 months, found that the addition of cattle manure increased the EC of the topsoil and resulted in an increase of heavy metals. White et al. (1997) in their study of the effect of applying biosolids to range land for about 9 years, found that after biosolids application the EC increased in proportion to the application rate, and after 8 years they found the EC declined to the control soil EC. In a two-year experiment of studying the effect of applying biosolids on the spring seasonal patterns of soil N mineralization, Cartron and Weil (1998) found that EC increased after the application of biosolids to the soil. Tsadilas et al. (1995) in their research of the influence of biosolids on soil properties and on the distribution and availability of heavy metals, found the application of biosolids increases the EC of the soil. The same conclusions were found by other researchers (Inman et al., 1982; Ticknor et al., 1985;Wong et al., 1996; Wong et al., 1998)

Dissolved organic matter:

Dissolved organic matter plays a major role in the soil ecosystem. Some researchers found a relationship between DOC and the transporting of heavy metals (Dunnivant et al., 1992). Some of the heavy metals tend to be highly complexed with

DOC such as Cu, and Pb, while other elements such Zn and Cd tend to complex with the organic substances, but in smaller fraction (McBride et al., 1997a). In a column experiment, Giusquiani et al. (1992) observed that 5% of DOC in a clay loam soil moved to 50 cm depth, while 10% of DOC in sandy loam soil reached 50 cm depth. Lehman and Mills (1994) in their study of dissolved Cu movement from the sediments to the water column as affected by the addition of sodium humate or phytoplankton, found the dissolved copper concentration in chambers amended with sodium humate increased about 500% and was well correlated with DOC concentrations. They concluded that long-term decomposition processes may enhance the formation of soluble organo-metallic complexes and therefore enhance the concentration of dissolved Cu in the water column.

The complexation of metals with organic molecules can increase their concentrations in soil solutions (Parfitt and Russell, 1977; Manley and Evans, 1986; Pohlman and McColl, 1986; and McBride, 1989). The addition of soluble organic matter to soil solutions enhances desorption of metals from soil particles to these organic ligands or into the soil solution (Elrashidi and O'Connor, 1982). Sposito et al. (1982) found that the water-soluble fraction of biosolids was similar to the low molecular weight (fulvic acid) fraction in natural soil organic matter. Others found that Fe and Mn concentrations increase and that their forms change from a less available to a more available form after the addition of organic matter (Shuman, 1988). In a column study, Hern et al. (1988) found that EDTA could be used to enhance the movement of Al from the sub-soil. The movement of Zn can also be enhanced by the addition of dissolved organic matter (Boyle and Fuller, 1987).

McBride et al. (1997a), found that 40% of the added Zn and Cu had been lost from the topsoil 15 years after a single heavy application of biosolids. They also concluded that soluble Cu seems to be in an organically complexed and mobile form. McBride et al. (1997b), in their work to develop a semi-empirical equation from metal complexation theory that relates the metal activity of soil solution with soil pH, organic matter content, and total metal content, found that the total Cu content of the soil correlated highly with the total soluble Cu, and that total Zn was also highly correlated with soil pH.

Temminghoff et al. (1997) found that DOC normally improves the solubility of Cu and Pb, and results in the formation of dissolved and colloidal organo-metal compounds. High concentrations of large molecule weight organic matter compounds such as fulvic acid can increase the retention and decrease the mobility of heavy metals by complexing the mineral with the organic ligand (Chubin and Street, 1981). In a different study, Zn soluble concentration was affected by pH in the topsoil in acid loamy-sand soil amended with cattle manure slurry, while it was affected by DOC in the subsurface soil (delCastilho et al., 1993). The DOC also affected the concentration of Cu. This is due to the strong complexation of DOC with Cu, by which the solubility of Cu is increased (Romkens and Salomons. 1998). Chairidchai and Ritchie (1990) found that the retention of organic matter could decrease the movement of heavy metals due to the complexation of immobile humic acid with the metal ion. In a column study of urban waste-amended soil, researchers found that 70-80% of soluble organic matter was retained in the top 10 cm of the soil, indicating that this retention most often occurs in the topsoil layer (Giusquiani et. al., 1992). McBride, (1989) mentioned that the addition of

organic wastes to soils could affect the solubility of heavy metals due to an increase in complexation capacities. It has also been found that organic components (organic acids, amino acids, and fulvic acid) can affect the solubility of heavy metals (Williams et al., 1980). These researchers found movement of heavy metals from the topsoil layer to the subsurface layers. Other researchers have reported that the only element that has a potential for movement is Zn (Dowdy and Volk, 1983). Totsche et al. (2000), in a study of the effects of fluoride on heavy metals' mobilization, found the main effect was the increasing of DOC. Chirenje and Ma, (1999) in a study on the affect on acidification of soils amended with paper mill ash, found that decreases in pH caused the concentration of both DOC and Cu to be reduced.

It is obvious from the literature that heavy metals may migrate from the layer of application to deeper depths. The mechanism of movement is not known and information on these mechanisms is needed if we are going to be able to predict heavy metals migration in soils.

REFERENCES

Alloway, B. J., and A. P. Jackson. 1991. The behavior of heavy metals in sewage sludge-amended soils. Sci. Total Environ. 100:151-176

Barriuso, E., U. Bear, and R. Calvet. 1992. Dissolved organic matter and adsorption. desorption of dimefurun, atrazine, and carbetamide by soils. J. Environ. Qual. 21 :359-367.

Baveye, P., M. B. McBride, D. B. Thomas D. H., M. S.A. Dahdoh, and M.F. Abdel-Sabour. 1999. Mass balance and distribution of sludge-borne trace elements in a silt loam soil following long-term applications of sewage sludge. Sci. Total Environ. 227:13-28.

Bevacqua, R. F., and V. J. Mellano. 1994. Cumulative effects of sludge compost on crop yields and soil properties. Common. Soil. Sic. Plant. Anal. 25:395-406.

Boyle, M. and W.H. Fuller, 1987. Effect of municipal solid waste leachate composition on zinc migration through soils. J. Environ. Qual. 16:357-360.

Brown, S., R. Chany, and J. S. Angle. 1997. Subsurface liming and metal movement in soils amended with lime stabilized biosolids. J. Environ. Qual. 26:724-732.

Cartron, J. M., and R. R. Weil. 1998. Seasonal trends in soil nitrogen from injected or surface incorporated sewage sludge applied to corn. Commun. Soil Sci. Plant Anal. 29:121-139.

Chairidchai, P., and G. S. P. Ritchie. 1990. Zinc and copper sorption and fixation on acid soil clay. Effect of selective dissolutions. Soil Sci. Soc. Am. J. 48:1050-1054.

Chirenje, T., and L. Q. Ma. 1999. Effects of acidification on metal mobility in a paper mill ash amended soil. J. Environ. Qual. 28:760-766.

Chubin, R. G., and J. J. Street. 1981. Adsorption of cadmium on soil constituents in presence of complexation ligands. J. Environ. Qual. 10:225-228.

delCastilho, P., W. J. Chardon, and W. Salomons. 1993. Influence of cattle-manure slurry application on the solubility of cadmium, copper, and Zn in a manure acidic, loamy-sand soil. J. Environ. Qual. 22:689-697.

Dixon, F. M., J. R. Preer, and A. N. Abdi. 1995. Metal levels in garden vegetables raised on biosolids amended soil. Compost Sci. Util. 3:55-63.

Domergue, F. L., and J. C. Vedy. 1992. Mobility of heavy metals in soil profiles. Intern. J. Environ. Anal. Chem. 46:13-23.

Dowdy, R. H., and V.V. Volk. 1983. Movement of heavy metals in soils. p. 227-240. *In* D. W. Nelson et al. (ed.) Chemical mobility and reactivity in soil systems. SSSA Spec. Pub. II. SSSA, Madison, WI.

Dowdy, R. H., J. J. Laterrell, ,T. D. Hinsely, R. B. Grossman, and D. L. Sullivan. 1991. Trace metal movement in an Aeric Ochraqualf following 14 years of annual sludge applications. J. Environ. Qual. 20:119-123.

Dunnivant, F. M., P. M. Jardline, D. L. Taylor, and J. F. McCarthy. 1992. Co-transport of cadmium and hexachlorobiphenyl by dissolved organic matter through columns containing aquifer material. Environ. Sci. Technol. 26: 360-368.

Elrashidi, M. A., and G. A. O'Conner. 1982. Influence of solution composition on sorption of zinc by soils. Soil Sci. Soc. Am. J. 46:1153-1158.

Gerritse, R. G. R., R. Vriesema, J. W. Dalenberg, and H. P. de Roos. 1982. Effect of sewage sludge on trace element mobility on soils. J. Environ. Qual. 11:359-364.

Giusquiani, P. L., G. Gigliotti, and D. Businelli. 1992. Mobility of heavy metals in urban waste-amended soils. J. Environ. Qual. 21:330-335.

Hern, J.H., H.A. Menser, R.C. Sidle, and T.E. Staley. 1988. Effects of surface-applied lime and EDTA on subsoil acidity and aluminum. Soil Sci. 147:52-57.

Inman, J. C., M. S. McIntosh, J. E. Foss, and D. C. Wolf. 1982. Nitrogen and phosphorus movement in compost-amended soils. J. Environ. Qual. 11:529-532.

Lehman, R. M., and A. L. Mills. 1994. Field evidence of copper mobilization by dissolved organic matter. Water Res. 28:2487-2497.

Manley, E.P., and L.J. Evans. 1986. Dissolution of feldspars by low-molecular-weigh aliphatic and aromatic acids. Soil Sci. 141:106-112.

Merrington, G., and C. Madden. 2000. Changes in cadmium and zinc phytoavailability in agricultural soil after amendment with paper mill sludge and biosolids. Commun. Soil Sci. Plant Anal. 31:759-776.

McBride, M.B. 1989. Reactions controlling heavy metals solubility in soils. Adv. Soil Sci. 10:1-57.

McBride, M.B., B.K. Richards, T.S. Steenhuis, JJ. Russo, and S. Sauve. 1997a. Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. Soil Sci. 162:487-500.

McBride, M. B., S. Sauve, and W. Hendershot. 1997b. Solubility control of Cu, Zn, Cd, and Pb in contaminated soils. Eur. J. Soil Sci. 48: 337-346.

Narwal, R. P., B. R. Singh and A. R. Panhar. 1983. Plant availability of heavy metals in a sludge treated soil: 1: effect of sewage sludge and soil pH on the yield and chemical composition of rape . J. Environ. Qual. 12:358-365.

Neilsen, D., P. B. Hoyt, and A. F. MacKenzie. 1986. Distribution of soil Zn fraction in British Columbia interior orchard soils. Can. J. Soil. Sci. 66:445-454.

Parfitt, R.L., and I. D. Russell. 1977. Adsorption on hydrous oxides: IV Mechanism of adsorption of various ions on geothite, 1. Soil Sci. 28:297-305.

Pohlman, A. A., and J. G. McColl. 1986. Kinetics of metal dissolution from forest soils by soluble organic acids. J. Environ. Qual. 15:86-92.

Romkens, P., and W. Solomons, 1998. Cd, Cu and Zn solubility in arable and forest soils: consequences of land use changes for metal mobility and risk assessment. Soil Sci. 163:859-871.

Shuman, L M. 1988. Effect of organic matter on distribution of manganese, copper, iron and zinc in soil fraction. Soil Sci. 146:192-198.

Sloan, J. J., and N. T. Basta. 1995. Remediation of acid soils by using alkaline biosolids. J. Environ. Qual. 24:1097-1103.

Sposito, G., L.J. Lund, and A.C. Chang. 1982. Trace metal chemistry in arid-zone field soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. Soil Sci. Soc. Am. J. 46:260-264.

Temminghoff, E. J. M., S. E. A. T. M van der zee, and F. A. M. de Hann. 1997. Copper mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved Organic Matter. Environ. Sci. Techno. 31:1109-1115.

Tester, C. F. 1990. Organic amendment effects on physical and chemical properties of a sandy soil. Soil. Sci. Soc. Amer. J. 54:827-831.

Ticknor, R. L., D. D. Hemphill Jr, and D. J. Flower. 1985. Growth response of Photinia and Thuia and nutrients concentration in tissue and potting medium as influenced by composted sewage sludge, peat, bark and sawdust in potting media. J. Environ. Hort. 3:176-180.

Totsche, K. U., W. Wilcke, M. Körber, J. Kobaz, and W. Zech. 2000. Evaluation of fluoride-induced metal mobilization in soil columns. J. Enviro. Qual. 29:454-459.

Tsadilas, C. D., T. Matsi, N. Barbayiannis, and D. Dimoyiannis. 1995. Influence of sewage sludge application on soil properties and on the distribution and availability of heavy metal fraction. Commun. Soil Sci. Plant Anal. 26:2603-2619.

U. S. Environmental protection agency. 1994. A plain English guide to the EPA part 503 biosolids rule. Washington, DC: EPA/832-R-93-003.

White, C. S., S. R. Loftin, and R. Aguilar. 1997. Application of biosolids to degraded semiarid rangeland: nine years responses. J. Environ. Qual. 26:1663-1671.

Williams, D. E., J. Vlamis, A. H. Pukite, J.E. Corey. 1980. Trace element accumulation, movement and distribution in soil profile from massive application of sewage sludge. Soil. Sci. 129:119-132.

Wong J. W. C., G. X. Li, and M. H. Wong. 1996. The growth of Brassica chinensis in heavy metal contaminated sewage sludge compost from Hong Kong. Bio. Res. Techno. 58:309-313.

Wong J. W. C., K. M. Lai, M. Fang, and K. K. Ma. 1998. Effect of sewage sludge amendment on soil microbial activity and nutrient mineralization. Environ. Int. 24:935-943.

CHAPTER II

EFFECTS OF BIOSOLIDS APPLICATION ON THE MOBILITY OF SOME HEAVY METALS IN TWO SOIL TYPES

ABSTRACT:

The agricultural use of biosolids improves a soil's physical properties and provides essential plant nutrients, but can affect some soil factors and heavy metal concentrations in the treated layer. Studies differ in their findings regarding the movement of these heavy metals. The objective of this study is to determine the effect of long-term application of biosolids on heavy metal concentrations in soil profiles. Soil profile samples were collected from a dryland soil, where biosolids had been applied since 1982, at 5 cm increments to a depth of 100 cm (Fine, smectitic, mesic Aridic Argiustoll). Similarly, samples were collected from an irrigated soil (Loamy, mixed, mesic Arenic Ustollic Haplargid), where application had occurred since 1988. Both soils received six biosolids applications at a rate of 26.8 and 28 Mg ha^{-1} yr^{-1}, respectively. The application of biosolids increased electrical conductivity (EC), organic matter (O.M.), and NO_3-N, and decreased the pH in the topsoil. The AB-DTPA extractable Zn, Cu, and Pb concentrations increased significantly in the treated layer. The ratio of AB-DTPA Zn and Cu to the total Zn and Cu increased by 4 and 12 times, respectively, but for Pb this ratio decreased to 0.5 times. There was significant movement for AB-DTPA Zn and Cu below the treated layer, but not for Pb. The total heavy metals did not show a significant movement below the treated layer.

There was a significant positive correlation between Zn, Cu and Pb and O. M., suggesting the transported metal to be in AB-DTPA extractable form. There was also a significant negative correlation between the two forms of Zn, Cu, and Pb and pH.

For the irrigated soil the two soils, treated and untreated, appeared to be different in origin. The study concluded that the increase of the element concentrations in the depths below the treated layer was due to the origins of the soils rather than the effect of the addition of biosolids to these soils. In summary, the total metal concentration of the soil did not show movement of total Zn, Cu, and Pb in the soil profile. However, it appears that the AB-DTPA extractable Zn, Cu, and Pb applied in the biosolids have redistributed and some have moved out of the soil surface by physical-chemical processes.

INTRODUCTION

In the present era, the land application of biosolids has become widespread. The most frequent practice is application to agricultural lands, and many countries have issued regulations to control this practice. The application of composted biosolids to agricultural lands may be a good method for adding rich, fertile material to the soil, but it can also contaminate the soil with toxic elements such as heavy metals, which are of major environmental concern. This concern has received much attention with regard to the accumulation of these metals in the topsoil, as well as their movement to surface water or ground water, since even their slow movement through the soil profile may increase their concentrations in ground or surface water.

Most investigations have revealed metals that occur as slightly soluble or insoluble compounds, and their movement is very low or non-existent. Camoberco et al. (1996) illustrated that heavy metals applied by the addition of biosolids in homogenized soil columns are not mobile. Other studies have also shown that these metals are trapped in the top layer and hence are not mobile.

However, some studies have shown that these elements do move through the soil profile, even though their mobility was relatively low. Except in acid soils, movement of heavy metals requires these elements to be in soluble forms and associated with other ligands. Schirado et al. (1986) found that three metals, Zn, Cd, and Ni, move from the plowed layer to the subsurface layer under high rainfall conditions. Other researchers also found that Cu and Zn move to the subsurface soil, and these metals were found to be complexed with humic acids (Waller and Pickering, 1992).

LITERATURE REVIEW

The mobility of heavy metals in soils is highly correlated with the chemical forms of these metals in the soil and the soil solution. Soil pH, organic matter, solubility of inorganic ions, and the presence of complexing agents are the important factors that can influence the distribution of metals in different forms (Karapanagiotis et al., 1991).

Some researchers believe that heavy metals have low solubility; therefore, they are considered to be immobile (Dowdy and Volk, 1983). Heavy elements such as Cu, Zn, and Pb were not found to move significantly in soils that had been amended with biosolids for eight years (William et al., 1987). Chang et al. (1984) showed that about 90% of the heavy metals applied to soil was found in the top 15 cm of the soil. William et al. (1980, 1987) studied the movement of heavy metals over nine years of experimentation with the application of biosolids to agricultural land, finding no significant movement among the heavy metals studied (Cd, Cu, Cr, Zn, Pb, and Hg) below the treated 20 cm.

Sloan et al. (1998) investigated the effects of long-term application of biosolids on the recovery of heavy metals from biosolids applied to the topsoil of a well-drained soil. They found there was no movement below 45 cm in depth and concluded that it is possible to get complete recovery of the heavy metals that are applied to a soil if the plot size is large enough to minimize the cross mixing of the treated layer with the subsurface layer.

Some researchers concluded that several of the extraction methods that had been used did not recover all the metal from the interior of soil minerals or from high

adsorption capacity sites (Dowdy et al., 1991). Camberco et al. (1996), in their study of the movement of heavy metals through undisturbed and homogenized soil columns, discovered that the four homogenized soil columns retained all the added metals (Cd, Zn, Cu, and Pb). Chairidchai and Ritchie (1990) found that the retention of organic matter could decrease the movement of heavy metals due to the complexation of immobile humic acids with the metal ion. High concentrations of large molecular weight organic matter compounds, such as fulvic acid, can increase the retention and decrease the mobility of heavy metals by complexing the mineral with the organic ligand (Chubin and Street, 1981).

Numerous experiments on long-term application of biosolids have demonstrated that it is not possible to recover all of the heavy metals that are added. Some researchers believe that a fraction of these elements move downward through the soil profile and possibly into ground or surface water. McBride et al. (1997) found that 40% of Zn and Cu had been lost from the topsoil15 years after a single heavy application of biosolids. In a long-term field experiment on biosolids addition, McGrath and Lane (1989) showed that about 68% of the added heavy metals were lost. In their 14-year long study of applying anaerobically digested biosolids to silt loam soil by furrow irrigation, calculations of mass balance carried out by Baveye et al. (1999) showed a relatively high proportion of Cd, Cr, Cu, Ni, Pb and Zn to be unaccounted for in the soil profile for each application rate. Mass balance calculations of losses ranged from a high of 60% for Ni to a low of 36% for Cu and Pb.

