Long-Term Copper Availability and Adsorption in a Sludge-Amended Davidson Clay Loam

by

Martha Ann Anderson

Dissertation submitted to the Faculty of the

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

IN

CROP AND SOIL ENVIRONMENTAL SCIENCE

APPROVED:

D.C. Martens, Co-Chair

L.W. Zelazny, Co-Chair   S.J. Donohue

R.D. Morse   E.R. Collins

April, 1997

Blacksburg, Virginia

Keywords: Copper, Sludge, Zinc, Adsorption, *Zea mays* L.

c.2

LONG-TERM COPPER AVAILABILITY AND ADSORPTION IN A SLUDGE-AMENDED DAVIDSON CLAY LOAM

by

Martha A. Anderson

Dr. David C. Martens, Co-Chair

Dr. Lucian W. Zelazny, Co-Chair

Crop and Soil Environmental Sciences

(ABSTRACT)

A single application of aerobically digested sewage sludge was applied by Rappaport et al. (1988) in 1984 at rates up to 210 dry Mt ha^{-1} on a Davidson clay loam (clayey, kaolinitic, thermic, Rhodic Kandiudults). The heavily contaminated sludge supplied up to 760 kg Cu and 620 kg Zn ha^{-1}, which are below current cumulative limits, but above annual loading limits for these metals (USEPA, 1993). Rappaport et al. (1988) reported an increase in DTPA extractable Cu and Zn with increasing sludge rate. They observed a linear increase in corn yields with an increase in sludge rate, which was attributed to high levels of available N supplied by the sludge. In the present residual study, conducted at the same research site, DTPA extractable Cu and Zn followed the trend observed by Rappaport et al. (1988). However, a linear decrease in corn and sorghum yields was observed with increasing sludge rate. The sludge-related decrease in yields was attributed to phytotoxicity (probably a combination of Al, Cu, Mn, and Zn) induced by low soil pH levels. Whole plant tissue concentrations of Cu and Zn at the high sludge rates were above the normal range, however grain concentrations were within the normal range. An

adsorption study was conducted, in which soils were amended with $Ca(OH)_2$ and $Al_2(SO_4)_3$, to ascertain the effect of decreased pH on Cu adsorption on the soil. Copper adsorption maxima decreased with a reduction in soil pH in all treatments. The effect of ionic strength on Cu adsorption was also investigated. Regardless of pH or ionic strength, Cu adsorption increased with an increase in sludge rate. This adsorption increase was attributed to the higher organic matter content of the sludge treatments. The organic matter at the highest sludge rate was approximately double that of the control after 11 years. The adsorption study shows that sludge amendment has long-term effects on metal retention in soils and the field study reveals that careful management of sludge-amended soils is necessary to prevent phytotoxicity.

Dedication

I dedicate this work to my parents Oscar and Virginia Anderson for their love and support. And to my sister Nancy, who passed away too early in life. And to my son, Jedidiah, who is deeply loved by his mother.

ACKNOWLEDGMENTS

I would like to express my greatest appreciation to my Co-Chair Dr. David C. Martens, who has taught me much over the years. I, in turn, have certainly taught him patience. It has been a privilege to work with him and my other Co-Chair, Dr. Lucian W. Zelazny.

I would like to thank Dr. Stephen J. Donohue for both his guidance and his financial support. It was a pleasure working with him in the classroom and in the greenhouse. I would also like to thank Steve Heckendorn for his assistance in interpretation of soil test and plant analysis data.

My deepest appreciation goes out to Hubert Walker for his friendship and his assistance in the lab. I also appreciate the assistance of Wes Atkinson and Dave Starner in collection of field samples and data. I would like to extend my thanks to the secretaries in the Department of Crop and Soil Environmental Sciences for their help over the years.

Over the years, I was fortunate to acquire a number of friends in the department, most of whom are no longer in the area. I can not express enough gratitude to Stewart Reed, who assisted me with the adsorption studies and who served as an inspiration. I will always cherish the friendship and comradery I shared with Sunetra Wijesudnara, who has returned her home country of Sri Lanka and is deeply missed. My thanks go out to all of the other individuals I have worked with in the lab: Dan Lucero, Ron Taraban, Edelgard Pavel, Alfredo Lopez, Hans and An Willems, Regine Mankolo, Wonae Pong and Archer Christian. Special thanks go out to Barry Stewart and Steve Feldman for their help over the many years. I would also like to acknowledge Dr. John Hall for his assistance

with special requests and for financial support.

And finally I would like to thank my family and my friends outside of the department for their encouragement. Special thanks go out to my father for his support over the years and to my son for his understanding and patience. Special thanks also go out to David Eborall and Vickie Altizer for the support they have provided over the years.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1

INTRODUCTION

Sludge Generation

Sewage sludge is generated during municipal wastewater treatment. The solid residues that remain after physical, biological, and chemical treatment of wastewater are referred to as sludge or biosolids. There is an increase in the volume of sludge generated as the level of treatment increases. Primary treatment generates 2,500 to 3,500 liters of sludge per million liters of wastewater treated; secondary treatment generates an additional 15,000 to 20,000 liters of sludge; and tertiary treatment generates an additional 10,000 liters (USEPA, 1993a). A typical family of four discharges 1134 to 1512 liters of wastewater day $^{-1}$, which sometimes contains household hazardous wastes and pesticides (USEPA, 1993a).

Sludge usually contains 3 to 7% solids and is dewatered at the wastewater treatment plant to concentrate solids. Sludge intended for landfilling and land application is usually concentrated to to 25% solids and 75% water (Cheremisinoff, 1994). The dewatered sludge may be mixed with wood chips and allowed to decompose, producing a compost product, or it may be dried to 95% solids and made into pellets.

Approximately 15,000 publicly-owned treatment works (POTWs) in the United States generate about 8 million dry mt (or 800 million to 1.7 billion wet mt) of sludge annually (Cheremisinoff, 1994). Seventy percent of all U.S. sludge is produced by 3% (about 400) of its POTWs, i.e., POTWs which generate more than 10 dry mt day $^{-1}$ (Cheremisinoff, 1994). The average amount of dry sludge generated per person is 21.4 kg yr $^{-1}$ (Jewell, 1994). The production of sludge in Virginia is approximately 400 dry mt day $^{-1}$, 90% of which is generated in the less than 100 POTWs with the largest flow volumes (Sawyer, 1996).

Application of Sludge on Cropland

Land application of human wastes to improve crop production is an age-old practice. Records of this practice date back to the Roman Empire. In Asian countries these wastes, referred to as "night soil", have long been applied to enhance crop production. Human wastes were applied in an unprocessed state until emergence of health concerns regarding use of raw wastes. Prior to the 1960s, little sewage treatment occurred. Direct application of wastes was discontinued with the passage of the Clean Water Act in 1977 and the advent of modern wastewater treatment.

Land application of the residues (sludge) from wastewater treatment was encouraged to prevent pollution of streams and rivers. Although the agricultural value of sludge was promising, large amounts were still either dumped in landfills or incinerated. Use of sludge on cropland increased as research revealed its agronomic benefits. Sewage sludge is a valuable resource because of its nutrient and organic matter content. The main benefits from sludge use on cropland are nutrient supply and soil conditioning (USDA, 1978). Related benefits include a decrease in dependence of chemical fertilizers and a reduction in fuel costs and emissions associated with incineration. Other land application options in which sludge use is beneficial include mine land reclamation (Sopper, 1991; Daniels and

Haering, 1994), rangeland restoration (Fresquez et al., 1990; Aguilar et al.,1994), and forest fertilization (Bayes et al., 1991; Taylor and Moffat, 1991; Henry and Cole, 1994; Outwater, 1994).

Despite the benefits, only about one third of the sludge generated in the U.S. is applied to land (USEPA, 1993a). The United Kingdom reuses 51% of its sewage sludge by land application. (USEPA, 1993a). Approximately 50% of Virginia's sludge is applied to agricultural land (Sawyer, 1996). The Blue Plains wastewater treatment plant in Washington, DC. generates 2,000 mt of sludge (3 to 7% solids) day $^{-1}$, of which northern Virginia is a contributor (Klemer, 1990). The total sludge output of this plant is recycled through composting and land application. Closure of existing landfills, more stringent restrictions on those which are opening, and increased disposal costs (tipping fees) are decreasing landfill disposal of sludge, thereby requiring other disposal options (Cheremisinoff, 1994). Only 1 to 2% of the nation's cropland would be required for land application of all the sludge generated in the U.S. (Peterson et al., 1994).

In the 1960s, Tennessee Valley Authority scientists investigated the possibility of land application of sludge (Klemer, 1990). Experiments conducted in the 1970s at the U.S.Department of Agriculture facility in Beltsville, Maryland revealed that the yield response produced by one dry ton of sludge was equivalent to that of 14 dollars of commercial fertilizer (Klemer, 1990). In 1991, Bio Gro Systems estimated that the first year savings from the use of anaerobically digested sludge for a 100-bu corn (*Zea mays L.)* crop was $90.55 (Forste, 1994). Sludge was evaluated as a commercial fertilizer substitute for corn by Kresse and Naylor (1983). Corn yields on sludge-amended sites were comparable to fertilizer-amended soils. Corn yields on sludge-applied land were higher than on fertilized control areas in a 20-year study conducted by the University of Minnesota in the Rosemount watershed (Knuteson et al., 1988). Corn grain and stover yields increased linearly as a function of sludge rate on three diverse Virginia soils that

received up to 210 mt ha $^{-1}$ sludge (Rappaport et al., 1988). Corn yields in a greenhouse study conducted by Cunningham et al. (1975) increased at sludge rates of 125 and 251 mt ha $^{-1}$, but decreased at the 502 mt ha $^{-1}$ rate. Yield decreases were attributed to heavy metal toxicity and high soluble salt levels.

Although numerous studies have shown crop response to sludge, it is regarded as an unbalanced, low-analysis nutrient source. Sommers (1977) investigated the potential use of sludges as fertilizers and reported considerable variation in nutrient content. He reported ranges of <1 to 176 g kg $^{-1}$ for total N, <1 to 143 g kg $^{-1}$ for total P, and 0.2 to 26.4 g kg $^{-1}$ for total K. Appreciable amounts of N and P are often present in sludge (Hall, 1984, 1985, 1986), however the K content of all sludges is low (Hall and Williams, 1986). Sludge can also supply other nutrients such as Ca, Mg, Cu, and Zn (Smith,1996).

Sludges have been applied to cropland at about half the rate of cattle manure (Fuller and Warrick, 1985). If sludges are relatively low in heavy metals and other toxic contaminants, loading rates should be similar to those for livestock manures. A conservative application rate of 10 mt ha $^{-1}$, based on N requirements of crops and N concentration of sludge, was used to calculate heavy metal limits for the Part 503 sludge regulations (USEPA, 1993b). The management practices portion of Part 503 states that the application rate of bulk sludge cannot exceed the agronomic rate. The agronomic rate is based on the N requirements of the crop or vegetation grown and minimizes the danger of nitrate leaching into groundwater. If no other sludge constituent limits the rate of application, then the rate should be based on nitrogen. Pierzynski (1994) recommends that the application rate should take into account the kinds and amounts of N present in sludge. Guidelines for N management with sludge application are discussed in the Proceedings of the 1993 National Land Utilization of Sludge Conference (Pierzynski, 1994). In these guidelines, Pierzynski points out that determination of the potentially available N is complicated by the difficulty of predicting the potentially mineralizable N.

The agronomic benefits of land application of sludge must be weighed against the risks. The risks depend upon the composition and application rate of sludge, soil properties, and crop species grown. As industrial inputs of contaminants in wastewater increased, environmental concerns regarding land disposal of sludge arose. This risk spawned a wave of research on assessment of the safe utilization of sludge on land.

Groundwater contamination through the leaching of Cu was initially a concern. Downward movement of sludge-applied Cu has been monitored in a few studies. Williams et al. (1987) applied up to 225 mt sludge ha^{-1} annually for an 8-year period and detected no movement of Cu below 0.3 m. Copper remained in the surface 0.2 m of soil 12 years after sludge application (84 mt ha^{-1}) in a field study conducted by Anderson and Nilsson (1972). Sludge-borne Cu did not appear to move into the subsoil in field plots that received 765 mt sludge ha^{-1} and 1070 kg Cu ha^{-1} over a 14-year period (Dowdy et al., 1991). Other research has revealed no movement of Cu below the sludge-soil interface (Robertson et al., 1982; Emmerich et al., 1982). Erosion of Cu-bearing soil particles into surface waters probably presents a greater water pollution hazard than groundwater contamination.

Phytotoxicity to crops was an additional concern regarding sludge-applied Cu. Copper, Zn and Ni accumulate more readily than other sludge constituents in crops and can reach phytotoxic levels (Smith, 1996). Copper concentrations in crops increased by 56% in more than 100 crop trials treated with sludge (Vigerust and Selmer-Olsen, 1986). Johnston et al. (1983) investigated copper toxicity in barley (*Hordeum vulgare* L.), ryegrass (*Lolium multiflorum* L.), and lettuce (*Lactuca sativa* L.) grown on sludge-amended plots. They concluded that it would require 30 years of sludge application at four times the normal rate to produce phytotoxicity in these crops. Copper phytotoxicity did not occur in corn grown on three diverse soils where sludge supplied 760 kg Cu ha^{-1} (Rappaport et al., 1988). The soil under study herein was one of the three soils utilized by Rappaport et al.

(1988) in their research. In a pathway risk analysis conducted by the USEPA, crop phytotoxicity was identified as the most limiting route of environmental exposure to Cu in sludge-treated soil (USEPA, 1992). It has been argued that the limits set for Cu in the recent 503 Regulation for sludge (USEPA, 1993b) are overly protective against potential crop phytotoxicity (Smith, 1996). Chang et al. (1992) determined that the probability of corn Cu concentrations on sludge-amended soils exceeding phytotoxic concentrations is <0.0001 for cumulative loading rates of 1550 kg Cu ha^{-1}, which is 50 kg ha^{-1} above the 503 Regulation cumulative loading rate of 1500 kg ha^{-1}.

Sludge Regulations

Concern in the 1970s over environmental contamination triggered expansive research on safe and efficient utilization of sewage sludge on land. For the last two decades, the research efforts of U.S. scientists in this area have culminated in the recent sludge regulations entitled *Standards for the Disposal and Utilization of Sewage Sludge* (Code of Federal Regulations, Title 40, Parts 257 and 503). Landgrant universites, including Virginia Polytechnic Institute and State University, played an important role in regulation decisions as they conducted research on the impact of sludge application on crops, soils, animals, and water quality. The technical information obtained from this research led many scientists to promote land application of sludge.

The USEPA realized the need for federal guidance on land application of sludge in 1979. The 257 rule was developed to fulfill that need and regulated sludge use on land until the 503 sludge rule was implemented in 1993. The 257 rule did not address all major sludge contaminates and regulated cumulative limits only for cadmium. Many states developed their own regulations as land application of sludge increased.

Prior to the recent Part 503 sewage sludge regulation, cumulative pollutant loading rates formed the basis for land application of sludge in Virginia. Virginia adopted the USEPA recommendation that guidelines for maximum Cu loading of cropland from sewage sludge application be based on soil cation exchange capacity and a soil pH greater than or equal to 6.5 (USEPA, 1983). For the soil under study, with a cation exchange capacity of 12.5 cmol kg^{-1}, the maximum safe cumulative sludge Cu application was 280 kg ha^{-1} according to USEPA guidelines (USEPA, 1983) and 250 kg ha^{-1} according to Virginia Sewerage Regulations (Kelley et al., 1984). In this study herein, a single application of sludge in 1984 supplied the soil with 760 kg Cu ha^{-1} at the highest sludge rate and exceeded both of the recommended maximum loading rates. Soil pH levels at the time of application and often thereafter were below the recommended pH of 6.5.

USEPA Part 503 sludge regulations are based on the assumptions of very high sludge application rates and worse case exposure. These regulations set numerical metal limits for sludge application to cropland (USEPA, 1993b). The ceiling concentration (maximum allowable) for Cu in any land applied sludge is 4300 mg kg^{-1}. The ceiling concentrations for heavy metals were based on the assumptions of a 100-year site life and an annual sludge application of 10 Mt ha^{-1}. Copper concentration in the sludge applied in this study was 3654 mg kg^{-1}, which is below the ceiling limit for Cu. However, the Cu concentration did exceed the pollutant concentration limit for Cu of 1500 mg kg^{-1}. The pollutant concentration limit is that concentration below which land application of sludge has no restrictive requirements and management practices. It is also the criteria for high quality sewage sludge. If the concentration of bulk sludge is below the ceiling, but above the pollutant concentration level, a cumulative loading limit has been set. The cumulative loading limit for Cu is 1500 kg ha^{-1}, about twice the amount of Cu applied in this study. An annual loading rate of 75 kg Cu ha^{-1} for containerized sludge was also established by USEPA Part 503 sludge regulations.

Management practices for land application of bulk sewage sludge are outlined in Part 503 regulations (USEPA, 1993b). Application is not permitted if there is a likelihood of adverse effects on threatened and endangered species. Bulk sewage sludge cannot be applied to flooded, frozen, or snow-covered land or to a site 10 meters or less from U.S. waters. Whole sludge application rates can not exceed the agronomic rate - a provision to ensure environmentally safe N levels.

Monitoring requirements are also outlined in Part 503 regulations (USEPA, 1993b). The frequency of monitoring is based on the amount of bulk or containerized sludge applied to the land. In all cases, monitoring must be performed at least once a year. After the sludge has been monitored for two years, the frequency may be reduced by the permitting authority. Appliers must maintain records on applicable management practices, cumulative amounts of pollutants applied, and pathogen and vector attraction reduction measures.

States may either adopt the federal sewage sludge program outlined in Part 503 or obtain separate USEPA permits (Bastian, 1994). Until the USEPA approves a separate program, states must comply with Part 503 requirements and state regulatory authorities and requirements. Section 510 of the Clean Water Act allows states and political subdivisions of states to enforce standards which are more stringent than those provided in Part 503.

Copper in Sludge

Local industrial inputs to treatment plants are a major source of Cu in sludge. Nonindustrialized sludge in Tucson, Arizona is reported to contain considerably less Cu than sludge from heavy industialized sludge in Chicago, Illinois (Fuller and Warrick, 1985). Stricter controls on industrial discharges have reduced the amount of Cu in sludge.

Baker and Chesnin (1975) reported that low levels of trace elements enter treatment plants via food and human wastes, plumbing, and surface runoff. Domestic sources account for most of the Cu discharge to sewers in the UK, primarily from corrosion of Cu plumbing systems (Smith, 1996). Critchley and Agg (1986) reported that only 3% of the Cu entering the sewer system in the UK was from industry.

The Cu content of sludge varies within and between treatment plants. Variation is due to the number and types of industries in the treatment plant district and the degree of pretreatment the wastewater receives. Primary treatment of wastewater (mechanical and physical removal of solids) removes a high percentage of metals from wastewater (Page and Chang, 1981). Trace metals removed from wastewater effluent are adsorbed onto sludge particles. Chen et al. (1974) reported a 69% reduction in total Cu content of effluent with secondary treatment. Bouwer and Chaney (1974) reported a median concentration of Cu in wastewater after primary treatment of 0.10 mg L $^{-1}$ compared with a median of 0.04 mg L $^{-1}$ after secondary treatment.

Variability in Cu content of sludges has been documented for a long time. Rudolfs and Gehm (1942) reported that U.S. sludges contained 160 to 400 mg Cu kg $^{-1}$. Kelley et al. (1984) combined data derived from studies by Page (1974) and Baker and Chesnin (1975) on metal concentrations in sludge obtained from 300 treatment plants located in Canada, England, Sweden, U.S., and Wales. Copper concentrations ranged from 52 to 11,700 mg kg $^{-1}$, with a median Cu content of 500 mg kg $^{-1}$. In 1989, the National Sewage Sludge Survey revealed that the mean concentration of Cu in U.S. sludges was 665 mg kg $^{-1}$ (O'Dette, 1991).

A comparison of fresh and composted sewage wastes revealed that composting of sludge increases Cu concentration (Ayuso et al., 1996). However, the higher quality of organic matter in composted sludge seems to offset the Cu increase in sludge. Ayuso et al.

(1996) concluded that the greater stability of organic matter in composted sludge permits more complexation with metals.

The chemical forms of Cu in sludge vary. Stover et al. (1976) fractionated metals from sludge and found Cu to be present in greatest amounts as sulfides, followed by carbonates, and organically bound forms. Their data indicate that less than 17% of total sludge Cu is readily available to plants (Kelley et al., 1984). The form of Cu in sludge also influences the behavior of the metal when placed in the soil-water environment.