In studies using different techniques to measure the mobility of metals, researchers found some migration of various heavy elements from the treated layer

toward the subsurface layer. McBride (1989) mentioned that the addition of organic wastes to soils could affect the solubility of heavy metals due to an increase in complexation capacities. Dowdy and Volk (1983) concluded that the only element that has potential for movement is Zn. In their study of the effect of long-term addition of biosolids to dryland crop soil, Zn was the only element found by Barbarick et al. (1998) to move below the treated layer. Yingming and Corey (1993) found that about 68% of the heavy elements added with the biosolids remained in the treated layer, and found more than 12% of these added elements in the subsoil section.

The objective of this study was to investigate the movement of heavy metals (Zn, Cu, and Pb) in two soils that had received long-term biosolids application: dryland soil and an irrigated soil. The dryland soil, under wheat-fallow, had received six applications of 26.8 Mg ha^{-1} biosolids over a period of 10 years, while the irrigated soil had received six applications of 28.0 Mg ha^{-1} biosolids over 9 years.

MATERIALS AND METHODS

Materials:

Soil samples and biosolid materials:

This study was conducted using two soils from two different locations in Colorado. The soil columns were collected in May 1998. The two locations had each received long-term biosolids application and each differed in soil and biosolid types. The first site, a dryland soil, was located west of Bennett, CO (Adams County). This plot was established in 1982. The mean annual long-term precipitation was 32 cm (Soil Conservation Service, 1974), and the soil type was a Platner loam (fine, smectitic, mesic Aridic Argiustoll). Biosolids from the Littleton/Englewood, CO sewage treatment facility were applied to this site in 1982, 1984, 1986, 1988, 1990 and 1992, with an application rate of 26.8 dry Mg biosolid ha^{-1} (Barbarick et al., 1998). The second site, an irrigated soil, was south of Roggen, CO (Weld County). This plot was established in 1988. The mean annual long-term precipitation was 37 cm (Soil Conservation Service, 1974), and the type of soil on this site was Osgod sand (loamy, mixed, mesic Arenic Ustollic Haplargid) (Table 1). Biosolids from the Metro Denver, CO treatment facility were applied to this site during 1988, 1989, 1992, January 1994, December 1994 and 1997 at a rate of 28 Mg ha^{-1}. Table 1 describes the properties of the biosolids.

Triplicate soil columns 100-cm deep were collected from each site (untreated and treated) and were separated into 5-cm sections. Soil samples from each section were air-dried, sieved (2 mm), and stored at 4° C. Selected soil properties are shown in Table 2.

Table 1. Typical biosolids chemical characteristics

Characteristics	Unit	LB†		DMB‡	
Moisture	g kg^{-1}	538		348	
pH		8.4		8.3	
EC	ds m^{-1}	9		11	
O.M.	%	22.5		21	
Solids	%	15.2		15.1	
		Total	**AB-DTPA**	**Total**	**AB-DTPA**
		g kg^{-1}			
P		40.7		26.9	
K		6.0		4.2	
NO_3-N		--	2.4	--	3.2
		mg kg^{-1}			
Zn		693	88	518	159
Cu		621	10.8	459	14
Pb		23.8	--	31	--

† Biosolids from Littleton/Englewood, CO sewage treatment facility.
‡ Biosolids from Metro Denver, CO sewage treatment facility.

Table 2. Chemical characteristics of control and treated dryland and irrigated soil.

Soil	pH	EC	O. M.	NO_3-N	Zn	Cu	Pb
		ds m^{-1}	%	g kg^{-1}	mg kg^{-1}		
Dl Un†	6.8	0.4	1.3	4.7	1.06	4.60	2.56
Dl Tr‡	6.1	0.6	2.2	11.0	23.3	32.2	3.60
Ir Un§	7.8	1.5	1.2	12.6	6.17	2.96	1.06
Ir Tr¶	6.7	2.1	1.6	23.0	9.75	6.35	1.62

†Dl Un: Dry land untreated soil
‡Dl Tr: Dryland treated soil
§Ir Un: Irrigated land untreated soil
¶Ir Tr: Irrigated land treated soil.

Methods:

AB-DTPA:

Heavy metals were extracted using the AB-DTPA method (Soltanpour and Schwab, 1977). This method is used to estimate the bio-availibility of heavy metals and other soil components using 1 M NH_4HCO_3-0.005 M DTPA

(Diethylenetriaminepentaacetic acid) at pH =7.6. The element concentrations were analyzed using a Jarrel-Ash ICP-AES Model 975 ATOCOMP instrument.

Total element digestion:

Total digestion of the soils was carried out using nitric, perchloric, and hydrofluoric acids (Hosner, 1990). The solution was analyzed using a Jarrel-Ash ICP-AES Model 975 ATOCOMP instrument.

General analysis:

For each profile, the twenty 5-cm core sections were combined into 6 samples (0-10, 10-20, 20-30, 30-50, 50-70, and 70-100 cm) for measurement of EC, pH, NO_3-N and O.M. Total soluble salts (EC) were measured in a saturated paste using the wheat-stone solubridge (Richards, 1954). The pH of the soil and biosolids was determined in the saturation paste using a pH meter (Richards, 1954). Organic matter content was determined according to the Walkley-Black method (Jackson, 1958). Particle size distribution was determined by the hydrometer method after dispersing the soil with sodium hexametaphosphate and sand sieving (Gee and Bauder, 1986). Nitrogen-nitrate (NO_3-N) was determined spectrophotometrically using a 2 M KCl extractant (Self and Rodriguez, 1997).

Statistical analysis:

Data were subjected to one-way ANOVA tests considering the means of the treatments, using SAS Windows Version 8.01 (SAS Inst. 1999-2000). Least significant difference (LSD) was used to evaluate the significance at the 0.1 probability level. For the general parameters (EC, pH, NO_3-N and O. M.) no statistical analysis was run due to the lack of the number of readings needed to run a

statistical analysis. (A means comparison analysis requires more than one reading for those parameters. However, only one reading for each sampling location or depth was available.

Table 3. Textural characteristics of untreated and treated soils from dryland and irrigated sites

Depth	Dryland Un†			Dryland Tr†			Irrigated soil Un†			Irrigated Tr†		
	SND§	CLY¶	SLT#	SND	CLY	SLT	SND	CLY	SLT	SND	CLY	SLT
Cm	%											
0-10	43.7	20.5	35.8	38.6	20.5	40.9	89.8	2.6	7.7	87.2	7.7	5.1
10-20	33.5	30.7	35.8	28.4	28.1	43.5	92.3	2.6	5.1	89.8	5.1	5.1
20-30	18.2	33.2	48.6	23.3	30.7	46.0	94.9	2.6	2.6	89.8	7.7	2.6
30-50	18.2	28.1	53.7	23.3	30.7	46.0	92.3	5.1	2.6	82.1	10.2	7.7
50-70	15.6	25.6	58.8	28.4	30.7	40.9	89.8	5.1	5.1	64.2	28.1	7.7
70-100	28.4	25.6	46.0	28.4	30.7	40.9	89.8	5.1	5.1	54.0	30.7	15.3

† Un: untreated soil, Tr: treated soil
§ SND=Sand
¶ CLY=Clay
# SLT=Silt

RESULTS AND DISCUSSION

Dryland soil:

The results of the dryland soil will be discussed first. The effect of biosolids application on the O.M. content in the soil profile is shown in figure 1. Organic matter content was greater in the biosolids amended soil than in the unamended soil. With respect to depth, O.M. content in the biosolids amended soil reflects the O.M. content in the biosolids material, strongly suggesting that the applied biosolids were the source of the additional O.M. in the amended soil. Organic matter carries negative charges that attract cations. Also, increasing O.M. in the soil profile may result in increased retention of heavy metals (Barrow, 1985).

The pH decreases with the addition of biosolids in the top layer of the dryland soil relative to untreated soil (Figure 2). This may be due to the release of organic acids from the biosolids as a result of the decomposition of the biosolids and microbiological activities (Al-Wabel et al., 1998). In addition, the cations' displacement of acidity from clays and organic matter, and bringing it to the soil solution, will decrease the pH. Oxidation of organic N and S to nitrate and sulfate also produce acidity and decrease the pH. Moreover, regarding the effect of biosolids application on the pH throughout the entire soil profile, the pH value at any soil depth in the treated profile was higher than the pH of the top layer in the same profile. The concentration of total soluble salts in the soil profile are shown in Figure 3 and expressed as EC. The addition of biosolids increases the EC in the soil profile as compared with the control. This was probably due to the leaching of salts which were applied with the biosolids from the treated layer into the deeper soil profile.

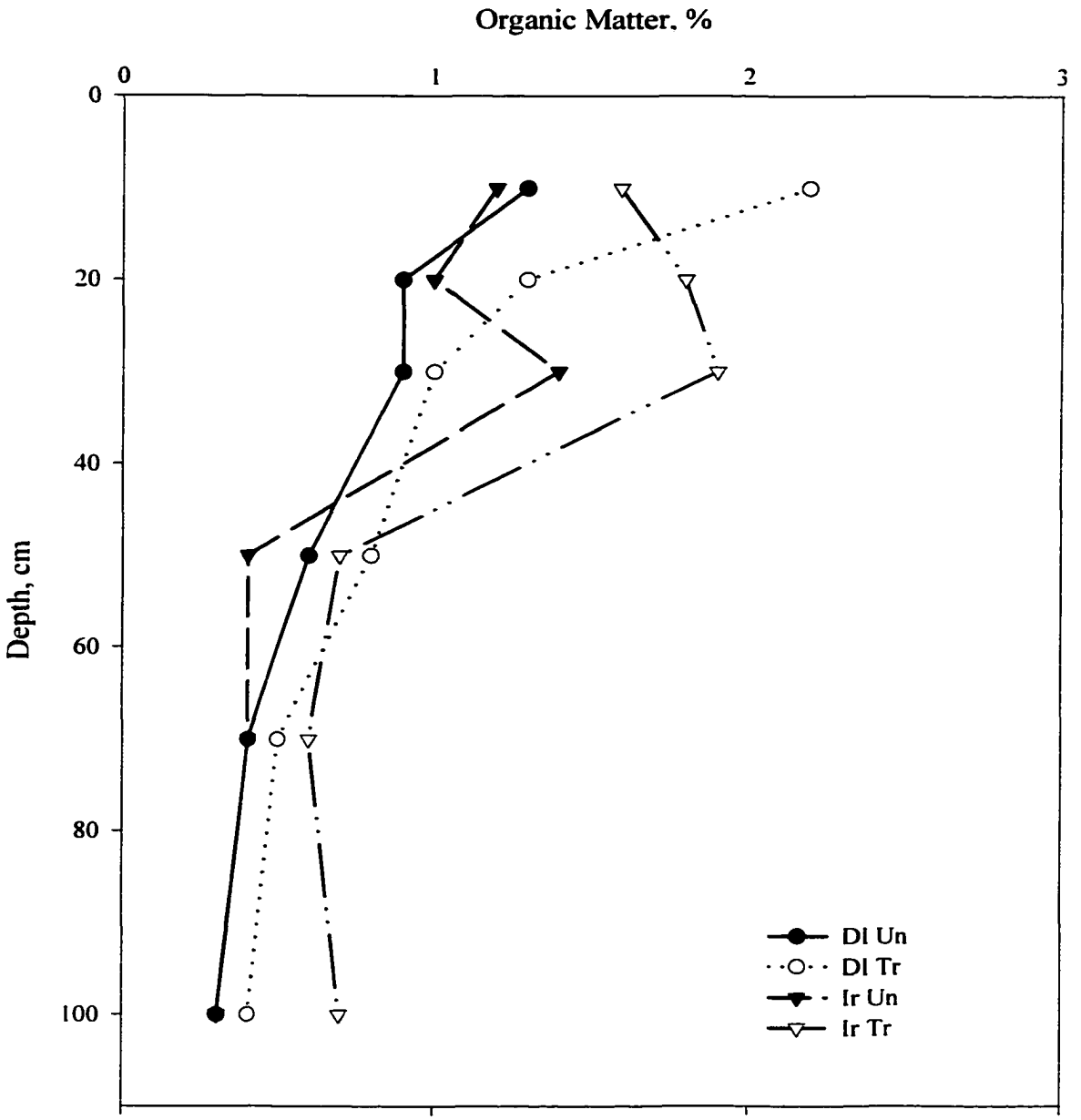

Figure 1 Organic mater percentage of the dryland and irrigated soils as related to profile depth.

Dl: Dryland soil.

Ir: Irrigated soil.

Dl Un: Dry land untreated soil; Dl Tr: Dryland treated soil, Ir Un: Irrigated land untreated soil; Ir Tr: Irrigated land treated soil.

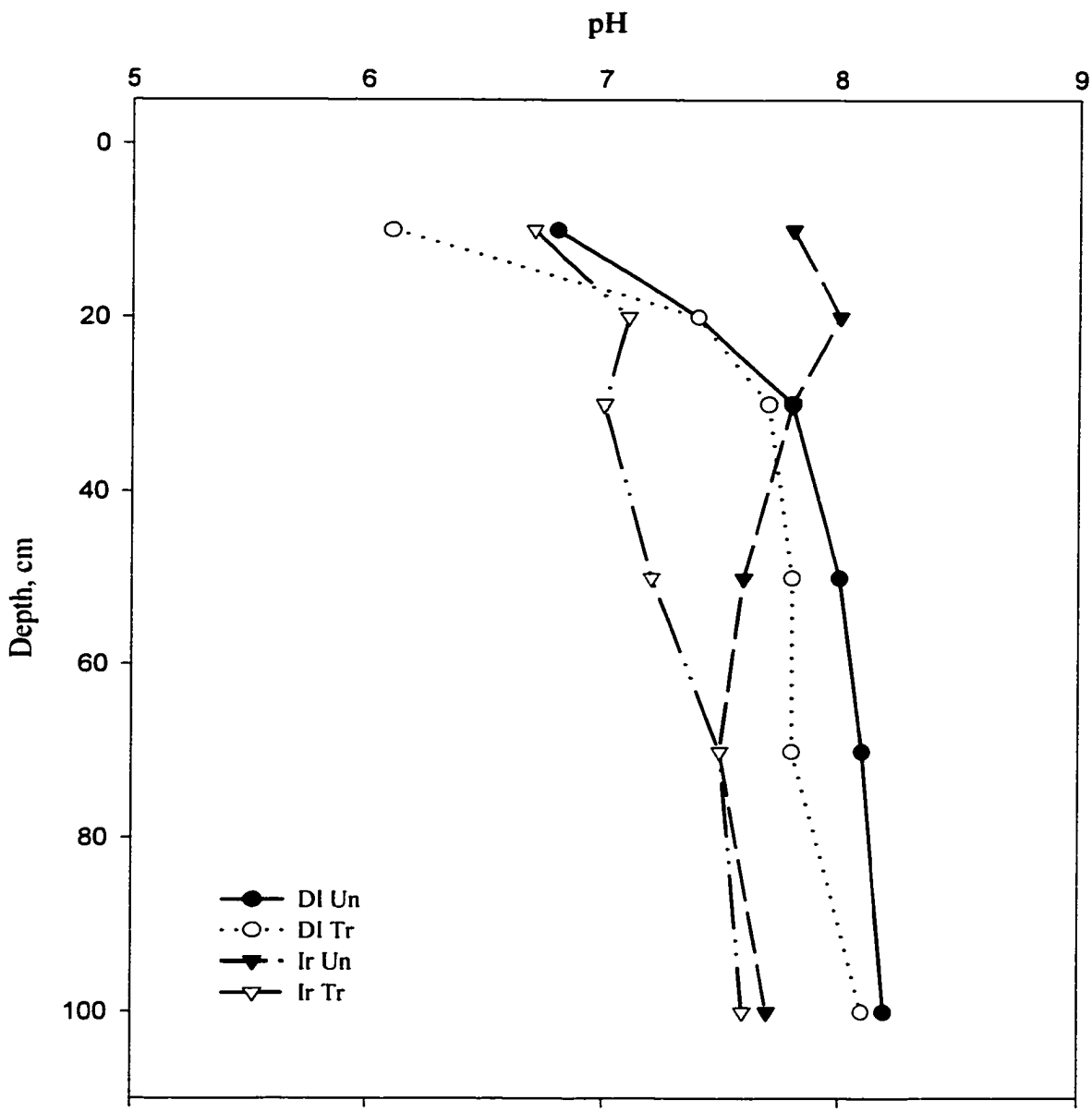

Figure 2 The pH of the dryland and irrigated soils as related to profile depth.

Dl: Dryland soil.

Ir: Irrigated soil.

Dl Un: Dry land untreated soil; Dl Tr: Dryland treated soil, Ir Un: Irrigated land untreated soil: Ir Tr: Irrigated land treated soil.

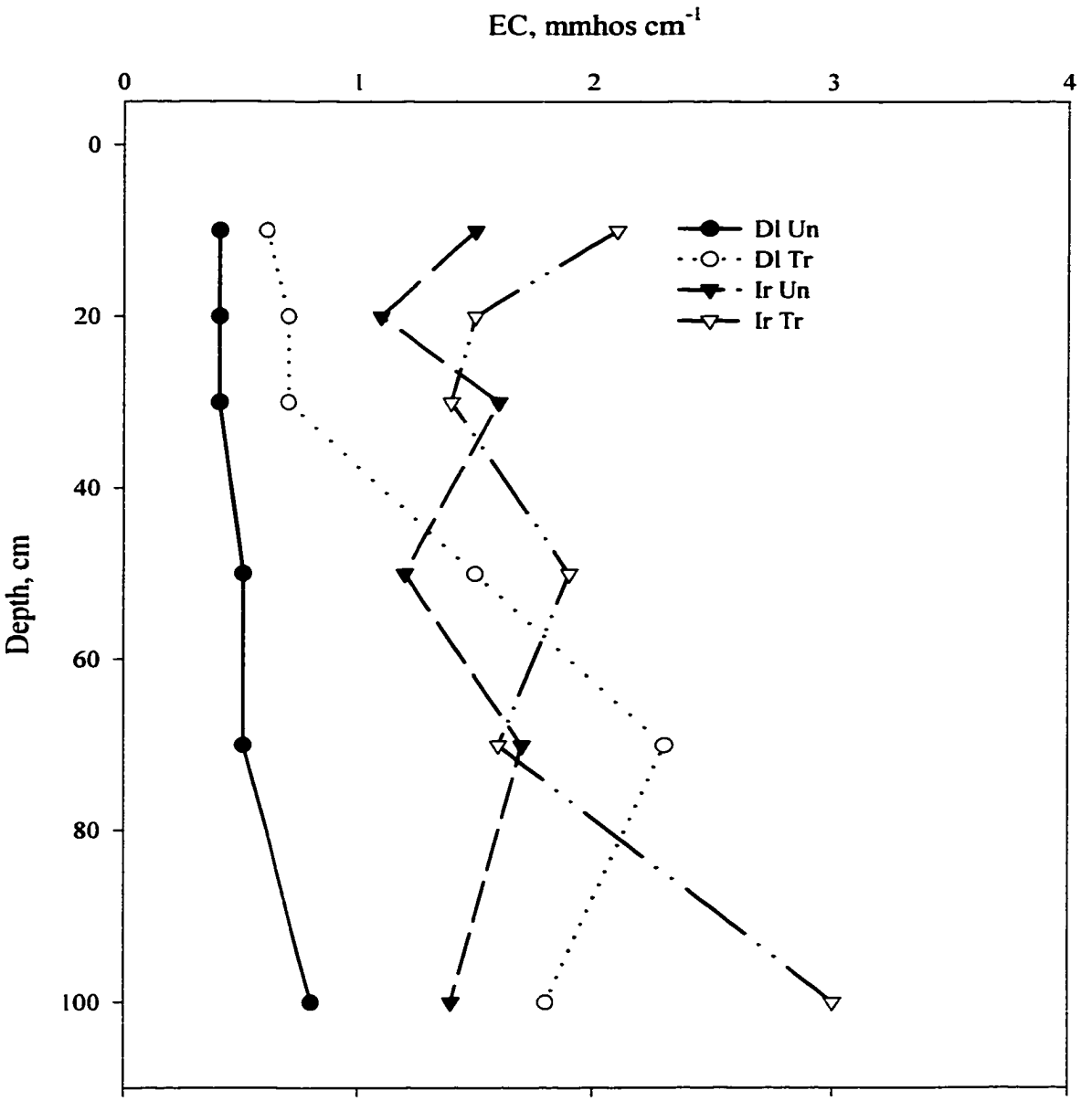

Figure 3 Electrical conductivity of the dryland and irrigated soils as related to profile depth.