Copper was classified as a potential hazard in land application of sludge by the Council for Agricultural Science and Technology in the 1970s (CAST, 1976). Recent U.S. sludge regulation contains a "Clean Sludge" provision referred to as Exceptional Quality Sludge, which deregulates sludge that meets certain requirements. One of the requirements for "clean sludge" is a Cu concentration below 1500 mg kg^{-1} (USEPA, 1993b). This deregulation provides incentive and creates pressure for treatment plants to produce less contaminated sludge.

Research Needs

Research needs for land application of sludge were identified in the Proceedings of the 1993 National Land Utilization of Sludge Conference (Clapp et al., 1994). These comments included the need for:

1. long-term studies (decades) on the gradual changes in assimilative capacity of soils that receive continuous sludge applications,
2. data on pollutant desorption in nonuniform media to support trace element transport models,
3. a better understanding of the ecological effects of sludge constituents,

4. more reliable methods of predicting N mineralization rates of sludges, and

5. an update on the magnitude of sludge generation and on the concentration of sludge constituents.

The USEPA has recognized future research needs for land-applied sludge (USEPA, 1993a). They urge continuing research on factors influencing plant availability of sludge-borne metals and on development of a model to predict metal uptake. The effects of different environmental conditions on bioavailability of sludge constituents also require further investigation. They point out that too small a portion of sludge research has been conducted under poor management conditions. Unfortunately during the last decade there has been little federal presence or funding for sludge research. Lack of funds has led to a decrease in sludge research to address current knowledge gaps.

The author anticipates that the research findings of this study will enhance current knowledge of land application of sludge and will also be utilized to improve environmental safety in sludge use. Objectives of this research were as follows:

1. to determine long-term effects of sludge amendment on Cu availability and adsorption,

2. to ascertain pH effects on Cu adsorption in a sludge-amended soil, and

3. to evaluate corn and sorghum (*Sorghum bicolor* L.) response to metal toxicity following sludge application.

REFERENCES

Aguilar, R., S.R. Loftin, and P.R. Fresquez. 1994. Rangeland restoration with treated municipal sewage sludge. p. 211-220. *In*: C.E. Clapp et al. (ed.) Sewage sludge: Land utilization and the environment. Soil Sci. Soc. Am.Misc. Publication, Madison, WI.

Anderson, A., and K.O. Nelson. 1972. Enrichment of trace elements from sewage sludge fertilizer in soil and plants. Ambio1:176-179.

Ayuso, M., J.A. Pascual, C. Garcia, and T. Hernandez. 1996. Evaluation of urban wastes for agricultural use. Soil Sci. Plant Nut. 42:105-111.

Baker, D.E. and L. Chesnin. 1975. Chemical monitoring for environmental quality and animal and human health. Adv. Agron. 27:305-74.

Bastian, R.K. 1994. Where do we stand on regulations?: pp.159-169. *In:* C.E. Clapp et al. (ed.) Sewage sludge: Land utilization and the environment. Soil Sci. Soc. Am. Misc. Publication, Madison, WI.

Bayes, C.D., C.M.A. Taylor, and A.J. Moffat. 1991. Sewage sludge utilization in forestry: the UK research programme. p. 115-138. *In*: J.E. Hall (ed.) Alternative uses for sewage sludge. Pergamon Press, New York, NY.

Bouwer, H., and R.L.Chaney. 1974. Land treatment of wastewater. Adv. Agron. 26:133-176.

Chang, A.C., T.C. Granato, and A.L. Page. 1992. A methodology for establishing

phytotoxicity criteria for chromium, copper, nickel, and zinc in agricultural land application of municipal sewage sludges. J. Environ. Qual. 21:521-536.

Chen, K.Y., C.S.Young, T.K. Jan, and N. Roghatgi. 1974. Trace metals in wastewater effluent. J. Water Pollut. Control Assoc. 45:2663-2675.

Cheremisinoff, P.N. 1994. Sludge:management and disposal. PTR Prentice Hall, Englewood Cliffs, NJ.

Clapp, C.E., W.E. Larson, and R.H. Dowdy (ed.). 1994. Sewage sludge: Land utilization and the environment. SSSA Misc. Publication. Am. Soc. Agron,. Madison, WI.

Council for Agricultural Science and Technology (CAST). 1976. Application of sewage sludge to cropland: appraisal of potential hazards of the heavy metals to plants and animals. USEPA Report No. 430/9-76-013. U.S. Environmental Protection Agency, Office of Water Program Operations, Washington, DC.

Critchley, R.F. and A.R. Agg. 1986. Sources and pathways of trace metals in the United Kingdom. Wrc Report No. ER 822-M. Wrc Medmenham, Marlow.

Cunningham, J.D., D.R. Keeney, and J.A. Ryan. 1975. Yield and metal composition of corn and rye grown on sludge-amended soil. J. Environ. Qual. 4:448-454.

Daniels, W.L, and K.C. Haering. 1994. Use of sewage sludge for land reclamation in the Central Appalachians. p. 105-121. *In*: C.E. Clapp et al. (ed.) Sewage sludge: Land utilization and the environment. Soil Sci. Soc. Am. Misc. Publication., Madison, WI.

Dowdy, R.H., J.J. Latterell, T.D. Hinesly, 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.

Emmerich, W.E., L.J. Lund, A.L. Page, and A.C. Chang. 1982. Movement of metals in sewage sludge-treated soils. J. Environ. Qual. 11:178-181.

Forste, J. 1994. Gaining public acceptance for biosolids. p. 81-85. *In*: C.E. Clapp et al. (ed.) Sewage sludge: Land utilization and the environment. Soil Sci. Soc. Am. Misc. Publication, Madison, WI.

Fresquez, P.R., R.E. Francis, and G.L. Dennis. 1990. Effects of sewage sludge on soil and plant quality in a degraded semiarid grassland. J. Environ. Qual. 19:324-329.

Fuller, W.H., and A.W. Warrick. 1985. Soils in waste treatment and utilization. CRC Press, Boca Raton, FL.

Hall, J.E. 1984. Predicting the nitrogen value of sewage sludges. *In:* P. L'Hermite and H. Ott (ed.) Processing and use of sewage sludge. D.Reidel Publishing Co., Dordrecht.

Hall, J.E. 1985. The cumulative and residual effects of sewage sludge nitrogen on on crop growth. *In:* J.H. Williams, et al. (ed.) Long-term effects of sewage sludge and farm slurry applications. Elsevier Applied Science Publishers Ltd., Barking.

Hall, J.E. 1986. The agricultural value of sewage sludge. Wrc Report No. ER

1220-M. Wrc Medmenham, Marlow.

Hall, J.E. and J.H. Williams. 1986. The use of sewage sludge on arable and grassland. p. 22-35. *In:* S. Berglund et al. (ed.) Utilization of sewage sludge on land: Rates of application and long-term effects of metals. D. Reidel Publishing Co., Boston, MA.

Henry, C.L., and D.W. Cole. 1994. Biosolids utilization in forest land. p.89-94. *In:* C.E. Clapp et al.(ed.) Sewage sludge: Land utilization and the environment.

Jewell, W.J. 1994. Engineering and cost considerations: sludge management and land application. p. 41-54. *In:* C.E.Clapp et al. (ed.) Sewage sludge: land utilization and the environment. Soil Sci. Soc. Am. Misc. Publication, Madison, WI.

Johnston, N.B., P.H.T. Beckett, and C.J. Waters. 1983. Limits of zinc and copper toxicity from digested sludge applied to agricultural land. p. 75-81. *In:* Davis et al. (ed.) Environmental effects of organic and inorganic contaminants in sewage sludge. D. Reidel Publishing Co., Boston, MA.

Kelley, W.D., D.C. Martens, R.B. Reneau, Jr., and T.W. Simpson. 1984. Agricultural use of sewage sludge: A literature review. VPI-VWRRC-Bull 143, Virginia Water Resource Center, Virginia Polytechnic Institute and State University, Blacksburg, VA.

Klemer, J. 1990. The ultimate recycling project. Chesapeake Bay Magazine, p. 45-47. January issue.

Knuteson, J., C.E. Clapp, R.H. Dowdy, and W.E. Larson. 1988. Sewage sludge management. Land application of municipal sludge to a terraced watershed in Minnesota. Minn. Agric. Exp. Sta. Misc. Publ. No. 56-1988. St. Paul, MI.

Kresse, E.J. and L.M. Naylor. 1983. Municipal sewage sludge: A three year
    research effort. Cooperative extension of Oneida County.

O'Dette, R.G. 1991. Clean sludge in Tennessee. Biocycle 32: 56-59.

Outwater, A.B. 1994. Reuse of sludge and minor wastewater residuals. Lewis Publishers,
    Ann Arbor, MI.

Page, A.L. 1974. Fate and effects of trace elements in sewage sludge when applied to
    agricultural lands. USEPA Report No. 670/2-74-005. U.S. Environmental
    Protection Agency, Washington, DC.

Page, A.L. and A.C. Chang. 1981. Trace metal in soils and plants receiving
    municipal wastewater irrigation. *In:* F.M. D'itri (ed.) Municipal wastewater in
    agriculture. Academic Press, NY.

Peterson, A.E., P.E. Smeth, R.B. Corey, and T.H. Wright. 1994. Effect of twelve
    years of liquid digested sludge application on the soil phosphorus level. p. 237-247. *In:*
    C.E. Clapp et al. (ed.) Sewage sludge: Land utilization and the environment. Soil Sci.
    Soc. Am. Misc. Publication, Madison, WI.

Pierzynski, G.M. 1994. Plant nutrient aspects of sewage sludge. p. 21-25. *In:*
    C.E. Clapp et al. (ed.) Sewage sludge: Land utilization and the environment.
    Soil Sci. Soc. Am. Misc. Publication, Madison, WI.

Rappaport, B. D., D.C. Martens, R.B. Reneau, Jr., and T.W. Simpson. 1988. Metal
    availability in sludge-amended soils with elevated metal levels. J. Environ. Qual.

17:42- 47.

Robertson, W.K., M.C. Lutrick, and T.L. Yuan. 1982. Heavy applications of liquid-digested sludge on three Ultisols.I. Effects on soil chemistry. J. Environ. Qual. 11:278-282.

Rudolfs, W., and W.H. Gehm. 1942. Chemical composition of sewage sludges, with particular reference to their phosphoric acid contents. New Jersey Agric. Exp. Stn. Bull. 699. New Brunswick, NY.

Sawyer, C.M. 1996. Personal communication.October, 1996. Director of Division of Wastewater Engineering. P.O. Box 2448, Richmond, VA.

Smith, S.R. 1996. Agricultural recycling of sewage sludge and the environment.CAB International, Wallingford, UK.

Sommers, L.E. 1977. Chemical composition of sewage sludges and analysis of their potential use as fertilizers. J. Environ. Qual. 6:225-232.

Sopper, W.E. 1991. Utilization of sewage sludge in the United States for mine land reclamation. p. 21-40. *In*: J.E. Hall (ed.) Alternative uses for sewage sludge. Pergamon Press, New York, NY.

Stover, R.C., L.E. Sommers, and D.J. Silivan. 1976. Evaluation of metals in wastewater sludge. J. Water Poll. Control Fed. 9:2165-2175.

Taylor, C.M.A, and A.F. Moffat. 1991. The potential for utilizing sewage sludge in forestry in Great Britain. p. 103-113. *In*: J.E. Hall (ed.) Alternative uses for

sewage sludge. Pergamon Press, New York, NY.

U.S.Department of Agriculture. 1978. Improving soils with organic matter. U.S.
   Gov. Printing Office, Washington, DC.

U.S. Environmental Protection Agency. 1983. Process design manual for land
   application of municipal sludge. USEPA Rep. EPA-625/1-83-016. U.S. Gov. Print.
   Office, Washington, DC.

U.S. Environmental Protection Agency. 1992. Technical support document for land
   application of sewage sludge. Vol. 1. Eastern Research Group, Lexington.

U.S. Environmental Protection Agency. 1993a. Preamble and final sludge rule. PB93-
   500478. National Technical Information Service, Springfield, VA.

U.S. Environmental Protection Agency. 1993b. Standards for use or disposal of sewage
   sludge. Final Rule, 40 CFR Part 503. U.S. Gov. Print. Office, Washington, DC.

Vigerust, E. and A.R. Selmer-Olsen. 1986. Basis for metal limits relevant to sludge
   utilization. *In:* R.D. Davis et al. (ed.) Factors influencing sludge utilization
   practices in Europe. Elsevier Applied Science Publishers Ltd., Barking.

Williams, D.E., J. Vlamis, A.H. Pukite, and J.E. Corey. 1987. Metal movement in
   sludge-amended soils: A 9-year study. Soil Sci. 143:124-131.

Chapter 2

LONG-TERM EFFECTS OF SLUDGE APPLICATION ON SELECTED SOIL CHEMICAL PROPERTIES

LITERATURE REVIEW

Introduction

Changes in soil physical and chemical properties in sludge-amended soils occur as the sludge and soil interact (Guidi and Hall, 1984; Epstein et al., 1976; Tester, 1990; Giusquiani et al., 1995). These changes may influence availability and adsorption of Cu and affect crop yield. Much of the research on metal retention focuses on the role of organic matter. Long-term changes in organic matter content, cation exchange capacity, and P levels of sludge-amended soils will be addressed in this chapter. The long-term effect of sludge application on soluble salt levels and their subsequent effect on crop yield will also be given consideration.

Organic Matter

The solid fraction of sludge is approximately 50% organic matter (Guidi, 1981). Sludge organic matter is composed of carbohydrates, proteins, fats, resins, waxes, cellulose, hemicellulose, and lignin (Guidi, 1981). The organic fraction of soil is the most chemically active fraction, and strongly affects physical and chemical properties (Bohn et al., 1985).

Soils often become deficient in organic matter when they are placed in continuous cultivation. Decomposition of soil organic matter occurs faster with cultivation, and crop residues return less organic matter to the soil than a full vegetation cover (Hall and Coker, 1983). Sludge additions increase soil organic matter (Epstein et al., 1976); however, Guidi and Hall (1984) observed that large applications of sludge are required for a detectable increase in organic matter. They recommend an application of 50 to 100 dry mt ha $^{-1}$ to increase organic matter sufficiently to improve soil properties. Robertson et al. (1982) calculated that 150 mt of organic matter (dry matter) were applied in a 335 mt ha $^{-1}$ sludge application. Total organic C increased two- to three-fold in a silt loam that received 298 dry mt sewage sludge ha $^{-1}$ (Hohla et al., 1978). An increase in organic matter improves soil structure and air-water relations and increases CEC, pH buffering capacity, and nutrient status (Bohn et al., 1985). Excessive addition of sludge organic matter can reduce aeration, create odor problems, and reduce root development (Miller, 1974).

Improvements in water infiltration and water holding capacity are associated with sludge applied organic matter (Oberle and Keeney, 1994). Soil organic matter can hold 20 times its weight in water (Stevenson, 1982) and, hence, can increase water retention. Epstein et al. (1976) observed that sludge and compost increased both water content and retention of a silt loam. Plant available water (between -0.33 and - 15 bar) was 18.5% in

the sludge treatments versus 12.5% in the control. Water retention and plant available water increased linearly with sludge compost addition in an investigation conducted by Giusquiani et al. (1995).

Addition of sludge to soil increases the complexation capacity for metals, although a reduction in binding strengths has been reported (Karapanagiotis et al., 1991). The affinity with organic matter is higher for Cu than for other metals. Organic matter is composed of humic acids and fulvic acids, which interact differently with heavy metals (Smith, 1996). Humic acids form more stable complexes with Cu^{2+} (Stevenson and Chen, 1991) and are considered to be an organic storage for many metals (Kiekens, 1984). Chelates formed with fulvic acids are soluble over a wide pH range, therefore a large percent of soil solution metals are associated with fulvic acids (Smith, 1996).

Organic matter levels decline as decomposition occurs and the beneficial effects concomitantly diminish. Soil and environmental conditions affect the rate of sludge decomposition. Decomposition rate varies with sludge application method (soil incorporation, deep plowing, etc.) and differs when sludge is applied in repeated small additions versus a single large addition (Miller, 1974). A certain amount of sludge organic matter is resistant to decomposition and plays an important role in long-term adsorption capacity for metals (Petruzzelli et al., 1986). Sposito et al. (1982) examined the fulvic acid fraction of organic matter in a sludge-amended soil, observed that it was more typical of sludge-derived material than soil-derived material, and concluded that a certain amount of sludge organic matter is resistant to degradation. About 23-26% of the total organic matter from anaerobically digested sewage sludge degraded in a five month incubation period in a column study (Karapanagiotis et al., 1991). Hohla et al. (1978) applied sludge for six years and concluded that 60% of the organic carbon had decomposed during that period. Lime-stabilized sludge appears to be more resistant to decomposition, probably due to a reduction in microbial activity as a result of increased sludge pH (Morel and

Guckert, 1983).

The stable fraction of the soil organic matter that remains after the major portion of residues have decomposed is humus. Humus plays an important role in the retention of heavy metals. The surface area and cation exchange capacity (at high pH) of humus colloids generally exceeds that of silicate clays. Humus buffers plant availability of trace elements through chelation, forming stable complexes with Cu^{2+} and other polyvalent ions (Bohn et al., 1985). Koskella (1983) compared the contribution of 0, 50, and 100 dry ton sludge ha^{-1} to the humus content of a sandy clay soil. After seven years, the soil humus content was 124.0, 140.9, and 151.4 g kg^{-1}, respectively, for the 0, 50, and 100 dry ton rates.

The long-term effect of organic matter decomposition on metal availability in sludge-amended soils has been debated. Beckett and Davis (1979), in what is known as the 'time bomb theory', speculate that even if pH is maintained at an acceptable level, availability of sludge applied metals will increase as sludge-supplied organic matter decomposes. Research has shown that heavy metals revert to an unavailable form over time (Chaney, 1973), although this reversion has not been universally demonstrated in sludge-amended soil (Smith, 1996). Metal availability does not increase over time if soil pH is held constant (Smith, 1996).

Cation Exchange Capacity

The cation exchange capacity (CEC) is the sum total of exchangeable cations that a soil can adsorb. The negative charges responsible for cation exchange arise from the dissociation of H^+ from functional groups of organic matter, isomorphous substitution in layer silicate minerals, and deprotonation of both hydroxyl groups on mineral edges and exposed AlOH groups (Sparks, 1995). It is not a fixed quantity because it is dependent on

soil pH, ionic strength, and the specific ions involved. Cation exchange capacity increases with an increase in soil pH due to ionization of hydroxyl groups on clay edges and hydrous Al and Fe oxides and dissociation of functional groups in organic matter (Sparks, 1995).

Cation exchange capacity is one of the soil properties that influence the retention and toxicity of heavy metals in sludge-amended soils (Smith, 1996).The strength of the link between CEC and metal bioavailability has been debated. Latteral et al. (1975) examined sludge-borne metal uptake by soybeans as a function of soil CEC and noticed no difference in the uptake of Cd, Cr, Cu, Pb, and Zn with an increase in CEC. King (1988) evaluated metal retention by several soils of the Southeastern United States. He concluded that Fe oxides and clay content would be better parameters than CEC for deciding metal limitations in southeastern soils. Korcak and Fanning (1985) investigated heavy metal availability as a function of soil type and reached the conclusion that low CEC soils were as suitable as high CEC soils for sludge application. Chang et al. (1983) observed a relationship between soil CEC and the retention and plant uptake of metals . Previous U.S. sludge regulations established heavy metal limits that were based on soil CEC (USEPA, 1983). The cumulative loading rates for Cu at a soil $pH \geq 6.5$, were as follows: CEC < 5: 140 kg ha $^{-1}$; CEC 5 to 15: 280 kg ha $^{-1}$; and CEC > 15: 560 kg ha $^{-1}$. Use of CEC for metal limitations was abandoned in the 503 Regulations (U.S.E.P.A., 1993).

Phosphorus Levels

The concentration of P in sludge is much higher than in other organic materials (Byrom and Bradshaw, 1991). The ratio of organic matter to P is very narrow in sludge (10:1) in comparison to cow slurry (100:1) and other organic fertilizers (Furrer and Stauffer, 1983). During wastewater treatment, $FeCl_3$ or $Al_2(SO_4)_3$ is added to precipitate P, increasing sludge P concentration (Peterson et al., 1994). The P content of sludge and sludge composts ranges from 10 to 40 g kg^{-1} (Epstein et al., 1976), with an average of 22

g kg $^{-1}$ in dry sludge solids (Smith, 1996). One hundred m^3 of sludge with 3% solids contains approximately 68 kg of P (Peterson et al., 1994).