Dl: Dryland soil.

Ir: Irrigated soil.

Dl Un: Dry land untreated soil; Dl Tr: Dryland treated soil, Ir Un: Irrigated land untreated soil; Ir Tr: Irrigated land treated soil.

The NO_3-N concentration increased in the treated dryland soil as compared to the untreated soil (Figure 4). The NO_3-N concentration increased dramatically below the treated layer in the treated soil profiles. These data show that there is a high correlation between the NO_3-N content in the treated layer with the EC (data not shown). This is due to the leaching of the NO_3-N from the treated layer to the lower depths of the profile. In the deeper soil profile the figures show the NO_3-N is higher in the treated soil profile than the untreated, which is due to the leaching, also it seems the leaching intensity was not enough to move NO_3-N below 100 cm. The application rate was aberrantly greater than the agronomic N demand of the system, thus the reason for an accumulation of NO_3 in the deeper soil profile. This was known at the initiation of the initial field study in 1982. The high biosolids application treatment was selected for this study in an attempt to identify the maximum potential effect of biosolids application.

The AB-DTPA extractable Zn of the dryland soil profiles is shown in figure 5. The dryland soil had been receiving biosolids in the amount of 26.8 tons ha^{-1} every other year starting in 1983. This increased the AB-DTPA Zn concentration in the topsoil from 1.3 to 28.4 mg kg^{-1}. Throughout the soil profile, the addition of the biosolids increased AB-DTPA Zn concentration significantly at most soil depths. At a depth of 20 cm and below, the difference in extractable Zn started to decrease but was still significant at most depths. These results are in agreement with McBride et al. (1997) in their study of the mobility and solubility of toxic metals in sludge amended soils. They found that about 40% of the Zn that had been added was lost from the top layer. The total Zn concentration in the dryland soil increased from 91.3 to 203.6 mg kg^{-1} in the treated layer (Figure 6). The data in figures 5 and 6 show that 1.4 % of the total Zn in the untreated

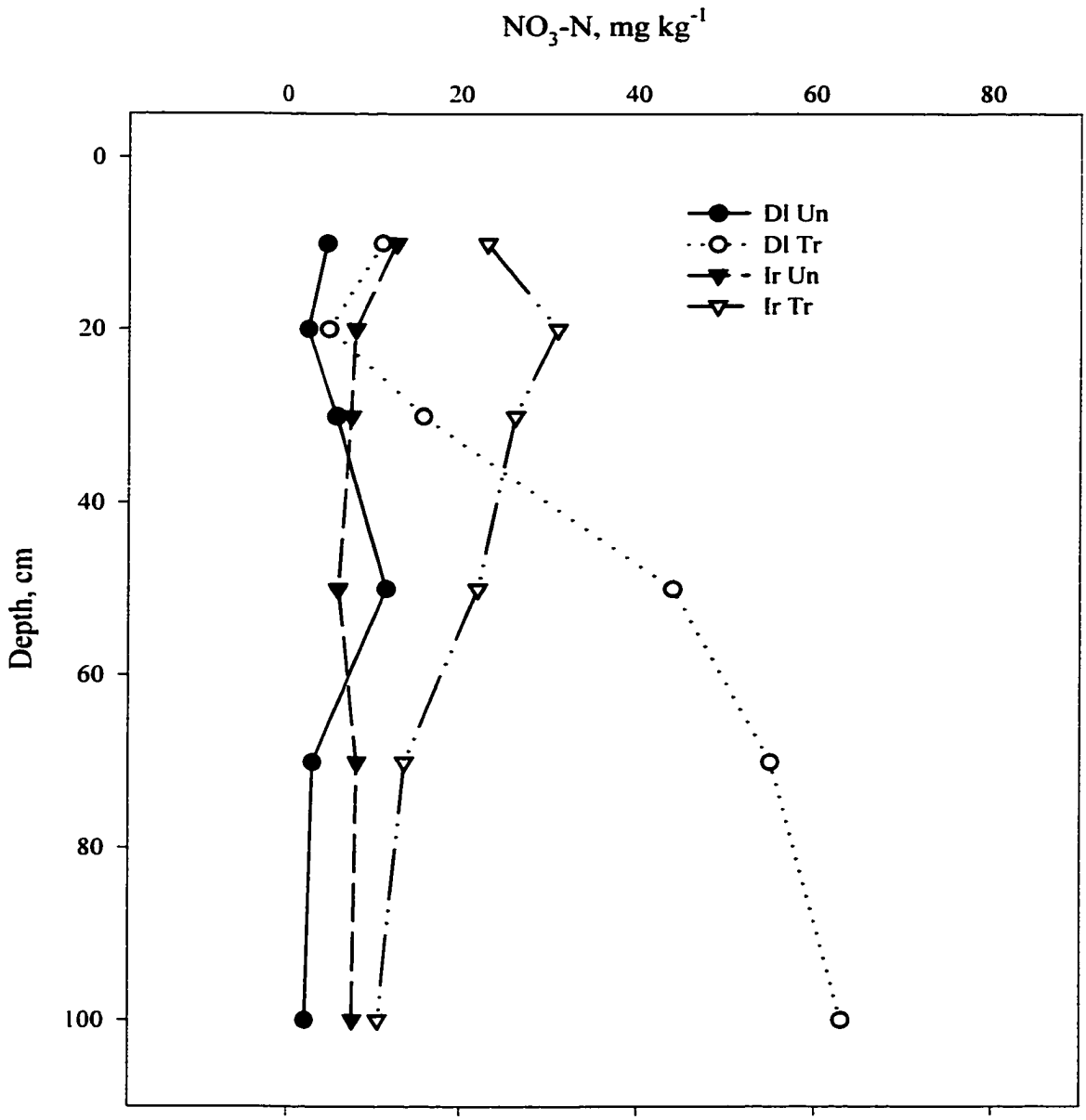

Figure 4 Nitrogen nitrate content of the dryland and irrigated soils as related to profile depth.

Dl: Dryland soil.

Ir: Irrigated soil.

Dl Un: Dry land untreated soil; Dl Tr: Dryland treated soil, Ir Un: Irrigated land untreated soil; Ir Tr: Irrigated land treated soil.

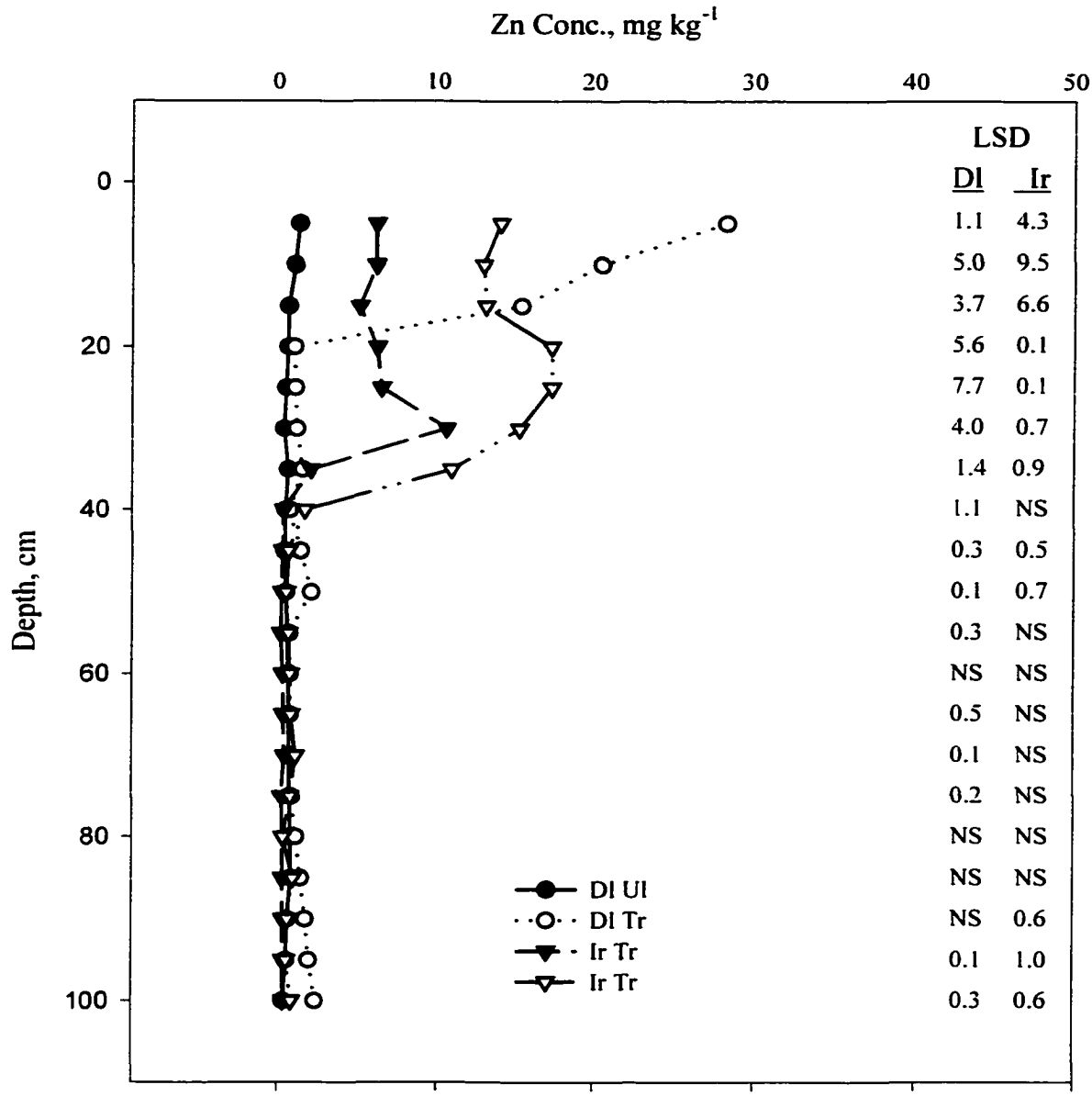

Figure 5 AB-DTPA extractable Zn concentration throughout the soil profile depths affected by the addition of biosolids to the dryland and irrigated soil.

Dl: Dryland soil.
Ir: Irrigated soil.
Dl Un: Dry land untreated soil; Dl Tr: Dryland treated soil; Ir Un: Irrigated land untreated soil; Ir Tr: Irrigated land treated soil.

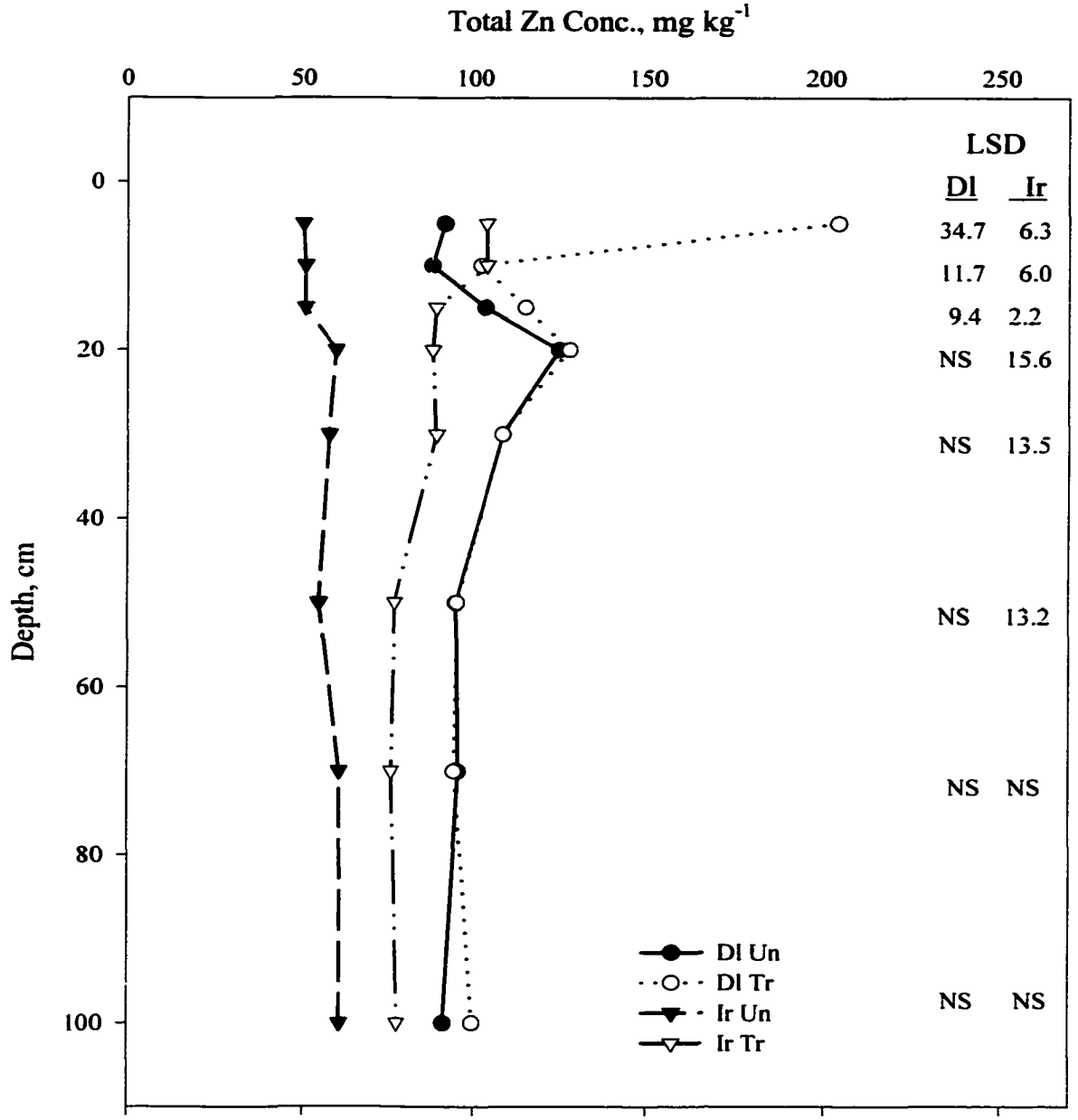

Figure 6 Total Zn concentration throughout the soil profile depths as affected by the addition of biosolids to the dryland and irrigated soil.

Dl: Dryland soil.
Ir: Irrigated soil.
Dl Un: Dry land untreated soil; Dl Tr: Dryland treated soil; Ir Un: Irrigated land untreated soil; Ir Tr: Irrigated land treated soil.

topsoil existed in extractable AB-DTPA form, whereas 16.8% of the total Zn in the topsoil of the amended soil existed as extractable AB-DTPA Zn. The previous results showed that the addition of biosolids increases AB-DTPA extractable Zn.

With the application of biosolids, the O.M. content increased in the topsoil; this large amount of O.M. may be the cause of the large amount of extractable Zn in the amended soil. This increase in O. M. may increase the DOC which could enhance the Zn movement when they complex together. This is would involve complexation or adsorption of Zn on the exchange sites of the organic matter. The data showed a significant difference between the AB-DTPA Zn in almost all the soil profiles, while the significant difference for the total Zn was only found in the treated layer. This was probably due to the differences in Zn concentration in the treated vs. untreated plots, less than 1 mg kg^{-1}, which is small compared to the total concentration, but large compared to the AB-DTPA Zn concentration. In quantitative terms, the LSD for total digest value is normally around 5 mg kg^{-1}, but the LSD for AB-DTPA is usually around 0.1 mg kg^{-1} . Therefore, the AB-DTPA showed a significant effect and indicated that the transported metals are AB-DTPA extractable. The results in Table 4 show that there is a significant positive correlation between AB-DTPA Zn and O. M., while it does have a significant negative correlation with the pH in the treated layer. The total Zn also has a significant positive correlation with O. M. and a significant negative correlation with pH.

The highest concentration of AB-DTPA Cu was in the top 20 cm of the dryland soil profile, as shown in figure 7. The effect of biosolids application on the AB-DTPA extractable Cu concentration was significant throughout the soil profile. The increase in AB-DTPA Cu at all depths may be the result of complexing Cu with DOC, which will

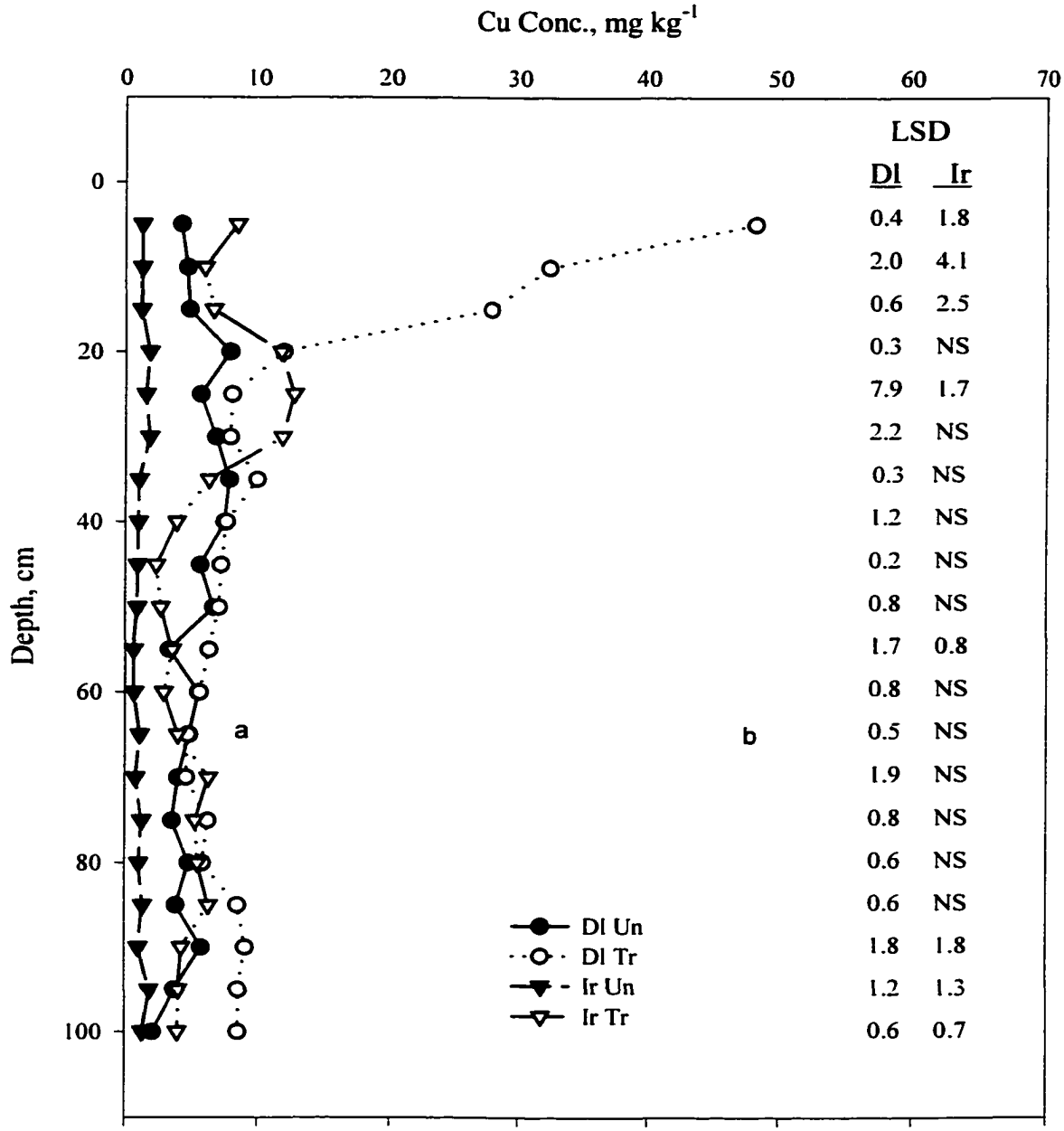

Figure 7 AB-DTPA extractable Cu concentration throughout the soil profile depths as affected by the addition of biosolids to the dryland and irrigated soil.

Dl: Dryland soil.
Ir: Irrigated soil.
Dl Un: Dry land untreated soil; Dl Tr: Dryland treated soil; Ir Un: Irrigated land untreated soil; Ir Tr: Irrigated land treated soil.

Table 4. The effect of biosolids application on dryland soil on the correlation between AB-DTPA or total of Cu, Zn, and Pb with some soil factors (pH, EC, and O.M)

		pH		EC		O. M.	
		Un‡	Tr‡	Un‡	Tr‡	Un‡	Tr‡
		AB-DTPA					
Un‡	Cu	-.011		-0.53		0.22	
	Zn	-0.75		-0.14		0.55	
	Pb	-0.90†		-0.55		0.83	
Tr‡	Cu		-0.97†		-0.65		0.95†
	Zn		-0.97†		-0.60		0.93†
	Pb		-0.98†		-0.81		0.94†
		Total					
Un‡	Cu	-0.32		-0.73		0.51	
	Zn	-0.06		-0.50		0.21	
	Pb	-0.89		-0.70		0.86	
Tr‡	Cu		-0.99†		-0.61		0.95†
	Zn		-0.96†		-0.75		0.96†
	Pb		-0.99†		-0.60		0.95†

‡ Un: untreated soil; Tr: treated soil

† significant at 0.1 the probability level

help the mobilization of Cu through the soil profile (Tyler, 1981). Figure 8 shows the total Cu in the dryland soil profile. The effect of biosolids application was significant in the top 15 cm. Below the treated layer the effect was not significant except at 50 cm in depth.

The percentage of AB-DTPA extractable Cu as compared to the total was high (66-68%). The correlation between the AB-DTPA Cu and total Cu with O.M. was 95 % (Table 4). This result is in agreement with Tyler and McBride (1982), who showed Cu to have strong complexation with complexation sites in organic matter. This high complexation can exist with soluble (humic or fulvic acids) or insoluble organic matter. This complexation will affect the mobility of Cu through the soil profile. The result may explain the mobility of Cu below the treated layer. For the correlation of AB-DTPA Cu

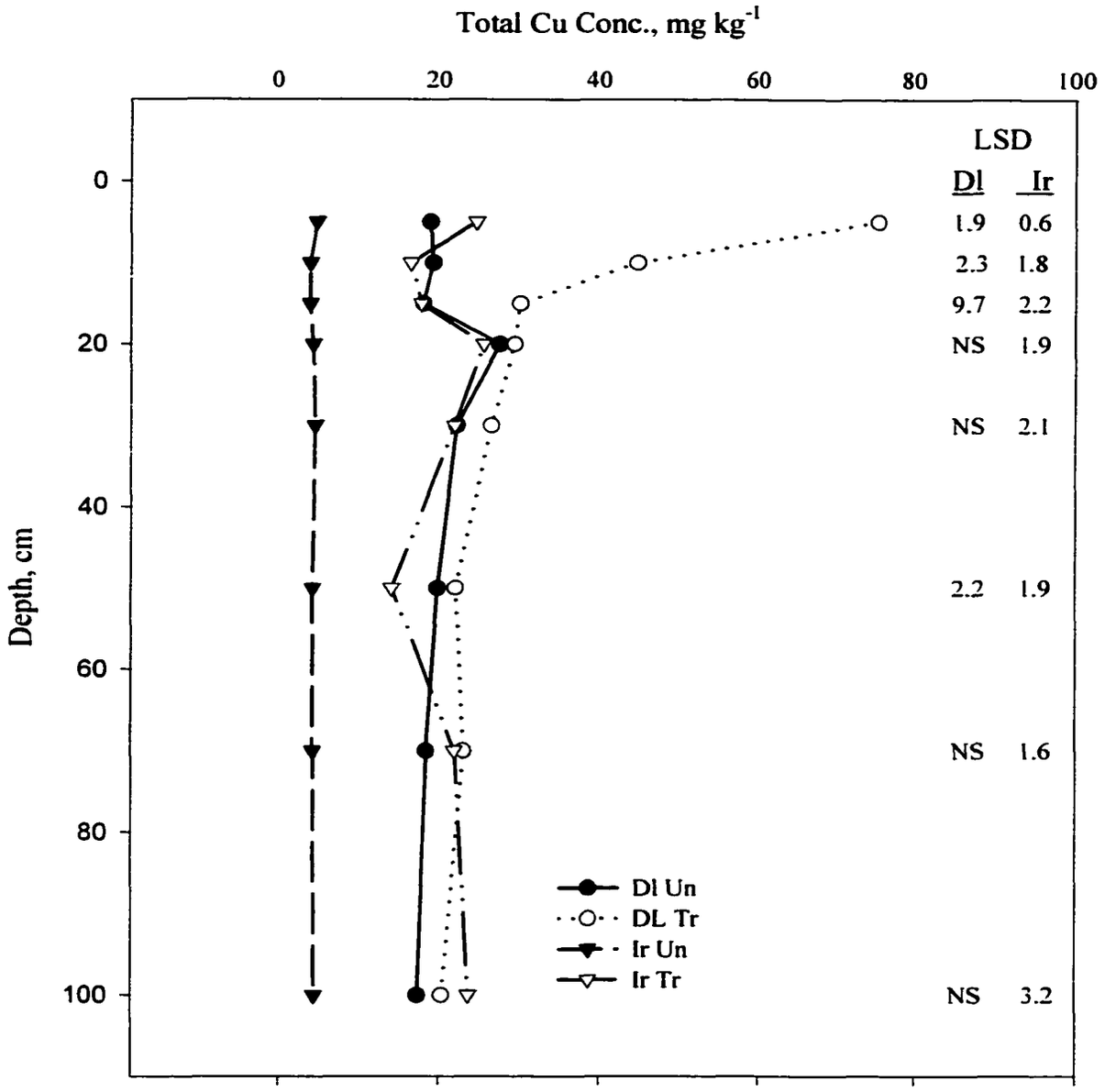

Figure 8 Total Cu concentration throughout the soil profile depths as affected l the addition of biosolids to the dryland and irrigated soil.

Dl: Dryland soil.
Ir: Irrigated soil.
Dl Un: Dry land untreated soil; Dl Tr: Dryland treated soil; Ir Un: Irrigated land untreated soil; Ir Tr: Irrigated land treated soil.

and the total Cu with some soil factors. Table 4 shows that AB-DTPA Cu and the total Cu have a significant positive correlation with O. M. and a significant negative correlation with EC, the same observation that we found with Zn.

The addition of the biosolids to the topsoil resulted in a significant increase in AB-DTPA Pb in the top 5 cm only (Figure 9) of the dryland soil. The Pb concentration increased from 2.56 to 3.61 mg kg^{-1}, but was not increased significantly throughout the remaining depths as a result of biosolids application. With regard to total Pb, the application of biosolids had significant effects on the total Pb in the top 15 cm; below this layer there was no significant change except at 50 cm (Figure 10). The percentage of extractable Pb compared to the total was low in the treated layer and increased below the 10-cm top layer. The correlation between AB-DTPA Pb and the total Pb with O.M. was not significant (Table 4), therefore, we can conclude that there is low complexation between Pb and O. M. This conclusion indicates that the mobility of Pb is not a concern in this type of soil. These results are not in agreement with Jordan et al., (1997) who studied Pb behavior in a soil-water system in the presence of dissolved natural organic matter (DOM). They concluded the presence of DOC enhanced the Pb mobility by a factor of 4-8 times. For the correlation of AB-DTPA Pb and total Pb with some soil factors, Table 4 shows that AB-DTPA and total Pb was significantly positive by correlation with O. M. and a significant negative correlation with EC, the same observation that has been found with Zn.

Table 4 shows the correlation between the studied heavy metals and some soil characteristics. The table shows that the correlation between AB-DTPA extractable heavy metals with EC, pH, and O.M. increased compared to the correlation with the

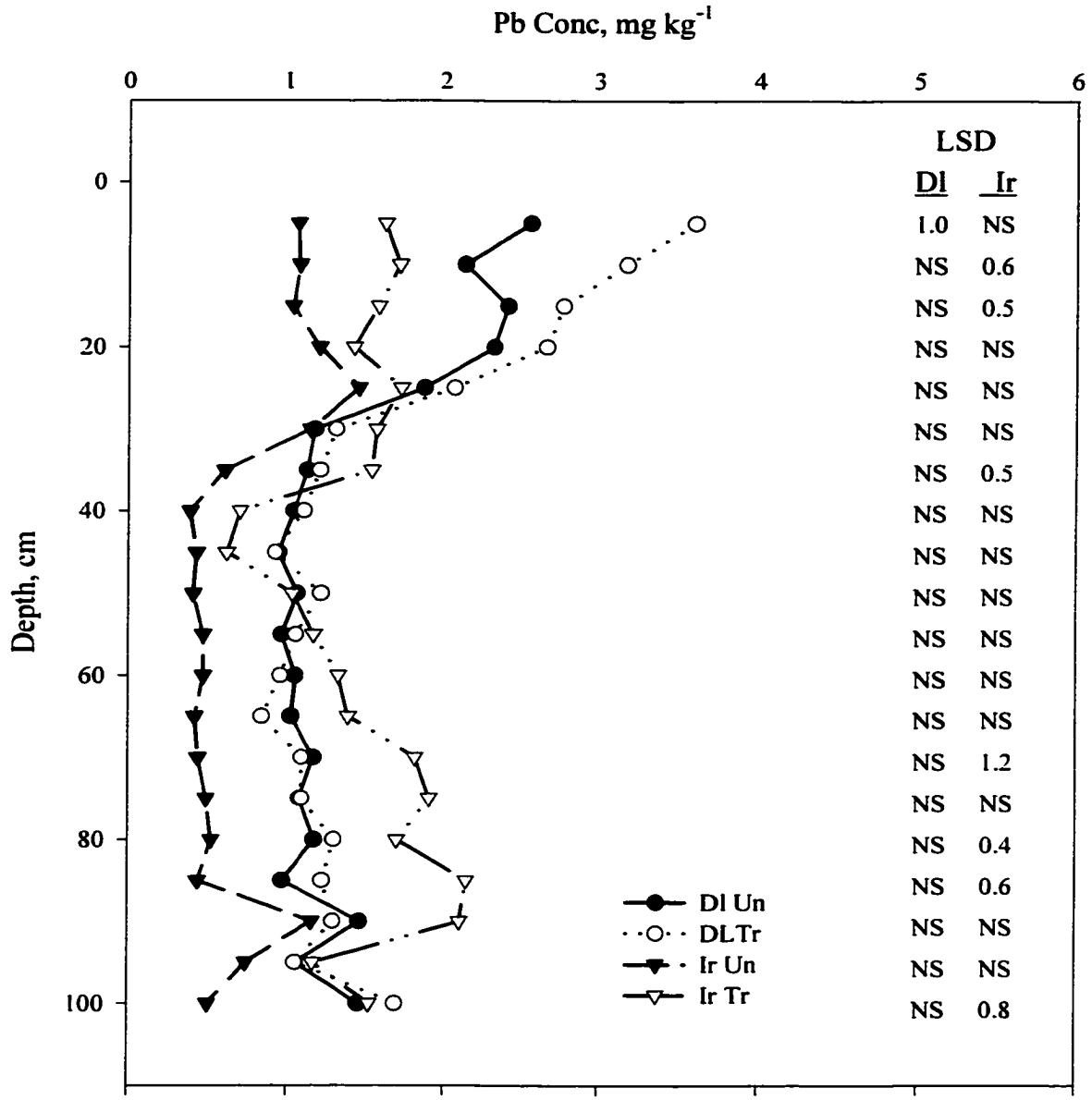

Figure 9 AB-DTPA extractable Pb concentration throughout the soil profile depths as affected by the addition of biosolids to the dryland and irrigated soil.

Dl: Dryland soil.

Ir: Irrigated soil.

Dl Un: Dry land untreated soil; Dl Tr: Dryland treated soil; Ir Un: Irrigated land untreated soil; Ir Tr: Irrigated land treated soil.

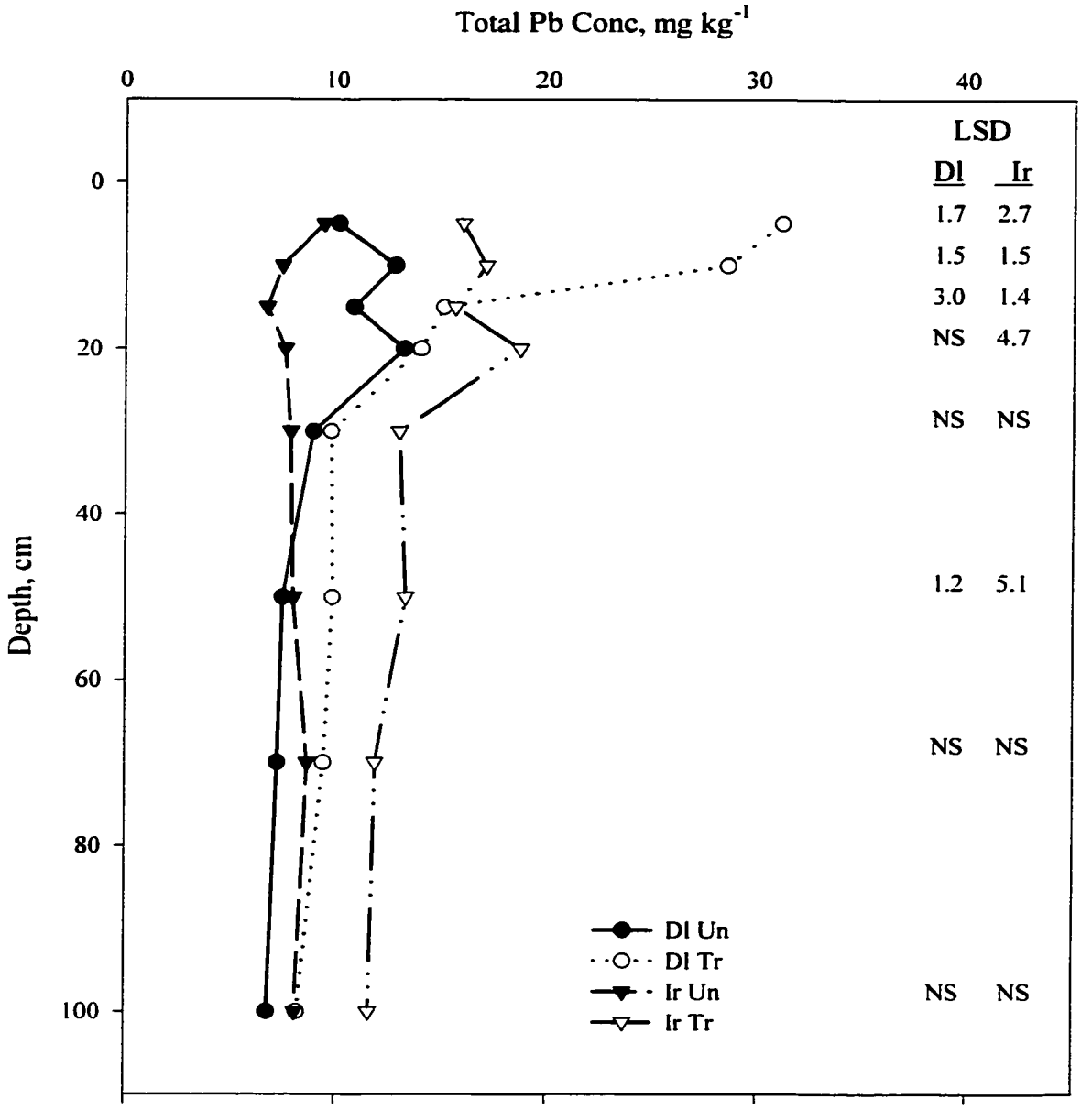

Figure 10 Total Pb concentration throughout the soil profile depths as affected by the addition of biosolids to the dryland and irrigated soil.

Dl: Dryland soil.
Ir: Irrigated soil.
Dl Un: Dry land untreated soil; Dl Tr: Dryland treated soil; Ir Un: Irrigated land untreated soil; Ir Tr: Irrigated land treated soil.

untreated soil. The correlation between heavy metals was negative with both EC and pH, while it was increased with O.M. Element totals also had good correlation with other soil characteristics except EC where the Cu and Pb correlation coefficients decreased.

Irrigated soil:

The effect of adding biosolids to the irrigated soil O.M. content is shown in figure 1. There was an increase in O.M. content in the treated soil as compared to the untreated soil. Organic matter content also increased throughout the entire soil profile. This increase may be due to the movement of some soluble organic matter from the treated layer to the subsurface soil and the remaining soil profile, or perhaps the treated and untreated soils were not identical. Soil texture analysis (Table 3) found that there were substantial differences in particle size distribution between the two soils. For instance, at a depth of 100 cm the untreated soil texture contained about 90% sand and 5% clay, while the treated soil contained 54% sand and 30% clay. This large difference in the soil particle analysis showed that these two soils were not identical and make comparison of treated and untreated soils very difficult. The data should interpreted with these differences in mind, because the two soils may not have been from the same population.

Figure 2 shows the effect of biosolids application on the soil pH in irrigated soil. The pH value decreased in the treated top layer as compared to the control; this may be due to the releasing of organic acids from the decomposition of the biosolids. Soil pH for both untreated and treated soil began to converge at a depth of 70 cm.

The EC in the top layer of the treated soil profile was higher than in the untreated soil profile (Figure 3). This may be due to the high content of salts in the biosolids.

However, below the treated layer there was no consistency between the untreated and treated soil profile. This finding suggested that these two soils (untreated and treated) were not from the same population. Another complicating actor was the fact that the treated soil was under central pivot irrigation while the untreated soil which was collected outreach the central pivot, never having been irrigated.

The NO_3-N concentration in the two soil profiles, as affected by biosolids application, is shown in Figure 4. Application of biosolids increased the NO_3-N content in the treated layer. Below the treated layer the figures show NO_3-N content remained higher in the treated profile than in the untreated profile throughout the entire soil profiles. The level of NO_3-N below the treated layer was almost the same and this may due the leaching of NO_3-N due to irrigation or the biosolids application rate (N loading) may have matched the N demand of the system.