Sludge contains both organic and inorganic forms of P. Sources of organic P include microbial tissue, plant residues, and metabolic by-products of living organisms (Loehr et al., 1979). Inorganic phosphates come from detergent residues and fertilizers. Organic forms of P predominate and are slowly mineralized in the soil (Loehr et al., 1979).

Sewage sludge often contains similar amounts of available N and total P (Peterson et al., 1994). In Virginia, the average P content of sludge is almost double that of available N content (Simpson et al., 1984). Sludge application rates are usually based on the next crop's requirement for available N (Smith, 1996). The N requirement for corn grain (for a yield of 8780 kg ha $^{-1}$) is 179 to 202 kg ha $^{-1}$ (Simpson et al., 1984). The recommended P amendment for corn grain in a soil testing low for P is 90 to 134 kg ha $^{-1}$; for a soil with a high P level, only 22 to 45 kg P ha $^{-1}$ are recommended (Donohue and Heckendorn, 1994b). Therefore P is applied in excess of crop needs and accumulation occurs at normal sludge application rates (Peterson et al., 1994). Furrer and Gupta (1985) applied a heavy rate of sewage sludge, which supplied a mean annual P rate of 329.4 kg ha $^{-1}$, for a 8-year period to a silty clay loam which was in a corn-wheat (*Triticum aestivum* L.)-clovergrass (*Trifolium* species) rotation. This application rate led to a serious P accumulation in soil, i.e., approximately 86% of the applied P was not taken up by the crops.

The major environmental concern with sludge applied P is eutrophication in surface waters from erosion of soil P. Downward movement of P is restricted by reactions with soil, therefore leaching of P is unlikely to cause groundwater pollution (Peterson et al., 1994). If sludge P rates were limited to crop removal (approximately 33 kg P ha $^{-1}$), eight times more acreage would be required for sludge application (Peterson et al., 1994).

Studies have shown that excess sludge applied P does not adversely affect crop yield or composition (Corey, 1992; Peterson et al., 1994). The (Al + Fe) to P ratio in sludge affects P solubility and therefore the P concentration in crops (Peterson et al., 1994). Corey (1992) investigated the effect of (Al + Fe) to P ratio of sludge on P concentration in soybeans. It was observed that the higher the (Al + Fe) to P ratio, the lower the P concentration was in plant tissue, which was attributed to precipitation of the P by Al and Fe. The P-induced Zn deficiency that normally occurs at high P levels is not a problem with sludge application, since sludge supplies Zn (Peterson et al., 1994).

Phosphorus in the soil is rendered relatively insoluble by a variety of fixation and precipitation reactions (Sanyal and DeDatta, 1991). The species of P is influenced by soil pH as follows (Lindsay and Moreno, 1960): at pH 2.0-6.5 $H_2PO_4^-$ is dominant, at pH 6.5-12.5 HPO_4^{2-} predominates, and at pH > 12.5 PO_4^{3-} is dominate. In very acid conditions, Fe, Al, and Mn are very soluble and react with $H_2PO_4^-$, forming an insoluble precipitate (Lindsay and Moreno, 1960). The ion also reacts with Fe and Al oxides and hydroxides in acid soils and is fixed into unavailable form (Brady, 1990). Under moderately acid conditions, phosphates are also fixed by kaolinite. Precipitation of insoluble calcium phosphates occurs in the alkaline range. The availability of P for crop uptake and leaching is at a maximum between pH 6 and 7 (Brady, 1990). Phosphorus availability decreases over time with sorption, i.e., adsorbed P penetrates by diffusion into calcium carbonate and Fe and Al oxides, leading to further adsorption of P (Sanyal and De Datta, 1991). Formation of the most insoluble P compounds does not occur with continuous sludge application, therefore resting periods between applications will increase P retention (Loehr et al, 1979).

Soluble Salts

A large amount of wastewater salts are removed with the effluent, therefore soluble salt levels in sludge are usually low (Stewart and Meek, 1977). The salt content of sludges varies and is affected by dilution with water. The simplest way to determine the soluble salts content of sludge is to measure the electrical conductivity of the sludge mixture. Salt content can also be determined by analysis of the sludge constituents. The sum of Ca, K, Mg, and Na is approximately half of the total salt content (Stewart and Meek, 1977). Vlamis and Williams (1971) analyzed sewage sludge in Georgia and found it contained the following (g kg $^{-1}$ dry weight): Na (3.9), K (7.4), Ca (34.3), and Mg (6.4). Cavallaro et al., 1993) analyzed two batches of a Puerto Rican municipal sludge and reported the following range (g kg $^{-1}$):0.9 to 1.6 Na, 1.3 to 3.6 K, 15.0 to 42.6 Ca, and 3.7 to 5.2 Mg.

Even though sludge salt content is usually low, high applications of sludge can increase soil salinity to a level detrimental to plants. Sludge application rates exceeding 80 mt ha $^{-1}$ can adversely affect salinity-sensitive crops (Epstein et al., 1976). Epstein et al. (1976) applied sludge at rates ranging from 40 to 240 mt ha $^{-1}$. The electrical conductivity of the soil was 2.5, 4.7, 5.2, and 5.5 dS m $^{-1}$, respectively, at sludge rates of 40, 80, 160, and 240 mt ha $^{-1}$. Plant growth can be adversely affected at EC values above 2 dS m $^{-1}$ (Bernstein, 1964).

The salinity hazards encountered most often in waste application to cropland are excess total salts and high Na levels (Stewart and Meek, 1977). Water availability is decreased if excess soluble salts are present in soil (Keeney and Wildung, 1977). The free energy of soil solution water is lowered under high salinity conditions, making it difficult for plant roots to extract soil water (McBride, 1994). Excess Na has a detrimental effect on soil structure and decreases infiltration (Keeney and Wildung, 1977). Sodium disperses

clays and organic colloids, which clog soil pores and reduce percolation (McBride, 1994).
Poor structure in dispersed soils can result in surface crusting, cementation, and soil
erosion (McBride, 1994). There is generally a good balance between Ca, K, Mg, and Na
in organic wastes, therefore the primary hazard in soil application of these wastes is total
salts rather than Na (Stewart and Meek, 1977).

Crop germination and growth can be adversely affected by excess total salts, therefore
root zone salinity should be a consideration in crop selection (Stewart and Meek, 1977;
Guidi et al., 1983).The major root activity of row crops occurs below the furrow, which is
less saline than soil surfaces (Richards, 1969). In general, crop responses to salinity at the
following soil EC values (dS m $^{-1}$ at 25° C) are: 0 to 2: effects are negligible; 2 to 4: yields
of sensitive crops are restricted; 4 to 8: yields of many crops are restricted; 8 to 16: only
salt tolerant crops have satisfactory yields; and >16: only a few very salt tolerant crops
have satisfactory yields (Bernstein,1964). Salt sensitive crops include beans (*Phaseolus
vulgaris* L.), lettuce (*Lactuca sativa* L.), and onions (*Allium sepa* L.) (Bernstein, 1964).
Barley (*Hordeum vulgare* L.), cotton (*Gossypium hirsutem*), and bermudagrass (*Cynodon
dactylon* L.) are very salt tolerant (Bernstein, 1964). Some crops such as sugarbeet (*Beta
vulgaris* L.) are very tolerant of salts in their later growth stages, but are very sensitive at
germination (Bernstein, 1964).

Symptoms of salt toxicity were accompanied by a reduction in growth and shoot N in
soybeans (*Glycine max* L.) grown with sludge application rates above 200 mt ha $^{-1}$ (Abd
El-Hay, and Angle, 1994). Maas and Hoffman (1977) reported that grain corn yields begin
to decline at a salinity threshold level of 1.7 dS m $^{-1}$, with a 12% yield decrease for each
unit increase in salinity beyond the threshold. Salinity effects on corn and sorghum yields
as reported by Stewart and Meek (1977) and adapted from research by Bernstein (1964)
are as follows:

Table 1. Approximate effect of salinity on corn and sorghum yields (Bernstein, 1964).

	Salinity EC	
Yield Reduction	Corn	Sorghum
%	-------------------------dS m^{-1} ----------------------	
10	5.5	6.0
25	6.1	9.0
50	7.2	12.2

Plants grown under high salt conditions may be stunted with a noticeable blue green coloration (Richards, 1969). The color is a result of a waxy coating on leaf surfaces and an increase in leaf chlorophyll content (Richards, 1969). Symptoms such as necrosis, tipburn, and firing of the margins are visible on some salt-affected plant species (Richards, 1969).

Soluble salts leach from sludge over time. The most hazardous salts, Na and K, are very soluble and readily leached (Stewart and Meek, 1977). However, a portion of the salts in sludge is not initially soluble and is released later during decomposition. A rise in salinity occurs during decomposition, as Ca and Mg are released and organic N is converted to inorganic forms (Stewart and Meek, 1977).

The basic principles of salinity management should be applied when amending cropland with sludge. One of the most important considerations is soil texture. Increases in salt levels influence the electrical conductivity (EC) of sandy soils more than that of clay soils. Stewart and Meek (1977) reported that the application of 30 mt ha $^{-1}$ of waste containing 7.5% salt would result in an EC value of 3 dS m $^{-1}$ in a fine textured soil and an EC value of 6 dS m $^{-1}$ in a sandy soil. Salinity buildup in clay soils is greater though, because salts leach more easily from sandy soils. The initial salt content of soils with very low infiltration rates is high. If a soil has a restrictive surface layer, addition of organic wastes

can improve the infiltration rate, counteracting some of the salinity. Under nonirrigated conditions, an annual application of 40 mt ha $^{-1}$ of organic wastes can be made without salinity buildup, if 10 cm yr $^{-1}$ of water moves through the soil profile (Stewart and Meek, 1977). Most of the eastern United States has > 10 cm yr $^{-1}$ of leaching water, therefore salt buildup is unlikely to occur unless waste application rates are high (Stewart and Meek, 1977).

Stewart and Meek (1977) developed the following guidelines for the prevention of salinity problems from organic waste application:
1) Determine soluble salt content of wastes prior to application.
2) Apply wastes prior to seeding to allow for leaching of salts.
3) Apply wastes at rates that do not exceed the nutrient needs of the crop.

The objectives of the research presented in this chapter are:

1. To determine long-term effects of sludge application on organic matter content,

2. To ascertain changes in CEC over time following sludge amendment,

3. To determine the long-term contribution of sludge application to soil P levels, and

4. To determine long-term soluble salts levels following sludge application.

MATERIALS AND METHODS

Long-term field experiments were initiated on four research sites in 1984 to determine metal availability in sludge-amended soils. Initial research was conducted by Dr. B.D. Rappaport at Virginia Polytechnic Institute and State University. Experimental results from this research are reported in his dissertation entitled "Availability and Distribution of Heavy Metals From Sewage Sludge in the Plant-Soil Continuum" (Rappaport, 1986). Rappaport's research findings were published (Rappaport et al., 1987, 1988) and are discussed in Chapters 2 and 3 of this research dissertation. Residual research on the site was conducted by the author from 1992 through 1995. Comparisons are made between chemical properties determined by Rappaport (initial field experiment) and by the author (residual field experiment).

Site Characteristics

The site is located on the Northern Piedmont Agricultural Research and Extension Center in Orange, Virginia.The experiment is located at the latitude longitude coordinates of 38 14 43N - 078 06 40W (Abate, 1991) and at an elevation of 157 m (Donohue et al., 1984). The site lies in the Piedmont physiographic region - an area of land approximately one thousand miles long with a north to south orientation. The geology of this region is characterized by a peneplain landscape underlain by deep saprolite formed from largely metamorphosed Paleozoic and Precambrian rock. Most of the soils in this region are residual, i.e., formed in place by the mixing of saprolite and organic matter.

The climate of the Piedmont physiographic region is fairly homogeneous. The growing season in the Piedmont, south of New Jersey, averages at least 180 frost-free days per year, with an average temperature of 21° to 27°C. The growing season for corn in the Piedmont runs from late April to late September. The length of the growing season at the Northern Piedmont Agricultural Research and Extension Center is 189 days (Donohue et al., 1984). Over the long term, precipitation is not a limiting factor for plant growth, averaging between 100 to 125 cm per year (Godfrey, 1980). Fifty-five to 60 % of that precipitation falls during the growing season. Mean annual precipitation and average monthly temperatures during the growing season at the Northern Piedmont Agricultural Research and Extension Center from 1961 to 1990 were reported by S.T. Reed (1993). The mean annual precipitation during the growing season for the 30 year period was 59.2 cm. Average daily maximum and minimum temperatures during the growing season ranged from a maximum of 19°C in April to 30° C in July and and a minimum of 5.8° C in April to 18.3°C in July. Climatological observations at the Northern Piedmont Agricultural Research and Extension Center for this research period are reported in Tables 2- 4.

Table 2. Precipitation (rainfall and melted snow in cm) at the Northern Piedmont Agricultural Research and Extension Center for the years 1992 through 1995.

	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec
1992	4.1	6.2	8.1	6.7	13.6	12.3	6.9	7.0	10.2	3.3	14.4	13.3
1993	9.4	6.6	21.3	11.2	8.8	5.6	5.5	8.8	6.2	5.7	16.2	9.4
1994	10.6	11.7	20.8	5.0	2.2	4.7	23.8	11.4	9.3	3.4	3.8	4.9
1995	10.5	3.6	6.4	3.7	12.2	29.2	11.5	1.2	8.9	15.7	10.3	5.6

Table 3. Mean daily maximum temperatures (°C) at the Northern Piedmont Agricultural Research and Extension Center for the years 1992 through 1995.

	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec
1992	7.8	9.8	11.3	19.1	20.9	25.1	29.8	26.7	24.2	18.2	12.3	7.4
1993	7.9	6.8	9.1	17.9	24.4	28.2	31.8	29.8	31.8	19.3	13.8	7.0
1994	2.7	7.9	13.1	22.8	22.8	30.2	29.7	27.4	24.7	19.1	16.1	10.2
1995	6.6	5.5	14.8	18.4	21.7	26.6	31.3	30.6	25.2	21.6	10.4	6.2

Table 4. Mean daily minimum temperatures (° C) at the Northern Piedmont Agricultural Research and Extension Center for the years 1992 through 1995.

	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec
1992	-2.9	-1.6	0.7	6.4	10.3	14.5	19.6	16.3	14.0	5.7	3.4	-1.4
1993	-1.7	-3.6	-0.3	5.7	12.3	16.1	20.1	18.3	14.9	6.2	2.6	-2.4
1994	-6.4	-2.6	1.2	7.8	9.7	17.9	19.3	16.4	12.6	4.6	4.0	-0.2
1995	-2.4	-5.4	1.4	4.6	10.9	16.8	19.6	19.3	14.0	8.1	-0.1	-4.4

Soil

The field plots were located on a Davidson clay loam (clayey, kaolinitic, thermic, Rhodic Kandiudults). This is a highly weathered soil formed from greenstone rocks on uplands in the Piedmont. Profile characteristics vary among the phases of the Davidson series. The following profile description is typical for a Davidson clay loam, ranging from 2 to 15% slope (Carter et al., 1967; USDA, 1985). Soils of the Davidson series are deep and well drained, with a root zone extending to a depth of approximately 1.52 m. Natural fertility is medium and organic matter content is moderate (20 to 30 g kg $^{-1}$). The Davidson

soil is commonly medium acid (5.6 to 6.0) to strongly acid (5.1 to 5.5) throughout. Permeability is moderate -1.5 to 5.0 cm hr^{-1}. The available water capacity is moderate - approximately 15 to 23 cm for a 1.52 m soil profile. The typical surface horizon of a Davidson clay loam is a reddish-brown to dark reddish brown clay loam, averaging 10 cm thick. The subsoil is a dark red clay up to 254 cm thick.

The Davidson series soil is well suited for crop production when limed and fertilized according to soil tests and has been rated above average in yield (Donohue and Hawkins, 1979). The Virginia Land Use Evaluation System (VALUES), which employs water quality oriented nutrient management, places this soil in Soil Management Group N (Donohue and Heckendorn, 1994b), with a realistic corn grain yield of 8150 kg ha^{-1}.

Initial Field Experiment

A single application of aerobically digested sewage sludge was applied in 1984. Sewage sludge for field experimentation was obtained from a wastewater treatment plant in Bristol, Va which received major industrial inputs. The water content of the sludge (105° C) was 370 g H$_2$O kg^{-1}. The sludge contained 16.0 g organic N, < 8 mg inorganic N, 31.7 g P, 1.1 g K, 21.5 mg Cd, 3654 mg Cu, 206 mg Ni, and 2982 mg Zn kg^{-1} on a dry weight basis. The pH of the sludge was 6.2.

Soil samples were taken from the 0- to15-cm layer of each plot prior to sludge application. The samples were air dried and ground to pass a 2-mm sieve. Soil pH was determined in a 1:1 soil/water suspension after a 1 hour equilibration period (McLean, 1982). A pipet method (Day, 1965) was used to determine particle size distribution. Cation exchange capacity (CEC) was measured by Ca saturation with subsequent displacement by Mg in acetate solutions buffered at pH 7.0 (Rich, 1961). Tamm's solution

(0.1 M oxalic acid and 0.175 M ammonium oxalate, pH 3.25) was used to extract noncrystalline and crystalline Al, Fe, and Mn under ultraviolet light as described by Samprath (1980). Aluminum, Fe, and Mn were determined by atomic absorption spectrophotometry. Mineralogical analyses were performed with clay fraction separation as described by Jackson (1979) and x-ray diffraction analysis.

Chemical and physical properties of the soil prior to sludge application were as follows (Rappaport et al., 1988).The particle size distribution was 15.3% sand, 47.1% silt, and 37.6% clay. The soil contained high levels of crystalline and noncrystalline Al, Fe, and Mn - 2430, 9070, and 80 mg kg $^{-1}$, respectively. The mineralogy of the Ap horizon was dominated by kaolinite . The mineral suite contained 68% kaolinite, 14% hydroxy interlayered vermiculite, 5% both montmorillonite and regularly interstratified mineral, 3% quartz, 2% both mica and feldspar, and 1% gibbsite. The pH of the soil was 6.3, considerably above the native pH of the Davidson series (Carter et al., 1967). The level of organic matter (18 g kg $^{-1}$) was medium for Virginia soils (Donohue and Heckendorn, 1994b). The cation exchange capacity was 12.5 cmol kg $^{-1}$.

Sewage sludge was incorporated to a 20 cm depth at rates ranging from 0 to 210 mt ha $^{-1}$, i.e., from 0 to 760 kg Cu ha $^{-1}$ (Table 5). The treatments were applied in quadruplicate in a randomized complete block design. Controlled lateral flow plots were constructed to isolate the soil volume of each plot in the following manner: a 20 cm wide ditch was excavated to a 0.9 m depth, aluminum flashing was placed around the plots, and the soil blocks were wrapped with 254 um polyethylene film, which was cut 20 cm above the soil and wrapped over the aluminum flashing. The controlled lateral flow plots measured 2.3 X 1.5 m and were 0.9m deep.

Table 5. Amounts of heavy metals applied to soil from sewage sludge application
(Rappaport et al., 1988).

Dry sludge application	Cd	Cu	Ni	Zn
Mt ha $^{-1}$	---------------------------------- kg ha $^{-1}$ ----------------------------------			
0	-----	-----	-----	-----
42	0.9	153	8.6	125
84	1.8	304	17.2	248
126	2.7	456	25.8	372
168	3.6	608	34.4	496
210	4.5	760	43.0	620

"Pioneer 3192" corn was planted in the spring of 1984 and grown at a population of 57,300 plants ha $^{-1}$. The control treatment received 200 kg N ha $^{-1}$ as NH_4NO_3 and 20 kg P ha $^{-1}$ as triple superphosphate. All treatments received 55 kg K ha $^{-1}$ as muriate of potash.

Residual Field Experiment

No further sludge was applied on the plots. "Pioneer 3136" corn was planted from 1991 through 1995. In 1994, drought (Table 2) caused crop failure and corn was replaced by a more drought tolerant crop, i.e., by "Softened Dekalb 41 Y" sorghum. The experimental area received an annual application of 1.12 t ha $^{-1}$ of 16-8-8 fertilizer prior to planting. A sidedressing of N was applied when necessary. Lime was applied in 1989 to raise pH levels, but not thereafter.

Soil samples were collected from the Ap horizon (0 to 15 cm) of each plot. Soil pH was determined in water with a 1:1 soil/solution ratio after an equilibration period of 15 minutes to 2 hours (Donohue and Heckendorn, 1994a). Soil organic matter was determined by a modified Walkley-Black method (Donohue and Heckendorn, 1994a; Walkley and Black, 1934). Phosphorus was extracted with Mehlich No. 1 extractant (0.05N HCl in 0.025N H$_2$SO$_4$) and analysed by an ICP (inductively coupled plasma spectrometer) procedure (Donohue and Heckendorn, 1994a). Soil CEC was measured by atomic absorption spectrometry after saturation with 0.5 M Ca acetate (pH 7.0) followed by displacement with 0.5 M Mg acetate (pH 7.0) (Rich, 1961). Soluble salts were determined by electical conductivity measurements in a 1:2 soil/water suspensions (Donohue and Heckendorn, 1994a).