The AB-DTPA extractable Zn concentration in the irrigated soil is shown in figure 5. The result in Table 5 shows there is a significant correlation between AB-DTPA Zn and O. M. in the treated soil profile, but with EC, the AB-DTPA Zn correlation was negative in the untreated soil profile and positive in the treated soil profile. The correlation results also indicate that the total Zn has a significant negative correlation with pH. The results showed a mix of positive and negative values. Biosolids application had a significant effect on the treated layer and down to 40 cm in depth. This indicates that some Zn moved from the treated layer downward. Figure 6 shows the total Zn distribution throughout the 100-cm soil profile. Total Zn concentration was different at most depths. Even though the difference is significant for all depths, it seems the source of the differences is related to the differences between the soils, rather than the effect of

the biosolids. The untreated and treated samples were taken 100 m from each other, but the results in Figure 6 point to the two soils not being from the same population

Figure 7 shows the effect of biosolids application on the distribution of AB-DTPA Cu concentration throughout the profile of the irrigated soil. Cu concentration differed significantly between the top layer (0-15 cm) of untreated and treated soil; it appears that the Cu then started to accumulate in the transition zone (20-35 cm). The effect of treatment then began to lessen and was significant only at some of the lower depths. Figure 8 shows that the total Cu concentration distribution was significant throughout all soil profile depths. But, similar to the results with Zn, the figures show that Cu is slightly different between the untreated and treated soil. This finding supports the idea that these two soils were not from the same population.

A mass balance calculation was performed to estimate the amount of Cu concentration for the one-meter soil profile of the irrigated soil. This was done to further elucidate the question of if the two soils came from the same population. This calculation depended on several factors, such as the loading rate of biosolids, incorporated layer depth, and bulk density. The bulk density was assumed to be 1.5 Mg m^{-3}, the mean Cu concentration in each load was 11.886 kg ha^{-1}, and the incorporation layer depth was 25.4 cm. After calculating the Cu concentration for all depths in both the treated and the untreated layers, it was found that the amount of Cu that been added to the soil was 52.44 kg ha^{-1}, while the difference in the amount of Cu between the untreated and treated soil profiles was 200.1 kg ha^{-1}. This difference occurred as a result of contribution from all the depths. From these mass balance calculations we concluded the two soils (untreated and treated) were not from the same population, even though the two soils were sampled

within 100 m of each other. The result in Table 5 shows that AB-DTPA Cu has a significant correlation with O. M., but it also has some mixed results between the untreated and treated soils with other factors such as pH. The same mixed results showed in the correlation between the total Cu and pH.

The AB-DTPA extractable Pb was 1.06 in the topsoil of the untreated layer, while it was 1.61 mg kg^{-1} in the treated soil (Figure 9). Figure 9 also shows some significant effects throughout several depths in the soil profile. For instance, at depths 10, 15, 35, 70, 80, 85, and 100 cm the effect was significant, while at all the others it was not. From this finding we can conclude that this effect was not due to the application of biosolids, but rather was due to different location of these two soils. In Figure 10, which illustrates the effect of the application on the total Pb distribution throughout the soil profile, we see significant effects from the addition of biosolids. The total Pb concentration ranged from 6.6 to 9.4 mg kg^{-1} in the untreated soil, and 11.6 to 18.7 mg kg^{-1} in the topsoil of the treated profile. The results in Table 5 also showed no consistent effect between the untreated and treated soil.

Table 5. The effect of biosolids application on irrigated soil on the correlation between some forms of Cu, Zn, and Pb with some other soil factors (pH, EC, and O.M.)

		pH		EC		O.M.	
		Un‡	Tr‡	Un‡	Tr‡	Un‡	Tr‡
		AB-DTPA					
Un‡	Cu	0.83		-0.18		0.74	
	Zn	0.30		0.35		0.70	
	Pb	0.83		-0.02		0.95†	
Tr‡	Cu		-0.56		-0.50		0.93†
	Zn		-0.83		-0.54		0.99†
	Pb		-0.06		0.32		0.42
		Total					
Un‡	Cu	-0.02		0.58		0.40	
	Zn	-0.45		0.34		-0.55	
	Pb	-0.79		0.77		-0.31	
Tr‡	Cu		0.32		0.19		0.24
	Zn		-0.90†		-0.16		0.78
	Pb		-0.76		-0.32		0.89

‡ Un: untreated soil; Tr: treated soil

† significant at 0.1 the probability level

CONCLUSION:

This study clearly shows that the long-term application of biosolids will affect the heavy metal concentration of the topsoil. The untreated soil shows low levels of heavy metals (Cu, Zn, and Pb). The long-term application of biosolids affected the topsoil by increasing the content of O.M., total soluble salts, and NO_3-N, and decreasing the pH. Specifically regarding the heavy metals, this study shows significant changes in Zn, Cu, and Pb concentrations between the untreated and treated soil in the treated layer. These findings suggest that the biosolids application increased the soil content of heavy metals (Cu, Zn, and Pb). The results also showed a significant difference in Cu and Zn between the untreated and treated profiles below the zone of biosolids incorporation in the dryland soil. This finding indicates that these two metals moved below the treated layer, while Pb does not show significant movement. There was a significant correlation between O.M. and the two forms of elements (AB-DTPA and the total), and negative significant correlation with pH. It appears that the two irrigated soils (untreated and treated) were not from the same population, and that the increase of the element concentrations in the lower depths of the treated layer was due to soil differences rather than the effect of the addition of biosolids.

REFERENCES

Al-Wabel, M. I., A.M. Al-Omran, A. A. Shalaby, and M. I. Choudhary. 1998. Effect of sewage sludge on some chemical properties of calcareous sandy soils. Commu. Soil Sci. Plant Anal. 29: 2713-2724.

Barbarick, K. A., I. A. Ippolito, and D. G. Westfall. 1998. Extractable trace elements in soil profile after years of biosolids application. J. Environ. Qual. 27:801-805.

Barrow, N. J. 1985. Reactions of anions and cations with variable charge soils. Adv. Agron. 38:183-215.

Baveye, P, M.B. McBride, D.B, Thomas D. Hinesly, M.S.A. Dahdoh, and M.F. AbJel-sabour. 1999. Mass balance and distribution of sludge-borne trace elements in a silt loam soil following long-term application of sewage sludge. Sci. Total Environ. 227:13-28.

Camobreco, V. J., B. Richards, T. S. Steenhuis, J. H. Peverly, and M. B. McBride. 1996. Movement of heavy metals through undisturbed and homogenized soil columns. Soil Sci. 161:740-750.

Chang A.C., J.E. Warmeke, A.L. Page, and J. Lund. 1984. Accumulation of heavy metals in sewage sludge-treated soils. J. Environ. Qual. 13: 87-91.

Chairidchai, P., and G. S. P. Ritchie. 1990. Zinc and copper sorption and fixation on acid soil clay. Effect of selective dissolutions. Soil Sci. Soc. Am. J. 48:1050-1054.

Chubin, R. G., and J. J. Street. 1981. Adsorption of cadmium on soil constituents in presence of complexation ligands. J. Environ. Qual. 10:225-228.

Dowdy, R.H., V.V Volk. 1983. Movement of heavy metals in soils. p. 227-240. *In* D. W. Nelson et al. (ed.) Chemical mobility and reactivity in soil systems. SSSA Spec. Pub. II. SSSA, Madison, Wisconsin

Dowdy, R. H., J. J. Latterell, T. D. Hinesly, R. B. Grussman. And D. L. Sullivan. 1991. Trace metals movement in an Aeric Ochraqualf following 14 years of annual sludge application. J. Environ. Qual. 20:119-123.

Gee, G. W., J. W. Bauder. 1986. Particle size analysis. P 383-412. *In* Klute, A. (ed.) Methods of soil analysis. Part 1. 2nd ed. Book series No. 5. ASA and SSSA, Madison, Wisconsin.

Hossner, L.R. 1996. Dissolution for total element analysis. *In* Methods of Soil Analysis. Part 3. Chemical Methods. Ed. Sparks. D. L. SSSA book series No. 5. Soil Science Soc. of Amer. Madison. Wisconsin.

Jackson, M. L. 1958. Soil chemical analysis. Prentice-Hall, Inc., Englewood Cliffs, N. J.

Jordan, R.N., D.R. Younge, and W.E. Hathhorn. 1997. Enhanced mobility of Pb in the presence of dissolved natural organic matter. J. Contaminant Hydrology. 29:59-8.

Karapanagiotis, N.K., R.M. Sterritt, and J.N. Lester. 1991. Heavy metals complexation in sludge-amended soil. The role of organic matter in metal retention. Environ. Tech. 12:1107-1116.

Li, Z. B., and L. M. Shuman. 1996. Heavy metals movement in metal-contaminated soil profiles. Soil Sci. 161:226-232.

McBride, M.B. 1989. Reactions controlling heavy metals solubility in soils. Adv. Soil Sci. 10:1-57.

McBride, M. B., B. K. Richards, T. S. Steenhuis, J. J. Russo, and S. Sauve. 1997. Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. Soil Sci. 162:487-500

McGrath, S. P., and P. W. Lane. 1989. An explanation for the apparent losses of metals in a long-term field experiment with sewage sludge. Environ. Pollut. 60:235-256.

Reed, S. T. and D. C. Martens. 1996. Copper and Zinc. *In* Methods of Soil Analysis. Part 3. Chemical Methods. Ed. Sparks. D. L. SSSA book series No. 5. Soil Science Soc. of Amer. Madison. Wisconsin

Richards, L. A., (ed.). 1954. Diagnosis and improvement of saline and alkali soils. U. S. D. A. Handbook No. 60.

SAS Institute. 1999-2000. The SAS system for Windows. Release 8.01. SAS Inst., Cary, NC.

Self, J. R., and J. B. Rodriguez. 1997. Laboratory manual for SC-564. Soil and plant chemical analysis. Ver. 4. Dept. Soil and Crop Sci. Colorado State Univ. Fort Collins, CO.

Schirado, T., Vergara, I., Schalscha, E. B., and Pratt, P. F. 1986. Evidence for movement of heavy metals in a soil irrigated with untreated wastewater. J. Environ. Qual. 15 (1): 9-12.

Sloan, J. J., R. H. Dowdy, and M. S. Dolan. 1998. Recovery of biosolids applied heavy metals sixteen years after application. J. Environ. Qual. 27:1312-1317.

Soil Conservation Serviece. 1974. Soil survey of Adams county, Colorado. Unites States Department of Agriculture. U. S. Gov. Print. Office, Washington, DC.

Soltanpour, P. N. and A. P. Schwab. 1977. A new Soil Test for Simultaneous Extraction of Macro and Micronutrients in Alkaline Soils. Commun. Soil Sci. Plant Anal. 8:195-207.

Tyler, G. 1981. Leaching of metals from the A horizon of spruce forest soil. Water Air Soil Pollute. 15: 353-369.

Tyler, L. D., and M. B. McBride. 1982. Mobility and extractability of Cd, Cu, Ni, and Zn in organic and mineral soil columns. Soil Sci. 143: 198-295.

Waller, P. A., and W. P. Pickering. 1992. Effect of time and pH on the avilability of Cu and Zn sorbed to humic acid particles. Chemical Speciation and Bioavailability. 4 (1): 29-41.

William, D. E., J. Vlamis, A. H. Pukite, and J. E. Corey. 1980. Trace element accumulation, movement and distribution in soil profile from massive application of sewage sludge Soil Sci. 129:119-132.

William, D. E., J. Vlamis, A. H. Pukite, and J. E. Corey. 1987. Metal movement in sludge-amended soils: a nine-year study. Soil Sci. 143:124-131.

Yingming, L., and R. B. Corey. 1993. Redistribution of sludge borne cadmium, copper, and zinc in cultivated plot. J. Environ. Qual. 22:1-8.

CHAPTER III

THE ROLE OF DISSOLVED ORGANIC MATTER AND ELECTROLYTE CONCENTRATION ON THE MOBILITY OF CU, ZN, AND PB IN SOILS AMENDED WITH BIOSOLIDS

To be submitted to the Journal of Environmental Quality

ABSTRACT

Many previous studies have implicated dissolved organic carbon (DOC) as an important contributor to the elevated mobility of trace metals in soils amended with biosolids. However, few of these studies have quantified both DOC and metal concentrations. Laboratory leaching column studies were conducted on a dryland (Fine, smectitic, mesic Aridic Argiustolls) and an irrigated soil (Loamy mixed, mesic Arenic Ustollic Haplargids), both with a history of biosolids application. The soils were neutral to slightly alkaline in pH prior to amendment. An additional application of biosolids was made to columns in the laboratory to simulate the effect of time following application on metal mobility. The effect of electrolyte concentration was studied by using both D.I. water and simulated irrigation water. Dissolved organic carbon concentration was significantly increased by the addition of biosolids at a rate of 28 Mg ha^{-1} in both soils, although the DOC had decreased to near background levels in the irrigated soil within one year of application. Zinc mobility was positively correlated with Electrical Conductivity (EC), suggesting that either a cation exchange mechanism or the formation of inorganic complexes influences Zn release. The application of biosolids increased both DOC and Cu in the column effluents resulting in a positive correlation between Cu and DOC across application treatments for both soils. Both Cu and Pb were mobilized under conditions of low EC, which is opposite to the observation for Zn. This may be the result of the release of a strong metal binding component of DOC under these conditions. Anodic Stripping Voltammetry (ASV) measurements indicated that only a small percentage of the total dissolved metals concentrations existed as free ions or inorganic

complexes; the remainder appears to be complexed to DOC or possibly dispersed mineral colloids. Although effluent metal concentrations were all below 1 mg L^{-1}, repeated applications of biosolids over a long time period could result in significant accumulation of metals below the zone of biosolids incorporation in these soils.

INTRODUCTION

A growing amount of evidence indicates that accelerated transport of metals is occurring in soils amended with biosolids. In many cases the annual export of metals from the surface-mixing layer represents a small fraction of the total amount of each metal added (Sidle and Kardos, 1977; Lamy et al., 1993; Holm et al., 1998). However, the cumulative transport of metals over a prolonged time period could result in a substantial redistribution of metals into the subsoil and possibly ground water (McBride, 1995). Furthermore, in some studies, water quality standards have been exceeded in soil pore water collected at depths below the zone of biosolids incorporation (Richards et al., 1998; McBride et al., 1999).

Several studies employing measurements of soil pore water collected by either laboratory column leaching experiments or field studies using lysimeters (solution samplers) or drainage tiles, have found that metal concentrations are elevated below the zone of incorporation of biosolids (Sidle and Kardos, 1977; Welch and Lund, 1987; Lamy et al., 1993; McBride et al., 1999; Richards et al., 2000). The amendment of soils with municipal solid waste has also been observed to cause elevated metal concentrations in effluents leached through the subsoil (Boyle and Fuller, 1987; Sawhney et al., 1994).

Many researchers have attributed the increased mobility of metals in amended soils to complexes with DOC released from the biosolids (Gerritse et al., 1982; Christensen, 1985; Lamy et al., 1993; Brown et al., 1997; McBride et al., 1997). The contribution of DOC to metal transport is expected to be magnified as pH increases, due

to both increased solubility (or mobility) of DOC and the very low solubility of metal ions in neutral or alkaline pH soils (Richards et al., 2000). The transport of metals through soil or aquifer materials has been proven to be enhanced by DOC derived from sources other than biosolids (Dunnivant et al., 1992; Wang and Benoit, 1996). However, relatively few studies on metal transport in soils amended with biosolids have directly evaluated the contribution of DOC. Only a few of these studies have quantified changes in DOC concentrations after the addition of biosolids or provided evidence of the association of metals with DOC.

A significant proportion of the water-soluble metals extracted from biosolids and biosolids-amended soils have been found to be associated with organic complexes. Dudley et al. (1987) used gel filtration chromatography to determine the extent of organic complexation of soluble metals in extracts of soils mixed with biosolids. From 80-100% of the total water soluble Cu, 48-100% of Zn, and 39-100% of Ni was found to be organically complexed. Further evidence of the association between metals and soluble organic matter in amended soils was revealed by the correlation between water soluble Cd, Cu, and Zn concentrations with absorbance at 650 nm, which is related to DOC concentration (McBride et al., 1997).

Experimental leaching studies indicate that the DOC-metal complexes released from soils amended with biosolids can be transported to a significant depth in the soil. Lamy et al. (1993) observed that both DOC and Cd concentrations collected in drainage tiles located at a depth of 80 cm below the soil surface increased by a factor of approximately 3 times compared to control samples 1 month after the addition of biosolids, and then both declined to background levels within 1 year. Concentrations of

Cu, Zn, and Ni were increased by a magnitude of 10- to 20-fold in soil solutions sampled by passive wick lysimeters placed 60 cm below the soil surface (40 cm below the depth of biosolids incorporation) 15 years after amendment with biosolids (McBride et al., 1999). In that same study, Differential Pulse Anodic Stripping Voltammetry was used to determine that only 30% of water soluble Zn, 18% of Cd, and 10% of Cu was present as ionic or inorganic complexes, and the remainder of the water soluble metals was considered to be complexed with DOC.

The definition of DOC is operational and includes all of the dissolved organic materials that pass through a 0.45 um filter (Buffle et al., 1992). These organic materials include a heterogeneous mixture of both organic colloids and true organic solutes. The humic components of DOC (humic acid and fulvic acid) possess colloidal properties (Stevenson, 1994). The mobility of organic colloids present in DOC could be affected by changes in pH, electrolyte concentration, or electrolyte composition (divalent vs. monovalent ions) (Tombacz and Meleg, 1990). Temminghoff et al. (1997) demonstrated that the mobility of dissolved humic acid through a soil column was substantially greater after the influent solution was changed from 0.001 M Ca $(NO_3)_2$ to demineralized water. This result is consistent with the expected response of colloid stability to a decrease in electrolyte concentration (Sposito, 1984). The colloidal stability of humic acid, because of its greater molecular weight, is more sensitive to changes in solution chemistry than is fulvic acid (Stevenson, 1994). In addition to the complexation of metals by DOC, other possible mechanisms of metal mobilization in biosolids amended soils include the displacement of exchangeable cations or ion-pair formation resulting from the potential high soluble salt content of biosolids, and acidification of soil pH (Gerritse et al., 1982;

Christensen, 1985; Boyle and Fuller, 1987). The first two mechanisms should be amplified in the presence of a high electrolyte concentration, which is the reverse of the relationship between electrolyte concentration and metal transport expected for the colloid mobilization mechanism described previously.

The objective of the current study was to determine the contributions of DOC and electrolyte concentration in the leaching water to metal transport in two soils of neutral to alkaline pH, which have a history of amendment with biosolids. We also evaluate the effect of time after biosolids amendment on metal mobility.

MATERIAL AND METHODS

Soil samples and biosolid materials:

This study was conducted using two soils from two different locations in Colorado. The two locations have received long-term biosolids applications and differed in soil and biosolids types. Site one is in summer fallow dryland winter wheat production (Platner loam soil: Fine, smectitic, mesic Aridic Argiustolls) located in west Bennett, CO (Adams County). Mean annual precipitation was 32 cm. Biosolids from the Littleton/Englewood, CO (LB) sewage treatment facility (Table 1) had been applied to this site on 1982, 1984, 1986, 1988, 1990, and 1992, at a rate of 26.8 dry Mg biosolids ha^{-1} (Barbarick et. al. 1995). Site two is an irrigated soil (Osgod sand: Loamy mixed, mesic Arenic Ustollic Haplargids) located in south Roggen, CO (Weld County). The mean annual precipitation was 37 cm (Soil Conservation Service, 1974). This plot was established in 1982. Biosolid from the Metro Denver treatment facility (DMB) was applied to this site in 1988, 1989, 1992, 1/1994, 12/1994, and 1997, at rate of 28 dry Mg biosolid ha^{-1}. Table 1 describes the properties of the biosolids.

Collection of undisturbed soil columns:

A total of 18 columns were made from polyvinyl chloride (PVC) pipe with I.D. of 10 cm and length of 28 cm. The depth of soil was 20-cm . The bottom of each of these column was trimmed to a wedge to facilitate insertion into the soil.

Undisturbed soil columns were collected in triplicate from control and sludge amended plots at each of the two sites in May 1998. An extra set of columns were collected from the amended plots at each site and later amended with additional biosolids in the laboratory. A hydraulic press was used to push the columns into the soil at a rate of 5 cm min^{-1}. Soil was then removed from around each column and the column was then removed from the soil-probe. After each column was collected, it was wrapped with plastic wrap on all sides to avoid any loss of soil, and kept at 4° C. In some studies the use Silicon bead on the inside walls of the column to avoid the occurrences of channels which could affect the water movement. Due to the nature of our study, we were aware of the fact that silicon could affect our experiment by contaminating or retaining some part of the metals in soil solution. To avoid the effect of channels we lightly tapped the columns five times in the lab.

Column stands and preparation:

On June 1999 (one year after the collection) the leaching experiment was started. Each column was closed from the bottom using a custom-made glass fiber filter and glass wool pad which was found in previous experiments to provide uniform flow patterns into the sediments (Dunnivant, et. al. 1992). Caps were constructed by inserting a plastic tube in the center of PVC end-caps. All columns were prepared by cutting the residual soil layer from the bottom and putting the two layers of glass fiber and glass wall-pad in place, then inserting the cap and sealing it using epoxy sealant. Wood stands, each holding three columns, were prepared to carry the columns upright. The columns were distributed randomly to the stands. Below each column a 250 mL Amber bottle was

placed to collect the effluent. There were two treatments in addition to the control (CT), these were the fresh addition (FT) and the old addition (OT). A fresh addition of biosolids from LB and DMB were added to the top layer (plowed layer) of the three columns (FT) at a rate of 26.8 and 28 dry Mg biosolids ha^{-1} for both the dryland soil and the irrigated soil, respectively. The addition of biosolids to the top 10 cm was done by removing the top layer and mixing it thoroughly with the appropriate amount of biosolid and returning it back to the top of the column. These columns were constructed and placed in a laboratory where the temperature was between 25-30^{o}C.

Collection of column effluent:

The irrigated soil was initially leached for the first 5 cycles with a synthetic solution prepared to simulate the chemical composition of irrigation water sampled at the field location (Table 2). In order to study the effects of leaching with a less saline water on the mobilization of DOC and metals, the irrigated soil columns were then leached with 5 cycles of D.I. water. The order of application of the two types of water to the dryland soil was the reverse, with D.I. water applied during the first five cycles and then the simulated irrigation water applied for cycles 6-10.

Initial wetting of the columns was done by applying D.I. water (dryland soil) or irrigation water (irrigated soil) to the bottom of the columns until they were saturated at the surface. Each of the columns remained saturated for 24 hrs and was then drained for 24 hrs. The first drainage water was not collected for analysis. Each of the 10 leaching cycles completed for each column was initiated by the addition of a volume of water equivalent to 50% of the field capacity of the soil (280 mL for the dryland soil, and 200

mL for the irrigated soil). Following the addition of this increment of water, the columns were allowed to drain into a glass bottle for a period of 48 hours. At that time, the collection bottles were replaced and the next leaching cycle was started. After collection, these solutions were kept in a refrigerator at $4^{O}C$ before and after filtration. A portion of each leachate was filtered using 0.45 μm Nuclepore® Polycarbonate. This filtered solution was used for the Differential Pulse Anodic Stripping Voltammetry (DPSAV), Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), and Dissolve Organic Carbon (DOC) measurements.

The pH of the effluent was measured with a glass electrode (Orion720). Electrical conductivity and total dissolved salts were measured in the effluent using an Orion model 108. A Shimadzu TOC-500 was used to analyze the filtrate samples for DOC. Hydrochloric acid was added to each filtered sample at a concentration of 1% followed by a purging with $N_{2(g)}$ for three minutes to remove inorganic carbon. A Perkin Elmer 4100 ZL with Zeeman background correction was used to analyze the total dissolved metal at $\mu g\ L^{-1}$ levels. Directly after filtering the samples, part of them was made up to 0.2% HNO_3 (ultra pure grade). Then the samples were analyzed using the GFAAS by using EDL lamps for Pb and Zn, and a hollow cathode lamp for Cu.

Differential Pulse Anodic Stripping Voltammetry (DPSAV):

Metal speciation was performed using Differential Pulse Anodic Stripping Voltammetry with a rotating disk electrode to differentiate between metals present as free ions or inorganic complexes vs. organically complexed metals in the sub-$\mu g\ L^{-1}$ concentration range (Wang and Benoit, 1996; Bruland, 1989; Rozan et al. 1999).

The system was RDE-1 a type of Bio-analytical Systems, Inc. It consists of CV-50 W Voltametric analyzer connected to RDE-1 Rotating disk electrode. The cell consisted of a 30-mL glass cell, a rotating glassy-carbon disk (RGCD) working electrode where a mercury film was deposited, an Ag/AgCl reference electrode, and a platinum wire counter electrode. The Teflon cap had two holes: one a N_2 inlet tube and a second for the addition of standards and other chemicals. This machine was connected to a PC and printer using CV-500 software (Bio-analytical Systems).

Mercury film formation:

Procedures of analyzing the samples with DPASV were adopted from Bruland (1989). Before the analysis all glassware was soaked in 2% pure HNO_3 for 24 hrs, followed by rinsing with ultra-pure D.I. In a glass cell, 300 µL of 1 M ultra-pure KCl (Suprapur®, EM Science) was added to 30 mL of ultra pure de-ionized water (UPDI). This cell was covered with parafilm and was purged for 10 min with grade 4.8 $N_{2(g)}$ to remove dissolved oxygen from the UPDI. After the sample was purged, it was moved to the RDE-1, and a stream of $N_{2(g)}$ was continuously passed through the top of the sample under a closed system to keep the system clean of dissolved oxygen. Following the addition of 60µl of 1000 mg L^{-1} Hg, the Hg film was deposited for 5 minutes under -1100 mV with a working electrode rotation of 4000 rpm. After the thin mercury film formation, the rotating glassy-carbon disk (TMF-RGCD) electrode was stopped and left for a 20 sec quiet time, then the film was stripped free of any deposited metals by scanning the potential from –1100 mV to –50mV (sample width, 17 msec; scan rate, 20 mV/sec; pulse amplitude, 50 mV; pulse period, 200 msec; sensitivity; $1X10^{-6}$ A/V). This

step was repeated three times. After each scanning the electrode was cleaned for 60 sec under a potential of −100 mV. The three-step deposition was performed to purify the system of metals, and ensure that the system was reproducible and ready for calibration.

System calibration:

After the TMF-RGCD was formed, another UPDI pre-purged sample was used to clean the RGCD electrode. Fresh 30-mL 0.01 M KCl solution was used to do the calibration curve, also using a 5 minutes deposition time. Successive standard additions in the rate of 0.2 μg L^{-1} of two standards (Cu-Pb, and Zn) to overcome the interference between Cu and Zn (Florence, 1986) was used to establish the calibration curve until the response was linear in accordance to the increase in element concentration. As a final point, addition normally stopped at about 3.5 μg L^{-1} of Zn, Pb, and Cu. Detection limits were 0.1, 0.1, and 0.2 μg L^{-1} for Cu, Pb, and Zn, respectively. The deposition potential was set to be −1300 to-900, -650 to −350, and -400 to −20 mV for Zn, Pb, and Cu, respectively.

Filtered effluent samples were placed in the glass cell, 300 μl of 1 M KCl was added, and then the sample was purged for 10 min under $N_{2(g)}$. Deposition and stripping of metals was completed using the same parameters as for calibration.

Separation of humic and fulvic acids:

Humic and fulvic acid fractions were quantified by the procedure of Kumada (1987). The effluents were acidified to pH 1 using 1:3 HCl solution, then kept for 24 hrs. After 24 hrs the solutions were centrifuged at 10,000 rpm for 20 minutes at 25°C

(Kumada, 1987). The supernatant solution was then analyzed to measure the fulvic acid concentration, and humic acid was calculated by the difference between total DOC and fulvic acid concentrations.

Table 1. Typical composition of the two types of biosolids.

Characteristics	Unit	LB†		DMB‡	
Moisture	g kg^{-1}	538		348	
pH		8.4		8.3	
EC	dS m^{-1}	9		11	
O.M.	%	22.5		21	
Solids	%	15.2		15.1	
		Total	AB-DTPA	Total	AB-DTPA
		g kg^{-1}			
P		40.7		26.9	
K		6.0		4.2	
NO_3-N			2.4		3.2
		mg kg^{-1}			
Zn		693	88	518	159
Cu		621	10.8	459	14
Pb		23.8	--	31	--

† Biosolid from Littleton/Englewood, CO sewage treatment facility
‡ Biosolid from Metro Denver treatment facility

Table 2. Chemical composition of irrigation water

EC	pH	Ca	Mg	Na	K	CO3	HCO_3	SO_4	Cl	NO_3	NO_3-N
dS m^{-1}		mg L^{-1}									
2.05	5.5	199.3	55.7	228.8	5.5	<0.1	339.1	552.1	198	75.1	17.2

Data Analysis:

All experiments were set up in a split-plot design where water is considered a block in a split plot design, treatment as the main effect, the cycles as subplots and carried out in triplicate. For the analysis, data were subjected to split-plot analysis using SAS windows version 8.01 (SAS Inst. 1999-2000). The Pearson correlation coefficient was used to study the significance of correlation at the 0.1 probability level. Correlation

analysis was first performed over all ten leaching cycles within each soil and biosolids application treatment (Fresh, Old, and Control). Correlation analysis was then performed for the separate water types used in cycles 1-5 and 6-10 both within (by analyzing data from the biosolids application treatments separately) and across (by analyzing data from the biosolids application treatments combined) biosolids application treatments. Correlation analysis across sludge applications for all ten cycles was not used due to the high number of observations (90) that were involved.

RESULTS AND DISCUSSION

Dryland Soil:

Within the first five cycles, the greatest Cu concentration was found in the second cycle for the recently amended soil (Fig. 1). Effluent Cu concentration was significantly greater for the fresh vs. old addition of biosolids amendment and also for the old amendment vs. control for cycles 1-5 and 6-10 (Table 3).

For Zn, the peak reading was in the first cycle and then decreased through cycle #6 (Fig. 1). After the influent was changed from D.I. to irrigation water, Zn concentration increased through the tenth leaching cycle. The highest soluble Zn concentrations were observed for the fresh addition (FT), followed by the control and the old addition (OT) (Table 3). The elevated mobility of the Zn in the fresh treated soil compared to the control is consistent with the results of Barbarick et al. (1998) who found an accumulation of extractable Zn below the zone of biosolids incorporation in a soil profile sampled from the same site as the dryland soil in this study. Although Zn mobility was low in the middle stages of the leaching experiment coinciding with low values of EC, the EC observed at the early and late stages of leaching is probably more representative of field conditions for this soil.

Effluent Pb concentration was significantly greater for the fresh and old amendments soils leachate compared to the control for cycles 1-5 but not cycles 6-10 (Table 3).

The DOC peak concentration was found in the 2^{nd} cycle and then decreased through the 10^{th} cycle (Fig. 1). The DOC concentration was significantly greater for the

fresh amendments as compared to the old amendment and also for the old amendment as compared to the control for both cycles 1-5 and cycles 6-10 (Table 3).

The EC peak was in the second cycle, indicating that the waterfront from the topsoil didn't reach the bottom until the second cycle (Fig. 1). The EC readings decreased as leaching progressed, due to the removal of inherent salts by D.I. water and then increased after switching to irrigation water. Significant differences in EC were observed between the two treated soils and the control soil (Table 3). Both EC and Zn reached minimum values near the sixth cycle for all three treatments. However, both Cu and Pb reached maximum values during the sixth cycle for the two amended soils when EC was at a minimum. Although Cu increased dramatically after switching from D.I. to SIM water beginning with the sixth cycle, the fact that EC did not begin to increase until the 7^{th} or 8^{th} cycles suggests that the Cu release in cycle 6 may reflect the later stages of leaching with D.I. water. The dispersion of Cu-bearing colloids, either organic or mineral, may be responsible for the elevated Cu concentration in cycle 6.The pH was significantly decreased for the FT compared to the other two treatments for all ten cycles (Table 3).

The increased concentration of both Zn and Cu and also DOC in the recently amended vs. old amended treatments is consistent with previous results, which indicated that leachate concentrations of DOC (Giusquiani et al. 1992), metals (Welch and Lund, 1987; Sawhney et al. 1994), or both DOC and metals (Dudley et al. 1986, Lamy et al. 1993) are the greatest immediately after the addition of biosolids, and both decrease as leaching progresses. The fast increase in these heavy metals and DOC may occur directly after applying biosolids to the soil, and may be due to the decomposition of organic

Table 3. Soil chemical components of the soil column leachate (pH, EC, Zn, Cu, Pb, and DOC) as affected by the addition of biosolids and time in the dryland soil.

	pH		EC		Zn		Cu		Pb		DOC	
Cycles	1-5	6-10	1-5	6-10	1-5	6-10	1-5	6-10	1-5	6-10	1-5	6-10
			dS m^{-1}		$\mu g\ L^{-1}$						mg L^{-1}	
Treatment												
Control	7.44	7.76	0.40	0.63	11.7	13.4	6.73	9.87	0.44	3.47	39.8	12.38
Old	7.54	7.54	1.02	0.92	4.87	12.6	52.4	91.1	2.66	3.19	117.8	51.9
Fresh	6.36	6.53	0.77	0.79	22.3	27.7	67.7	178.8	2.39	3.47	185.8	70.0
$LSD_{0.1}$	0.2	0.2	0.2	0.2	6.1	6.6	13.1	42.6	0.7	NS	35.8	13.4
Cycles												
1	6.83	7.18	0.55	0.52	24.1	8.0	28.9	148.9	1.27	9.67	119.74	63.48
2	7.12	7.20	0.91	0.56	15.2	12.2	47.0	118.1	1.26	4.78	132.04	51.66
3	7.10	7.62	0.80	0.80	11.6	19.6	48.9	102.7	1.81	0.86	125.37	43.26
4	7.29	7.25	0.73	0.96	8.3	22.1	46.1	52.56	2.14	0.92	101.18	35.44
5	7.24	7.15	0.66	1.06	5.67	27.9	40.6	44.0	2.68	0.66	93.93	30.11
General interaction¶	NS		NS		<0.01		<0.01		<0.01		0.02	

¶ Cycle X Treatment (water)

compounds which can produce soluble organic matter and can form complexes with various heavy metals. The form of the heavy metals also play a major role in this increase, as some of these elements were in simple or complexed ions in the soil, and can be directly present in the soil solution.

Metal Speciation:

From analyzing effluent from the 3rd cycle and the 8th cycle, the ASV signals were very small and near or below the detection limits, which were 0.1, 0.1, and 0.2 $\mu g\ L^{-1}$ for Cu, Pb, and Zn, respectively, based on the smallest concentration needed to produce a peak that was easily identified. Therefore, the results showed that more than 99% of Cu and Zn and at least 90% of Pb complexed with either DOC or mineral colloids, and were not present as free metal ions or inorganic complexes, which are ASV labile. Temminghoff et al. (1997) found that when the pH was over 6.6 the complexation of Cu with DOC comprised more than 99% of the total dissolved element. This is in agreement with our results where the pH was above 6.6.

The results of the ASV analysis are consistent with the relationship between Cu and DOC, observed in Fig. 1. The fact that soluble Zn increased with EC suggests that exchangable Zn may have been released. However, this Zn is apparently complexed by DOC or colloids once displaced from exchange sites. Although Rozan et al. (1999) have verified the accuracy of ASV for the speciation of Cu in the presence of fulvic acid at concentrations up to 25 mg L^{-1} as DOC, the accuracy of this method has not been validated for metal speciation in the presence of the extremely high concentrations of

DOC released from soils recently amended with biosolids. Therefore, these metal speciation results must be considered tentative and interpreted with caution.

Irrigated soil:

Effluent Cu concentrations were significantly greater for the FT than OT or CT for all of the cycles after the first, and also for OT vs. CT for both cycles 1-5 and 6-10 (Fig. 2, Table 4). Zinc was greatest in the 4th cycle for both the OT and FT (Fig. 2). Similar to the dryland soil, effluent Zn concentration was the greatest in the FT, followed by CT and OT for cycles 1-5 (Table 4). The relatively low concentration of Zn in the old amended soil may be the result of depletion of exchangeable Zn due to the high salt content of the biosolids. The presence of organic matter on the old amended soil may be one of the reasons for this as a result of its production of large amount of dissolved organic matter, which can keep complexing with the heavy metals and decrease their concentrations even below their initial values. The other effect of the presence of organic matter is the improvement of the physical structure of the soil so the water and solutes can travel more easily than in the unamended soil. This conclusion is in agreement with McBride et al. (1997).

Lead readings were low and highly variable and no differences between treatments were evident (data not shown).

Dissolved organic matter concentration was significantly greater for the fresh addition of biosolids compared to the other two treatments for both cycles 1-5 and 6-10 (Fig. 3, Table 4). However, DOC was very similar for the old treatment and the control, indicating that most of the DOC from the biosolids was leached out of the surface layer within one year of application. After DOC concentration peaked in the 3rd cycle, DOC

Table 4 . Soil chemical components of the soil column leachate (pH, EC, Zn, Cu, Pb, and DOC) as affected by the addition of biosolids and time in the irrigated soil.

	pH		EC		Zn		Cu		Pb		DOC	
Cycles	1-5	6-10	1-5	6-10	1-5	6-10	1-5	6-10	1-5	6-10	1-5	6-10
			dS m^{-1}		$\mu g\ L^{-1}$						mg L^{-1}	
Treatment												
Control	7.95	7.99	2.42	1.08	121.7	53.3	57.7	134.0	3.4	1.9	27.2	25.2
Old	7.31	7.17	3.26	1.11	91.5	58.1	92.5	226.9	4.1	0.3	24.1	23.7
Fresh	7.26	7.39	3.76	2.0	153.9	64.5	184.2	417.3	4.9	2.3	175.8	97.7
$LSD_{0.1}$	0.13	0.29	0.53	0.42	24.6	NS	29.8	45.8	1.3	1.5	19.3	5.1
Cycles												
1	7.35	7.68	2.92	2.13	108.1	92.2	81.9	227.3	2.6	1.6	51.2	50.3
2	7.62	7.80	3.64	1.75	94.3	74.?	99.9	211.6	4.2	1.8	78.3	42.9
3	7.46	7.77	3.6	1.32	114.4	63.3	137.3	223.9	6.1	4.1	97.6	46.7
4	7.54	7.26	3.04	0.99	157.0	39.6	124.0	338.0	4.0	0	79.6	51.3
5	7.56	7.08	2.53	0.77	137.9	23.8	114.1	296.2	3.9	0	71.9	53.1
General Interaction ¶	0.003		NS		<0.01		<0.01		<0.01		<0.01	

¶ Cycle X Treatment (water)

decreased between cycles 3 through 7 and then increased slightly through cycle 10. The increase in DOC concentration during the later stages of leaching when EC reached minimum values indicates that a colloidal component of DOC that is sensitive to low EC was released. If this fraction of DOC that was released under conditions of low EC binds Cu very strongly, this could explain why soluble Cu increased dramatically between cycles 5 and 6 even though total DOC concentration decreased. A slight increase in the concentration of a strongly Cu-binding DOC component could be masked by an overall decrease in the total DOC concentration. The existence of multiple components with a range of metal binding constant has been illustrated for DOC extracted from biosolids (Dudley et al., 1986; Dudley et al., 1987).