Soil organic matter, cation exchange capacity, Mehlich-1 extractable P, and soluble salts data were evaluated by analyses of variance and by the least significant difference (LSD) test (Steele and Torrie,1980). The 0.05 level of probability was chosen for these statistical techniques. The relationship between organic matter and cation exchange capacity was determined by Pearson correlation coefficients.

RESULTS AND DISCUSSION

Soil pH

The pH of the soil prior to sludge application in 1984 was 6.3 (Rappaport et al., 1988) and was limed prior to planting to bring it to the USEPA recommended level of ≥ 6.5 at that time for sludge-amended soils (USEPA, 1983). By early corn silk in 1984, the pH had dropped (Table 6) and continued to drop until lime was applied in 1989. No further amendments were used to adjust soil pH and the soil became more acidic.

Soil pH values in 1995 were much lower than in 1994 and unusually low for a Davidson series soil (Table 6). The 1995 pH analysis was repeated with the same methodology, with no more than 0.1 difference in pH units between any of the readings in the two analyses (Table 7). A salt effect was suspected as the reason for the unusually low pH. Soil pH can decrease more than 1 unit with an increase in salt concentration (McLean and Brown, 1984). Salt concentrations affect soil pH through cation exchange. Cations of salts displace H ions and exchangeable Al. There is an increase in H ions in solution upon hydrolysis of the displaced Al, resulting in a lower pH (McLean, 1982). Possible sources of salts in soil include fertilizer residues and microbial decomposition of organic matter.

Normally leaching prevents salt accumulation in humid areas, but a temporary salt buildup could occur during a period of limited rainfall. The soil was leached with 125 ml of distilled water prior to pH determination and levels were 0.4 to 0.5 units higher in the leached soil (not shown). Leaching of soil prior to pH determination is not a

recommended practice; however the use of $0.01M$ $CaCl_2$ has been recommended for pH determination of soils with salt content (Schofield and Taylor, 1955; Woodruff, 1967). The substitution of 0.01 M $CaCl_2$ for distilled water masks differences in salt concentration without displacing large amounts of H or Al ions (McLean, 1982). Determination of pH was repeated, using the original method except for the substitution of 0.01 M $CaCl_2$ for distilled water. The pH levels were 0.3 to 0.5 units lower than those obtained with distilled water (Table 7). The lower pH was expected as studies have shown that 0.01 M $CaCl_2$ pH measurements are 0.4 to 0.6 units lower than those measured in water (McLean and Brown, 1984).

Table 6. Soil pH in the sludge-amended soil experiment from 1984 to 1995.

Sludge Rate	Soil pH						
Mt ha $^{-1}$	1984	1988	1989	1992	1993	1994	1995
0	5.7b*	5.4b	5.8b	5.3b	5.4c	5.3b	4.4b
42	6.0a	5.7a	6.2a	5.4ab	5.7b	5.6a	4.9a
84	5.8ab	5.8a	6.0ab	5.4ab	5.8ab	5.6a	4.8a
126	5.9a	5.7a	6.2a	5.6a	5.9a	5.7a	4.9a
168	5.9a	5.8a	6.2a	5.5a	5.8ab	5.7a	4.9a
210	5.9a	5.8a	6.1a	5.5a	5.8ab	5.7a	4.9a

* Column means followed by different letters are significantly different at the 0.05 probability level.

Table 7. Comparison of 1995 soil pH readings for the sludge-amended experiment with different methods.

Sludge Rate	Soil pH		
Mt ha $^{-1}$	Initial/ distilled H_2O	Repeat/ distilled H_2O	Repeat/0.01 M $CaCl_2$
0	4.4	4.5	4.2
42	4.9	4.9	4.4
84	4.8	4.8	4.4
126	4.9	4.9	4.4
168	4.9	4.9	4.5
210	4.9	4.9	4.5

In every year, soil pH in the control treatment was lower than in the sludge treatments (Table 6). This suggests that sludge amendment had an effect on soil pH. The increased organic matter would have increased the buffering capacity of the sludge-amended soils, therefore lime should have had more of an effect on the control soils. A lower pH in the sludge treatments was expected since organic acids produced during organic matter decomposition and nitrification acidify the soil. The pH of the sludge (6.2) was probably not high enough to have a long-term effect on soil pH; however, if the sludge contained high amounts of bases the overall effect could be an increase in soil pH (Coker, 1978).

Organic Matter Content

Soil organic matter increased with sludge application rate (Table 8). Soil organic matter also increased in a 20-year study in which a cumulative total of 224 mt sludge ha $^{-1}$ was applied to soil cropped with corn (Clapp et al., 1994). Soil organic matter levels were 5 to 14 g kg $^{-1}$ higher in their sludge treatments than in the control treatment. In this study,

levels at the highest sludge rate were 17 to 21 g kg^{-1} higher than in the control.

Table 8. Long-term effect of sludge application on soil organic matter.

Dry Sludge Application	Soil Organic Matter			
	1992	1993	1994	1995
Mt ha^{-1}	-------------------------- g kg^{-1} --------------------------			
0	22.3d*	21.0c	23.5e	23.0d
42	24.5d	24.3c	28.0de	25.0d
84	28.3c	28.0b	31.8cd	29.3c
126	33.3b	29.3b	36.3bc	32.3bc
168	37.5a	35.3a	39.0ab	36.0ab
210	40.0a	38.0a	43.8a	39.0a

* Column means followed by different letters are significantly different at the 0.05
  probability level.

Soil test calibrations for organic matter were as follows: low: 0 to 9; medium: 10 to 19;
high: 20 to 29; and very high: >29 g kg^{-1} (Donohue and Heckendorn, 1994b). Organic
matter levels were very high at sludge rates of 126 to 210 mt ha^{-1}. The organic matter
was in the high range for the control and 42 Mt sludge ha^{-1} treatments and bordered
between high and very high for the 84 Mt ha^{-1} sludge treatment.

Cation Exchange Capacity

Soil CEC was measured in 1995 to determine the long-term effect of sludge
application on residual CEC. The CEC method used by Rapppaport (Rich, 1961) was
chosen for comparison purposes. Except at the highest sludge rate, CEC values were
below the 12.5 cmol kg^{-1} reported by Rappaport for CEC prior to sludge application

(Table 9). Differences in technique, pH, and sample could be responsible for the variation between 1984 and 1995 CEC values. Determination of CEC in acid soils is complicated by their variable charge and the high amount of Al-hydroxy cations, which are difficult to exchange (Rhoades, 1982). The method of Gillman (1979), recommended for acid soils, would have been a more appropriate method for measuring both initial and long-term CEC. In Gillman's method, unbuffered solutions are used throughout to ensure that the natural pH of the soil is not altered. This provides a better estimate of the exchange capacity of the variable charged matrices in highly weathered soils (Rhoades, 1982). The pH of the soil at the time Rappaport measured CEC was 6.3, considerably above the pH values of the 1995 soil (Table 6). Gilman's method would have provided a better comparison between initial and residual CEC, however, the method by Rich (1961) probably was required for CEC determination when CEC was included in the USEPA guidelines for sludge application.

Table 9. Long-term effect of sludge application on residual soil cation exchange capacity.

Dry Sludge Application	Soil Cation Exchange Capacity
Mt ha $^{-1}$	cmol kg $^{-1}$
0	10.4d*
42	10.6cd
84	11.2bcd
126	11.8bc
168	12.2ab
210	13.2a

* Column means followed by different letters are significantly different at the 0.05 probability level.

The CEC increased with level of sludge application (Table 9). Epstein et al. (1976) observed a similar trend in a study in which they applied sludge at the rates of 40 and 240 mt ha^{-1} on an Aquic Hapludult soil. The CEC at their highest sludge rate increased almost threefold (from 5.5 to 15.4 cmol kg^{-1}) in one month. It decreased to 8.7 cmol kg^{-1} within two years, but remained higher than in the control. The increase in CEC was attributed to the increase in organic matter supplied by the sludge. Soil CEC increased in proportion to the amount of organic-C remaining in the soil after termination of sludge applications when 232.5 mt sludge ha^{-1} were applied over a five year period (Hinesly et al., 1979). The coefficient of correlation between CEC and soil organic-C concentrations in their study was r = 0.78. A positive correlation (r = 0.69, P = 0.0002) was also observed between CEC and organic matter in this study.

The clay complex of soils that are dominated by kaolinite, such as the soil under study, has a low CEC, ranging between 5 and 20 cmol kg^{-1}. Most of the CEC in this soil arises from negative charges in kaolinite, organic matter, and hydous oxides of Fe and Al. The total negative charge and the percentage that is pH dependent, respectively, in colloids is as follows: kaolinite (7 cmol kg^{-1}, 57%); organic colloids (240 cmol kg^{-1}, 75%), gibbsite (6 cmol kg^{-1}, 100%); and goethite (4 cmol kg^{-1}, 100%) (Brady, 1990). This variable, pH dependent charge, is generally high at high pH and low at low pH.

Phosphorus Levels

The sludge contained 31.7 g P kg^{-1} on a dry weight basis, supplying the soil with up to 6657 kg P ha^{-1} (Table 10). Available P was extracted from the soil with a mixture of dilute HCl and H_2SO_4 - a method developed by Nelson et al. (1953) and referred to as the Mehlich -1 method. The mixed acids are effective for extracting P from soils which fix P strongly and the results correlate well with plant response (Olsen and Sommers, 1982). Soil test P levels were calibrated as follows: Low - 0 to 6 , Medium - 6 to 18, High - 18 to

55, and Very High - >55 mg kg $^{-1}$ (Donohue and Heckendorn, 1994b). All sludge amended plots had P levels in the High to Very High range, compared to the control which remained in the Medium to Medium High range (Table 10). Fertilizer recommendations for grain corn based on calibrations for the Mehlich-1 procedure are as follows: Low- 39 to 59, Medium- 20 to 39, High- 10 to 20, and Very High - 0 kg P ha $^{-1}$ (Donohue and Heckendorn, 1994b).