Electrical conductivity was the highest in the 2nd or 3rd cycle and after that decreased through cycle 10 (Fig 2). As with the dryland soil experiments, peak Zn concentrations were observed near a maximum in EC. Effluent Zn concentration and EC both reached peak concentrations during the 3rd or 4th cycle, and both decreased during cycles 6-10.

Both the old and recent amendments with biosolids significantly decreased effluent pH compared to the control (Table 4). This difference in pH could be responsible for the greater Cu concentration in the OT vs. the CT, even though DOC was very similar for these two treatments.

As for the dryland soil, ASV measurements indicated that > 99% of soluble Cu and Zn were complexed, based on analyses of effluent collected during the 3rd and 8th cycles. This highly complexed Cu and Zn indicate that most of these two metals are present as organic complexes.

Separation of humic and fulvic acid:

For effluents from all soil-treatment combinations, most of the DOC was in the fulvic acid fraction (Table 5). This result is consistent with the expected greater mobility of fulvic acid (FA) compared to humic acid (HA) (Stevenson, 1994). With the presence of fulvic acid in the solution, the chemical equilibria for some heavy metals enhanced to be in aqueous form and this may lead to an increase in the mobility of these metals in the soil profile (Lamy et al., 1993).

Correlation analysis:

Dryland Soil

Correlation analysis within each biosolids application treatment over all ten cycles for the dryland soil revealed a significant positive relationship between Zn and EC for the control and fresh amendment (Table 6). This relationship is consistent if a cation exchange mechanism is controlling Zn solubility. Boyle and Fuller (1987) found that the total soluble salt concentration contributed more than DOC concentration in increasing the transport of Zn through soils amended with municipal solid waste. They attributed their results to competition between Zn and soluble salts for nonspecific exchange sites. For cycles 1-5 and 6-10 the overall results for each group of cycles showed a negative correlation between Zn and pH; these findings are in agreement with Dutta et al. (1989).

Effluent Cu concentration was negatively correlated with DOC over all ten cycles for the fresh and old amended treatments. If DOC is responsible for Cu mobility, we would expect a positive correlation. This result appears to be in contradiction with many previous observations that DOC contributes to the solubility and mobility of Cu in soi

Table 5. The separation of humic and fulvic acid in the soil†.

	Dryland Soil‡		Irrigated Soil§	
	%		%	
	humic	**fulvic**	**humic**	**fulvic**
Control	11.5	88.5	8.4	91.6
Old Addition	8.3	91.7	10.9	89.1
Fresh Addition	9.4	90.6	16.6	83.4

† The readings were for the cycle with the highest DOC concentration.
‡ The highest DOC was in the second cycle.
§The highest was in the third cycle.

(Campbell and Beckett, 1988; McBride et al., 1997; Temminghoff et al., 1997; McBride et al., 1999). However, Cu and DOC were positively correlated for both cycles 1-5 and 6-10 when data from all three treatments were combined (Table 6). The lack of correlation between Cu and DOC within treatments over the duration of the leaching experiments could be the result of the release of chemically different components of DOC under high vs. low electrolyte concentrations with respect to metal binding properties.

Effluent concentrations of Pb were negatively correlated with EC within the fresh and old amended treatments over all ten leaching cycles. A cation exchange mechanism should cause a positive relationship between EC and soluble metals, as we found for Zn. This negative correlation between Pb and EC may be the result of the release of Pb-bearing organic colloids under low EC.

Irrigated Soil

Similar to the dryland soil, effluent Zn concentrations were positively correlated with EC over all ten cycles for the control, old, and fresh amendment treatments (Table 7). Zinc was also positively correlated with DOC for the fresh amended soil over all ten

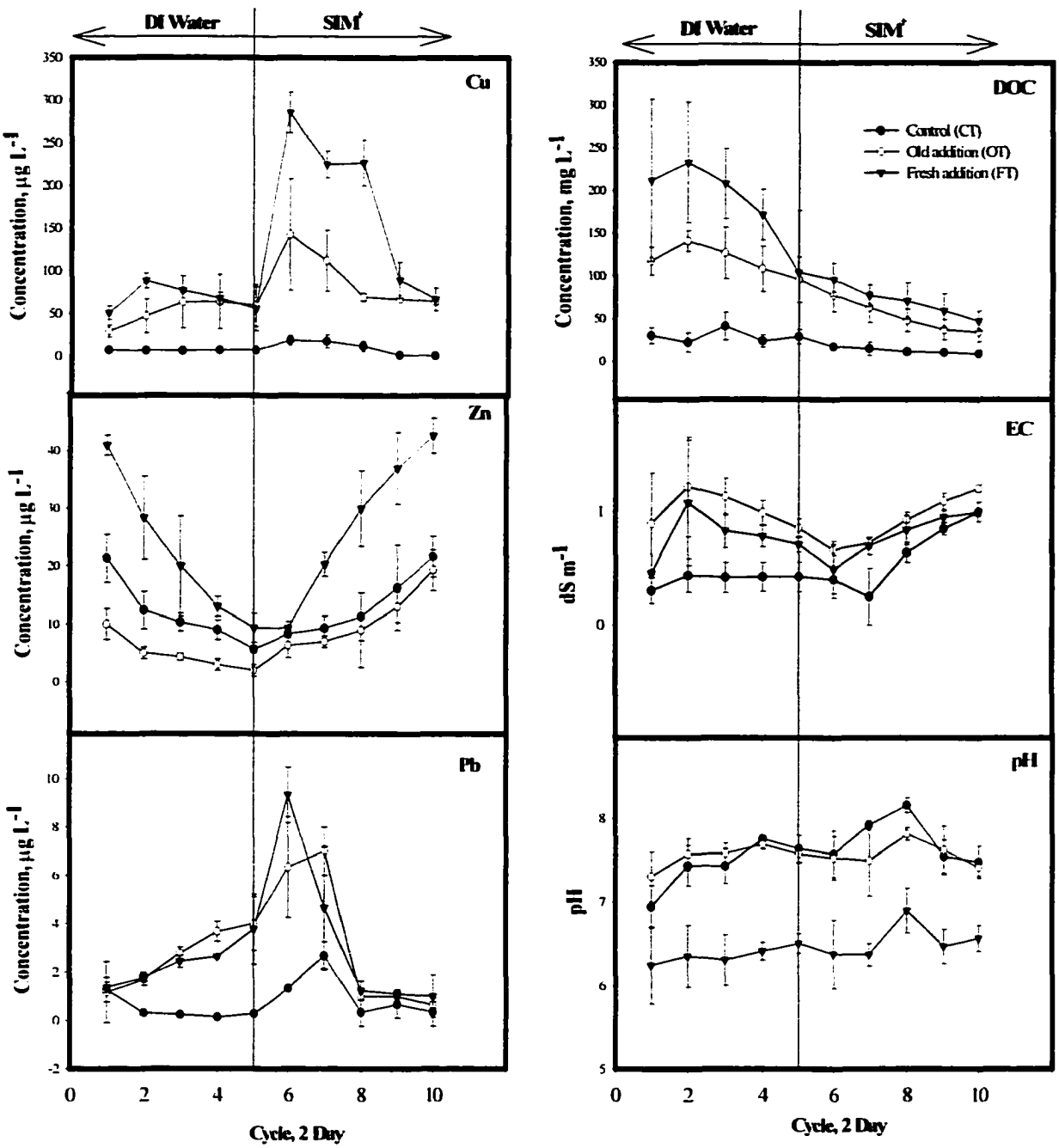

Fig. 1. Chemical analyses of effluent solutions collected from ten leaching cycles of the dryland soil.

† Simulated Irrigation Water

Error bars are ± standard error of the mean.

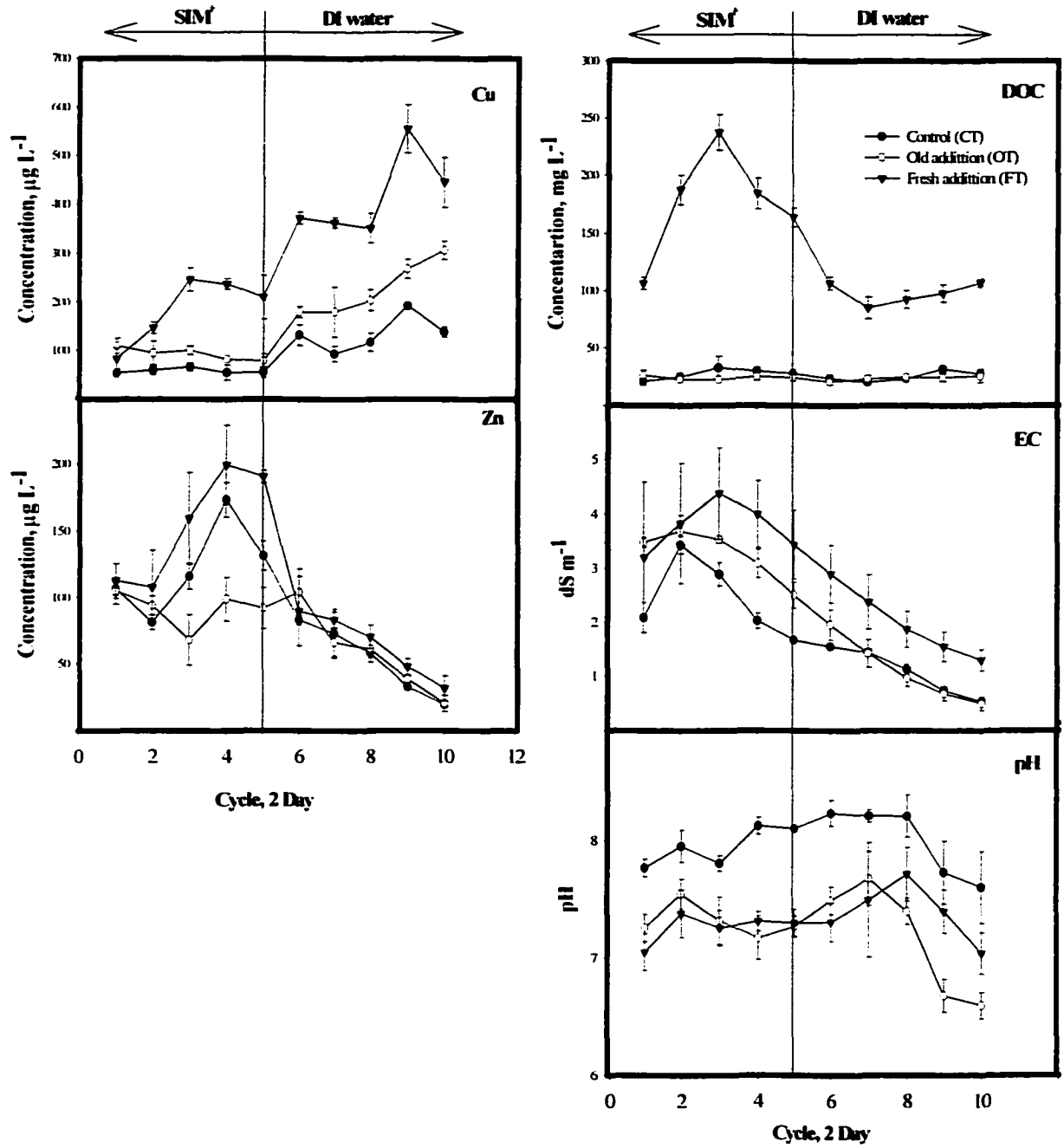

Fig. 2. Chemical analyses of effluent solutions collected from ten leaching cycles of the irrigated soil.

† Simulated Irrigation Water
Error bars are ± standard error of the mean.

cycles and across all three biosolids application treatments for cycles 1-5. The organic matter started to be more soluble when the pH >6.6, and this may enhance the leaching of heavy metals with strong ability to complex with Zn.

Table 6. Correlation analysis[†] for Cu, Zn, and Pb Vs. pH, EC, and DOC in the dryland soil.

Treatment	Cu			Zn			Pb		
	pH	EC	DOC	pH	EC	DOC	pH	EC	DOC
Cycles 1-5									
Control[a]	0.55^{-}	0.10^{-}	0.69^{+}	$<0.01^{-}$	0.09^{-}	0.17^{-}	$<0.01^{-}$	0.12^{-}	0.70^{-}
Old[a]	0.75^{+}	0.09^{+}	0.08^{-}	0.02^{-}	0.82^{-}	0.31^{+}	0.07^{+}	0.62^{-}	0.03^{-}
Fresh[a]	0.59^{-}	0.07^{+}	0.13^{+}	0.05^{-}	0.94^{-}	0.03^{+}	0.68^{+}	0.83^{+}	0.01^{-}
Over all[b]	$<0.01^{-}$	$<0.01^{+}$	$<0.01^{+}$	$<0.01^{-}$	0.25^{-}	$<0.01^{+}$	0.20^{-}	$<0.01^{+}$	0.08^{+}
Cycles 6-10									
Control[a]	0.16^{+}	$<0.01^{-}$	$<0.01^{+}$	0.18^{-}	$<0.01^{+}$	0.01^{-}	0.27^{-}	0.05^{-}	0.03^{+}
Old[a]	0.65^{+}	$<0.01^{-}$	0.08^{+}	0.66^{+}	$<0.01^{+}$	0.02^{-}	0.19^{-}	$<0.01^{-}$	$<0.01^{+}$
Fresh[a]	0.97^{-}	$<0.01^{-}$	$<0.01^{+}$	0.48^{+}	$<0.01^{+}$	$<0.01^{-}$	0.22^{-}	$<0.01^{-}$	$<0.01^{+}$
Over all[b]	$<0.01^{-}$	0.42^{-}	$<0.01^{+}$	$<0.01^{-}$	$<0.01^{+}$	0.68^{+}	0.31^{-}	$<0.01^{-}$	0.05^{+}
Cycles 1-10									
Control[a]	0.09^{+}	$<0.01^{-}$	0.89^{-}	$<0.01^{-}$	0.04^{+}	0.06^{-}	0.91^{-}	0.22^{-}	0.43^{-}
Old[a]	0.62^{+}	0.20^{-}	0.04^{-}	0.74^{-}	0.34^{+}	$<0.01^{-}$	0.46^{-}	$<0.01^{-}$	0.89^{+}
Fresh[a]	0.35^{+}	0.17^{-}	0.05^{-}	0.73^{-}	0.09^{+}	0.88^{-}	0.48^{-}	0.02^{-}	0.47^{-}

$^{-/+}$ Negative or positive correlation

[†] Significant at 0.1 the probability level

a within treatments

b acroos treatments

Copper was negatively correlated with DOC over all ten cycles only for the soil receiving fresh amendment of biosolids. However, as for the dryland soil, Cu was positively correlated with DOC when data from the fresh, old, and control treatments were combined for both cycles 1-5 and 6-10. This negative correlation may due to the summation of ten cycles, where we used two different waters. However, the data in Table 7 showed that there is a positive correlation for over all of the first and the last five cycles.

Table 7. Correlation analysis† for Cu and Zn Vs. pH, EC, and DOC in the irrigated soil.

Treatment	Cu			Zn		
	pH	EC	DOC	pH	EC	DOC
Cycles 1-5						
Control[a]	0.26^{-}	0.21^{+}	0.06^{+}	0.03^{+}	$<0.01^{-}$	0.40^{+}
Old[a]	0.88^{-}	0.08^{+}	0.66^{-}	0.41^{-}	0.99^{+}	0.14^{+}
Fresh[a]	0.32^{+}	0.25^{+}	$<0.01^{+}$	0.69^{+}	0.37^{+}	0.19^{+}
Over all[b]	$<0.01^{-}$	$<0.01^{+}$	$<0.01^{+}$	0.91^{+}	0.46^{+}	$<0.01^{+}$
Cycles 6-10						
Control[a]	0.07^{-}	0.05^{-}	$<0.01^{+}$	$<0.01^{+}$	$<0.01^{+}$	$<0.01^{-}$
Old[a]	$<0.01^{-}$	$<0.01^{-}$	0.33^{+}	$<0.01^{+}$	$<0.01^{+}$	0.07^{-}
Fresh[a]	0.58^{-}	0.06^{-}	0.48^{+}	0.20^{+}	$<0.01^{+}$	0.24^{-}
Over all[b]	$<0.01^{-}$	0.04^{+}	$<0.01^{+}$	$<0.01^{+}$	$<0.01^{+}$	0.60^{+}
Cycles 1-10						
Control[a]	0.34^{-}	$<0.01^{-}$	0.47^{+}	0.07^{+}	$<0.01^{+}$	0.67^{+}
Old[a]	$<0.01^{-}$	$<0.01^{-}$	0.87^{+}	$<0.01^{+}$	$<0.01^{+}$	0.53^{-}
Fresh[a]	0.29^{+}	$<0.01^{-}$	$<0.01^{-}$	0.68^{-}	$<0.01^{+}$	$<0.01^{+}$

$^{-/+}$ Negative or positive correlation

† Significant at 0.1 the probability level

a within treatments

b across treatments

CONCLUSION:

The addition of biosolids significantly increased effluent DOC concentration in both soils studied. One year following the field application of biosolids, DOC concentration was at background levels in the irrigated soil but still elevated in the dryland soil. In both soils, elevated Cu concentrations accompanied increased DOC concentrations; however, the concentrations of these two variables were not proportional throughout each leaching experiment. This could be the result of differential release of multiple components of DOC from the biosolids. Mobile Zn concentrations were more closely related to EC. The fraction of each of the metals (Cu, Zn, and Pb) present as free metal ions or inorganic complexes was extremely low, indicating that the mobile metals

were associated with DOC or possibly mineral colloids. Mobile concentrations of Cu and Zn were the greatest immediately after the addition of biosolids, and decreased within 1 year of application. However, an increase in EC caused the release of mobile Zn in the dryland soil, and a decrease in EC caused the release of high concentrations of Cu in the irrigated soil.

Although the measured concentrations of all three metals were below 1 mg L^{-1} for all effluents collected, the metal mobility was significantly greater in the amended soils, and this could lead to significant redistribution of metals from the mixing layer to the subsoil after several years.

REFERENCES

Barbarick, K. A., I. A. Ippolito, and D. G. Westfall. 1995. Biosolids effect on phosphorus, cooper, zinc, and molybdenum concentrations in dry land wheat. J. Environ. Qual.24: 608-611.

Barbarick, K. A., I. A. Ippolito, and D. G. Westfall. 1998. Extractable trace elements in the soil profile after years of biosolids application. 27:801-805.

Boyle, M., and W.H. Fuller. 1987. Effect of municipal solid waste leachate composition on zinc migration through soils. J. Environ. Qual. 16:357-390.

Brown, S., R. Chaney, and J.S. Agle. 1997. Subsurface liming and metal movement in soils amended with lime-stabilized biosolids. J. Environ. Qual. 26:724-732.

Bruland, K., 1989. Complexation of zinc by natural organic ligands in the central north pacific. Limnol. Oceanogr. 34:269-285.

Buffle, J., D. Peret, and M. Newman. 1992. The use of filtration and ultrafiltration for size fractionation of aquatic particles, colloids, and macromolecules. *In* Environmental Particles Volume 1., J. Buffle and H.P. van Leeuwen, eds., Lewis Publishers, Boca Raton, p. 171-230.

Campbell, D. J., and P. H. Beckett. 1988. The soil solution in a soil treated with digested sewage sludge, J. Soil. Sci. 39:283-298.

Christensen, T.H. 1985. Cadmium sorption at low concentrations. IV. Effect of waste leachates on distribution coefficients. Water Air Soil Pollut. 26:265-274.

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

Dudley, L.M., B.L. McNeal, and J.E. Baham. 1987. Characterization of soluble organic compounds and complexation of copper, nickel, and zinc in extracts of sludge-amended soils. J. Environ. Qual. 16: 341-348.

Dunnivant, F.M., P.M. Jardine, D.L. Taylor, and J.F. McCarthy. 1992. Co-transport of Cadmium and hexachlorobiphenyl by dissolved organic carbon through columns containing aquifer material. Environ. Sci. Technol. 26: 360-368.

Dutta, D., B. Mandal, and L. N. Mandal. 1989. Decreas in availability of Zinc and copper in acidic near neutral soils on submergence. Soil Sci. 147:187-195.

Gerritse, R.G., R. Vriesema, J.W. Dalenberg, and H.P. de Roos. 1982. Effect of sewage sludge on trace element mobility in soils. J. Environ. Qual. 11:359-364.

Giusquiani, P.L., G. Gigliotti, and D. Businelli. 1992. Mobility of heavy metals in urban waste-amended soils. J. Environ. Qual. 21:330-335.

Holm, P.E., T.H. Christensen, S.E. Lorenz, R.E. Hamon, H.C. Domingues, E.M. Sequeira, and S.P. McGrath. 1998. Measured soil water concentrations of cadmium and zinc in plant pots and estimated leaching outflows from contaminated soils. Water Air Soil Pollut. 102:105-115.

Kumada, Kyoichi. 1987. Chemistry of Soil Organic Matter. Elsevier. New York. 34-37.

Lamy, I., S. Bourgeois, and A. Bermond. 1993. Soil cadmium mobility as a consequence of sewage sludge disposal. J. Environ. Qual. 22:731-737.

McBride, M. B. 1989. Reactions controlling heavy metals solubility in soils. Adv. Soil Sci. 10:1-57

McBride, M.B. 1995. Toxic metal accumulation from Agricultural use of sludge: Are USEPA regulations protective? J. Environ. Qual. 24:5-18.

McBride, M.B., B.K. Richards, T. Steenhuis, J.J. Ruiso, and S. Suave. 1997. Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. Soil Sci.162:487-500.

McBride, M.B., B.K. Richards, and T. Steenhuis. 1999. Long-term leaching of trace elements in a heavily sludge-amended silty clay loam soil. Soil Sci. 164:613-623.

Rozan, T. F., G. Benoit, H. March., and Y. Chin. 1999. Intercomparison of DPASV and ISE for the measurement of Cu complexation characteristics of NOM in freshwater. Environ. Sci. Technol. 33: 1766-1770

Richards, B.K., T.S. Steenhuis, J.H. Peverly, and M.B. McBride. 1998. Metal mobility at an old, heavily loaded sludge application site. Environ. Pollut. 99:365-377.

Richards, B.K., T.S. Steenhuis, J.H. Peverly, and M.B. McBride. 2000. Effect of sludge-processing mode, soil texture and pH on metal mobility in undisturbed soil columns under accelerated loading. Environ. Pollut. 109:327-346.

Sawhney, B.L., G.J. Bugbee, and D.E. Stilwell. 1994. Leachability of heavy metals from growth media containing source-separated municipal solid waste compost. J. Environ. Qual. 23: 718-722.

SAS Institute. 1999-2000. The SAS system for Windows. Release 8.01. SAS Inst., Cary, NC.

Sidle, R.C., and L.T. Kardos. 1977. Transport of heavy metals in a sludge-treated forested area. J. Environ. Qual. 6:431-437.

Soil Conservation Serviece. 1974. Soil survey of Adams county, Colorado. Unites States Department of Agriculture. U. S. Gov. Print. Office, Washington, DC.

Sposito, G. 1984. The Surface Chemistry of Soils. Oxford University Press, New York, NY.

Stevenson, F.J. 1994. Humus Chemistry: Genesis, Composition, Reactions. 2nd ed. John Wiley and Sons. New York, NY.

Temminghoff, E.J.M., S.E.A.T.M. Van Der Zee, and F.A.M. De Haan. 1997. Copper mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved organic matter. Environ. Sci. Technol. 31:1109-1115.

Tombacz, E., and E. Meleg. 1990. A theoretical explanation of the aggregation of humic substances as a function of pH and electrolyte concentration. Organic Geochemistry. 15:375.

Wang, E., and G. Benoit. 1996. Mechanisms controlling the mobility of lead in the spodosols of a northern hardwood forest ecosystem. Environ. Sci. Technol. 30:2211.

Welch, J.E., and L.J. Lund. 1987. Soil properties, irrigation water quality, and soil moisture level influences on the movement of nickel in sewage sludge-treated soils. J. Environ. Qual. 16:403-410.

APPENDIX I

DEVELOPMENT OF DATA FOR GENERATION OF MODEL TO PREDICT RELATIONSHIP BETWEEN DOC AND CU ON CU MOVEMENT IN BIOSOLIDS AMENDED SOILS

INTRODUCTION

The application of biosolids to agricultural lands has become very popular due to its advantages in the disposal of these wastes and the fact that they supply soils with nutrients and organic matter. On the other hand, this application may increase the soil content of heavy metals, which can be harmful to plants and human beings. Models that predict the transport of heavy metals in different soil conditions have been created. The major consideration of the models is the adsorption and desorption of heavy metals between soil particles and the components of a soil solution. This model approach can be equilibrium or kinetic. The equilibrium model assumes an immediate reaction between the solute and soil matrix, while the kinetic model is time-dependent.

Biosolids contain high levels of organic matter that lead to a high content of fulvic and humic acids. Fulvic acid tends to be a large molecular weight substance that can complex heavy metals. Moreover, these humic substances can be absorbed to the soil minerals. The humic substances that have been sorped into the soil mineral surface may increase the adsorption of some heavy metals. There is some competition between the soil particles and the dissolved organic matter (DOC) in absorbing the heavy metals; this complexation depends on the pH, ionic strength, DOC concentration, the form of humic substances, and the soil matrix from minerals and organic materials.

The goal of this laboratory work was to develop a model and to simulate the transport of Cu and DOC from biosolid amended layers to subsurface layers during the flow of water through the soil profile.

This work contains four experiments, the first to study the adsorption and desorption of Cu in the subsurface soil. The second experiment is a study of the adsorption of dissolved organic carbon from biosolids (SS-DOC) to subsurface-soil and desorption of Cu from SS-DOC to subsurface-soil at pH 7.1. The third experiment is a study of the desorption of Cu from SS-DOC in the soil solution. The fourth experiment is a study of the desorption of SS-DOC from the treated surface-soil at pH 6.6.

MATERIALS AND METHODS

Materials:

1) Soil samples from irrigated land (Osgod sand) located in south Roggen, CO (Weld County). The mean annual precipitation was 37 cm (Soil Conservation Service, 1974). This plot was established in 1982. Biosolids from the Metro Denver treatment facility (DMB) were applied to this site since 1988 at rate of 28.00 dry Mg biosolid ha^{-1}. Table 2 on chapter 2, describes the properties of the soils. The most recent application of biosolids to the site was approximately 1 year prior to sampling.

2) Biosolids from the Metro Denver treatment facility (DMB). Table 2 describes the properties of the soils.

3) Chelex-100 resin

4) Cu standard

Methods:

I. Cu adsorption-desorption experimental procedure

Adsorption experiment:

Amounts needed:

1) Concentration Range (for Cu^{2+}) 0, 1, 2.5 , 5, 10, 25, 50 mg L^{-1}

2) Retention time for adsorption: (1, 2, 4, 8, and 21 day); and desorption: (2 hrs 1, 2, 3, 5, and 8 days).

3) Shaking time: 30 min (140 osc min^{-1}) once every 4 hrs.

4) Sample volume: for graphite furnace atomic absorption analysis the needed volume is about 3 mL.

A mass ratio of 1:10 soil to solution was used. The extractant used was the irrigation water. After the soil was weighed, the desired amount of extractant with the needed concentration of Cu was added to the soil. After the addition, the tubes were closed and put in the horizontal direction shaker; the tubes had been attached to an empty box and this box was attached to the shaker. The shaker was run for 30 minutes every 4 hrs. After one day of reaction, the shaker was stopped and the necessary tubes were removed to represent a 1-day span of time. The pH of the solution was read, and then the tubes were placed on the refrigerator centrifuge for 10 minutes at 25° C before the centrifuge was started (to allow the temperature of the sample to be in the temperature range of 25° C). After the 10 minutes, the centrifuge was run at 10,000 rpm for 10 minutes. After 10 additional minutes the sample was collected from the tubes. Then the samples were run for the other set of times until we reached the end of the adsorption experiment. At the end of this experiment, we collected the solution from the tubes and we used these tubes for the desorption experiment.

Desorption experiment:

A period of 21 days was allowed (for what to reach equilibrium?) to reach equilibrium. Solutions were decanted and replaced with a solution free of Cu with the same ratio of soil: extractant. The process was then repeated 6 times. Each time 35 mL of solution free of Cu was added to the tube.

Analysis:

Cu using GFAA, Ion activity using Cu electrode, pH using pH meter, and free Cu ion after 1 day samples using ASV.

II. Extraction of DOC and Cu from Biosolids (pH 6.6)

1. I first extracted DOC from the biosolids by adding 86 mL (I added 120.5 mL for five cycles) of laboratory prepared irrigation water (fixed ionic strength) to 10 g biosolids "dry basis" of sludge in 250 mL centrifuge bottles. This calculation depends on the application rate, which was 28 Mg ha-1, and we assumed the bulk density was 1.45 g cm-3, the moisture for the biosolids was 472 %. The calculations resulted in the addition of 10 g of dry biosolids to the 1194 gm soil (similar to the weight of 10 cm ID and 10 cm depth). These biosolids and soil were mixed for 48 hours, at a speed of 140 cpm, (some solution was collected during this time to study the effect of time on releasing SS-DOC and Cu) then we centrifuged it at 10,000 rpm for 15 minutes and collected DOC in supernatant and filtered it through <0.45 μm. The extract from the sludge is called "SS-DOC".
2. The DOC concentration was measured in the extract (as Total DOC) using a TOC analyzer.
3. The total dissolved Cu concentration was measured by GF AA.
4. The extractant was refrigerated and to be used immediately for experiments to avoid decomposition.

III. Adsorption of SS-DOC to subsurface-soil and desorption of Cu from SS-DOC to subsurface-soil (pH 7.1)

1. Different concentrations of SS- DOC (1.0, 0.75, .50,0.25,0.1, and 0.05 times that of the SS-DOC) were prepared in duplicate using the SS-DOC solution and prepared irrigation water.
2. The solution pH was adjusted to pH 7.1.
3. From the different concentrations of SS-DOC solution we added 120 mL to 40 gm of subsurface soil in 250 mL plastic bottle, plus blank of SS-DOC (just irrigation water with no contact with biosolids).
4. Mixture was shaken for 2 hours on rotary shaker.
5. Mixture was centrifuged at 10,000 rpm for 15 minutes
6. We measured the total soluble Cu, Cu^{+2} ion activity, and labile Cu by the following methods:
    - 5 mL of the solution was collected and filtered through <0.45 μm, for analysis of total Cu and DOC in solution by GFAA and Shimadzu instrument.
    - The Cu^{+2} activity was measured using Cu-ISE electrode, by placing the Cu ISE and reference electrodes directly into the 250 mL bottles. The pH was also checked by placing pH electrodes directly into the bottles.
    - The labile Cu was measured using DPASV; this was done by removing 60 mL of solution from duplicate bottles at 24-hr. time. The glass DPASV cell was rinsed with the first 30 mL of solution, then the 2^{nd} 30 mL was used to obtain a reading. These duplicate solutions were then discarded.

- We returned the 250 mL centrifuge bottles containing 115 mL solution and 40 g soil to the shaker and repeated the analysis at time intervals of 24, 48, and 72 hours.

IV. Desorption of Cu from SS-DOC

1. The chelex-100 resin was prepared by washing it with 0.1M $CaCl_2$ and adjusting the pH to 7.0-7.5 using 0.1 M HCl.
2. Different amounts of chelex-100 metal chelating resin bottle (0.25, 0.5, 0.75,1.0,2.0, and 3.0 g) were added to each bottle. Preliminary experiments were done before the experiment to determine the amount of resin needed to extract Cu from the SS-DOC.
3. One hundred mL of SS-DOC extract solution was added to 250 mL centrifuge bottles.
4. The mixture was shaken for 2, 24, 48, and 72 hours, the total soluble Cu, Cu^{2+} ion activity, and DOC measured using GFAA, ISE electrode and Shimadzu instrument.
5. The pH was checked every time the sample was collected

V. Desorption of SS-DOC from the treated surface-soil (pH 6.6)

1. In 50 mL centrifuge bottle 20 mL of irrigation water was added to 20 g of treated soil (89.51 surface soil +10.49 g of biosolids).
2. Quadruplication was performed (4 replications).
3. Mixture was shaken for 24 hrs, then centrifuged at 10,000 for ten minutes and the solution was collected.
4. Another 30 mL was added and repeated 10 times, each time was a one-day interval.
5. The total Cu and DOC were measured using GFAA, and Shimadzu instrument.

RESULTS

The model requires the relation between the adsorption and desorption of Cu^{2+} from the topsoil, at the relevant pH. It also required the adsorption of SS-DOC to the subsurface-soil and desorption of Cu^{2+} from SS-DOC to the subsurface-soil at fix pH (7.1). The desorption of Cu^{2+} from SS-DOC was also required. Finally, desorption of SS-DOC and Cu^{2+} from the treated surface-soil at fixed pH (6.6) was also required. This work was not finished due to the lack of time with the Prof. Magdi Selim from Lousiana State University, who will be the one to provide the help in generating the multi reaction model (MRM)

I. Adsorption and desorption experiments:

Table 1. pH readings for adsorption of Cu to irrigated surface soil as a function of time

Cu mg l^{-1}	1	2	4	8	12	21
	day					
	pH					
control	7.65	7.35	7.1	5.57	5.59	4.51
1	7.26	7.09	6.55	5.91	5.84	4.85
2.5	7.18	6.95	6.43	6.1	6.08	5.05
5	6.63	6.49	6.38	6.24	6.17	5.16
10	6.02	5.99	5.89	6.38	6.67	5.28
25	4.31	5.02	5.48	6.49	6.85	6.36
50	3.02	4.58	5.2	6.65	6.91	6.69

Table 2. pH readings for desorption of Cu to irrigated surface soil as a function of time

Cu mg l^{-1}	1	2	3	5	8
			day		
			pH		
control	6.7	6.5	6.29	6.21	6.05
1	6.94	6.56	6.44	6.31	6.16
2.5	6.84	6.52	6.51	6.41	6.23
5	6.83	6.43	6.38	6.31	6.19
10	6.35	6.17	6.14	6.15	6
25	5.47	5.27	5.23	5.25	5.36
50	3.31	3.48	3.58	3.65	3.7

Table 3. Free Cu in solution in the adsorption experiment as a function of time

Cu mg l^{-1}	1	2	4	8	12	21
			day			
			Cu µg l^{-1}			
control	0.8	1.4	0.4	0.0	0.2	0.5
1	0.4	0.4	0.1	0.0	0.2	0.6
2.5	0.3	0.6	0.0	0.0	0.1	0.5
5	0.4	0.4	0.0	0.0	0.5	0.9
10	1.2	0.9	0.1	2.6	0.4	1.2
25	29.4	19.5	5.9	4.4	1.9	1.3
50	108.8	65.0	13.1	9.2	5.0	3.1

Table 4. Free Cu in solution in the desorption experiment as a function of time

Cu mg l^{-1}	1	2	3	5	8
			day		
			Cu µg l^{-1}		
control	6.4	2.9	3.8	3.5	2.4
1	11.2	1.7	2.3	2.4	1.4
2.5	14.9	1.8	2.2	2.9	1.7
5	22.4	3.0	3.0	5.3	2.2
10	37.8	5.1	5.1	7.0	4.4
25	347.5	153.8	151.1	127.9	127.7
50	1242.6	841.7	795.2	673.5	461.6

Table 5. Total dissolved Cu in solution in the adsorption experiment as a function of time

Cu mg l^{-1}	1	2	4	8	12	21
	day					
	Cu µg l^{-1}					
control	4	10.5	11	12.5	12.5	11.5
1	16	15	14.5	53.5	11	10
2.5	23	16	19.5	73.5	9	8.5
5	35.5	33	32	92	11.5	9.5
10	119	60.5	61	149	17.5	11
25	5321.5	4130	3393.5	2492	21	15.5
50	26166.5	25592	22308	21057	22.5	19.5

Table 6. Total dissolved Cu in solution for the desorption experiment as a function of time

Cu mg l^{-1}	1	2	3	5	8
	day				
	Cu µg l^{-1}				
control	15	22	10	11	11
1	24	7	4	4	11
2.5	26	10	5	5	12
5	23	18	12	12	16
10	74	85	18	19	23
25	327	241	215	180	176
50	3349	1260	701	393	282

II. Adsorption of SS-DOC to subsurface-soil and desorption of Cu from SS-DOC to subsurface-soil (pH 7.1):

Table 7. Dissolved organic carbon levels as a function of time and concentration of DOC in soil solution

SS-DOC %	Origion DOC	2	24	48	72
		hour			
	mg l^{-1}	mg C l^{-1}			
control	0	25	25.5	28.6	29.8
5	13	36.9	34.9	37.6	35.7
10	26	47.8	45	48.7	48.5
25	64	75.3	85.6	72	66.4
50	128	136.4	129.4	116.7	110
75	191	177.1	149.6	140.5	134
100	255	218.5	219.9	170.8	142

Table 8. Free Cu concentration in solution as a function of time and concentration of DOC in soil solution

SS-DOC %	2	24	48	72
	hour			
	Cu μg l^{-1}			
control	0.050	0.265	2.627	2.854
5	0.012	0.085	1.395	2.233
10	0.006	0.044	0.467	1.400
25	0.004	0.019	0.287	0.911
50	0.003	0.010	0.141	0.497
75	0.002	0.007	0.097	0.425
100	0.001	0.004	0.067	0.318

III. Desorption of Cu from SS-DOC

Table 9. Total dissolved Cu in solution as a function of the amount of chelex resin added and time.

Chelex-100 Weight gm	2	24	48	72
	hour			
	Cu μg l^{-1}			
Control (0)	260	251.5	249.5	247.5
0.25	183	58.5	50	43.5
0.5	132	49	38.5	36
0.75	113.5	45.5	37.5	34
1	97.5	44.5	37.5	30.5
2	76	40.5	32.5	27.5
3	71	37.5	29.5	26.5

Table 10. Free Cu in solution as a function of the amount of chelex resin added and time

Chelex-100 Weight gm	2	24	48	72
	hour			
	Cu μg l^{-1}			
Control (0)	0.034	0.023	0.015	0.010
0.25	0.022	0.008	0.007	0.006
0.5	0.019	0.006	0.005	0.004
0.75	0.017	0.006	0.004	0.003
1	0.014	0.005	0.004	0.003
2	0.013	0.004	0.003	0.002
3	0.011	0.003	0.002	0.002

Table 11. Dissolved carbon solution as a function of the amount of chelex resin added and time

Chelex-100 Weight gm	2	24	48	72
	hour			
	mg C l^{-1}			
Control (0)	329.5	288	278.5	267
0.25	288.5	282.5	273.5	271.5
0.5	277	272	267.5	264.5
0.75	274.5	271	266.5	262.5
1	271.5	264.5	254	251.5
2	249	244.5	243.5	238.5
3	240	239.5	239	233.5

IV. Desorption of SS-DOC from the treated surface-soil (pH 6.6)

Table 12. Total dissolved Cu concentration and dissolved organic matter concentration as a function of time in biosolids amended layer

Day	Cu $\mu g\ l^{-1}$	DOC $mg\ l^{-1}$
1	62.33	236.33
2	41.00	160.67
3	26.00	112.00
4	17.00	61.33
5	12.67	33.67
6	8.67	29.33
7	5.00	25.00
8	3.33	17.67
9	2.00	12.33
10	1.00	8.67