Extractable P increased with level of sludge application (Table 10). This increase has also been observed with a variety of different P extractants. Cavallaro et al. (1993) observed that dilute acid-flouride extractable P increased by 2 to 19% when sludge P was added to an Ultisol. Bray-extractable P increased from 10 mg kg $^{-1}$ in a control treatment to 253 mg kg^{-1} in a 240 mt sludge ha^{-1} treatment in a study by Epstein et al. (1976). In a fractionation study by Chang et al. (1983) the concentration of soil P in every chemical fraction increased with sludge addition.

Table 10. Long-term effect of sludge application on Mehlich-1 extractable soil P levels.

		Mehlich-1 extractable soil P			
Sludge Rate	Sludge Applied P	1992	1993	1994	1995
Mt ha $^{-1}$	kg ha $^{-1}$	----------------------- mg kg $^{-1}$ -----------------------			
0	0.0	17.1f*	25.4e	20.1f	23.1f
42	1331.4	27.4e	35.6e	37.3e	33.6e
84	2662.8	41.9d	53.6d	61.2d	49.4d
126	3994.2	63.5c	68.6c	79.3c	68.4c
168	5325.6	73.9b	89.9b	101.5b	78.3b
210	6657.0	91.9a	112.5a	115.0a	92.7a

* Column means followed by different letters are significantly different at the 0.05

The availability of sludge P is high, even in soils with high P-fixing capacity (McLaughlin and Champion, 1987). The higher availability of P in the sludge-amended soil is attributed to its higher organic matter content (Table 8). The increase in P availability from the decomposition of organic matter has been explained by replacement of phosphate on exchange sites by organic anions and by the reduced P-fixing capacity of soils in which sesquioxide particles have been coated by humus (Nagarajah et al., 1970; Lopez-Hernandez et al., 1986; Hue, 1991). Certain organic anions form stable complexes with Fe and Al and are not easily displaced by other anions (Hue, 1991). The soil in this study contains high amounts of amorphous and crystalline Fe and Al (42,500 mg kg^{-1} Fe and 4,740 mg kg^{-1} Al), therefore organic anion complexes would be likely to form.

Corey (1992) applied 22.3 mt sludge ha^{-1} (3800 kg P ha^{-1}) on a clay soil with high P availability and reported no significant increase in the P concentration of corn ear leaf and grain and only a slight increase (8 g kg^{-1}) in the P content of sorghum-sudan (*Sorghum bicalor* L. Moench). Phosphorus concentrations in corn grain and stover were unaffected by applications of anaerobically digested sludge at rates supplying up to 1,600 kg N ha^{-1} (Soon et al., 1978).

It is doubtful there was much downward movement of sludge applied P for the Davidson soil under study. Robertson et al. (1982) applied 335 mt sludge ha^{-1} to an Ultisol , supplying 4,801 kg P ha^{-1}, and observed that the majority of P remained in the top 90 cm of the soil. King and Morris (1973) applied 40 cm of liquid sewage sludge to a sandy clay loam and concluded that water pollution from leaching of sludge P is unlikely. Their conclusion was supported by the absence of sludge treatment effect on the dilute acid extractable P content of the 15- to 45-cm layer of soil.

Soluble Salts

The soluble salt content of the applied sludge and of the soil during the initial field experiment was not determined. The sludge was on a drying bed for a long time prior to sludge application, therefore salt content should have been reduced. In the residual study, soluble salt levels were determined as part of an investigation into decreased crop yield on high-sludge treatments. The 10-year residual levels of soluble salts ranged from 64 to 115 mg kg^{-1}. These soil soluble salt contents are considerably below the level of 844 mg kg^{-1} which causes salt injury to field crops (Donohue and Heckendorn, 1994b), therefore reductions in plant growth and yields were not attributed to soluble salts.

Sludge rates, 10 years after application, did not affect soluble salt levels (Table 11). The control soil had salt levels similar to the sludge-amended soils, therfore salts present in all treatments can probably be attributed to salts supplied by fertilizer. Soluble salts were not higher in treatments amended with an average of 11 mt dry sludge ha^{-1} yr^{-1} than in control treatments by the end of the growing season (Clapp et al., 1994). Soil EC values (Table 11) were well below the 4 dS m^{-1} at which a soil is considered saline (Bohn et al., 1985) and the 6 dS m -1 at which a 10% reduction in corn and sorghum yields occurs (Stewart and Meek, 1977; Bernstein,1964).

It is likely that sludge-borne salts leached out of the root zone long before the soluble salt analysis was conducted. Guidi et al. (1983) investigated salinity increases from the addition of aerobic sludge, anaerobic sludge and composts of aerobic and anaerobic sludge. All treatments increased salinity and by the end of the growing season EC values had dropped considerably. Epstein et al. (1976) observed a considerable drop in EC values (from 5.5 to 3.9 dS m^{-1}) by the end of the next growing season in an Aquic Hapludult soil amended with 240 mt sludge ha^{-1}. By the end of the next growing season, the EC value had dropped to 1.5 dS m^{-1}. Rapid leaching of sludge-borne salts was

reported by Madariaga and Angle (1992). Sludge compost with an EC of 18 dS m^{-1} was applied to a sandy loam, which was then leached with distilled, demineralized water. The EC of the sludge compost/mixture dropped from 6 to less than 3 dS m^{-1} after the compost was completely saturated with water six times. Madariaga and Angle (1992) concluded that the majority of salts are leached from the crop root zone after it has rained once or twice. Abd El-Hay and Angle (1994) flushed soluble salts from a sludge-amended soil in an investigation on sludge-borne salt effects on soybeans. They concluded that adverse effects of salts can be reduced if rainfall or irrigation water remove root zone salts prior to planting.

Table 11. Ten-year residual effect of sludge application on soil salinity.

Sludge Application Rate	Soluble Salts	Salinity EC (25° C)
Mt ha^{-1}	mg kg^{-1}	dS m^{-1}
0	80.0a*	0.06
42	67.3a	0.05
84	70.5a	0.06
126	73.8a	0.06
168	73.8a	0.06
210	77.0a	0.06

* Column numbers followed by the same letter are not significantly different at the 0.05 probability level.

CONCLUSIONS

In this study, sludge application had long-term effects on soil organic matter, CEC, and Mehlich-1extractable P, but not on the soluble salt content of the soil. Soil organic matter levels increased with sludge rate, with levels in the high-sludge treatment almost double that of the control treatment. The CEC also increased with sludge rate and was attributed to the increase in organic matter supplied by the sludge. Mehlich-1 extractable P also increased with sludge rate and was attributed to high P availability from the decomposition of organic matter. Sludge rates did not affect the soluble salt levels, which were well below the level at which reduction in corn and sorghum yields occur.

The changes in chemical and physical properties of soil induced by sludge application should be considered in agricultural utilization of sludge. For the most part, the changes are beneficial for crop production; however careful management of sludge-amended soil is required. Soluble salt levels following sludge application should be determined prior to planting. Soil P levels should be monitored and the addition of fertilizers containing P should be avoided if soil test levels are satisfactory. Nutrient management on sludge-amended soils is more complicated because sludge is not a balanced fertilizer. Maintenance of an appropriate pH is important for control of heavy metal availability. Erosion control is very important to prevent surface runoff of sludge-supplied N, P, and heavy metals.

Sludge contribution of organic matter becomes more important as worldwide demand for cropland increases the utilization of soils with marginal productivity. Crop production

on productive soils can be limited by inadequate rainfall. One of the major factors determining crop yields on non-irrigated, well drained soils in Virginia is soil retention of plant accessible water (Donohue and Heckendorn, 1994b). The increase in plant available water from sludge organic matter application is advantageous, regardless of soil productivity.

REFERENCES

Abate, F.R. (ed.) 1991. Omni gazetteer of the United States. Vol. 3. Southeast. p. 697. Omnigraphics, Inc., Detroit, MI.

Abd El-Hay, G.H., and J.S. Angle. 1994. Sludge-borne salt effects on soybean growth. p. 185. *In*: C.E. Clapp et al. (ed.) Sewage sludge: Land utilization and the environment. Soil Sci. Soc. Am., Madison, WI.

Beckett, P.H.T., and R.D. Davis. 1979. The disposal of sewage sludge onto farmland: The scope of the problem of toxic elements. Water Pollution Control 78:419-445.

Bernstein, L. 1964. Salt tolerance of plants. USDA Agric. Inform. Bull. No. 283. 24p.

Bohn, H., B. McNeal, and G. O'Connor. 1985. Soil chemistry, 2nd ed., John Wiley and Sons, NY.

Brady, N.C. 1990. The nature and properties of soils, 10th Edition. MacMillan Publishing Co., NY.

Byrom, K.L. , and A.D. Bradshaw. 1991. The potential value of sewage sludge in land reclamation. p. 1-19. *In*: J.E. Hall (ed.) Alternative uses for sludge. Pergamon Press, New York, NY.

Carter, J.B., G.R. Epperson, and J.C. Estes. 1967. Soils of Orange County. Soil Conservation Service Report No. 9. Agronomy Dept., Virginia Polytechnic Inst. And State Univ., Blacksburg, VA.

Cavallaro, N., N. Padilla, and J. Villarrubia. 1993. Sewage sludge effects on chemical properties of acid soils. Soil Sci. 156:63-69.

Chaney, R.L. 1973. Crop and food chain effects of toxic elements in sludges and effluents. p. 129-141. *In*: Recycling municipal sludges and effluents on land. National Assoc. State Univ. and Land Grant Colleges, Washington, DC.

Chang, A.C., A.L. Page, F.H. Sutherland, and E. Gfgurevic. 1983. Fractionation of phosphorus in sludge-affected soils. J. Environ. Qual. 12:286-290.

Clapp, C.E., R.H. Dowdy, and D.R. Linden. 1994. Crop yields, nutrient uptake, soil and water quality during 20 years on the Rosemount sewage sludge watershed. p. 137-148. *In*: C.E. Clapp et al. (ed.) Sewage sludge: Land utilization and the environment. Soil Sci. Soc. Am., Madison, WI.

Coker, E.G. 1978. The utilization of liquid digested sludge. p.110-129. *In*: S.Berglund et al. (ed). Utilization of sewage sludge on land: Rates of application and long-term effects of metals. Oxford, UK.

Corey, R.B. 1992. Phosphorus regulations: Impact of sludge regulations. Crops Soils Newsletter 20:5-10.

Day, P.R. 1965. Particle fraction and particle-size analysis. In C.A. Black et al. (ed.) Methods of soil analysis. Part 1., Agronomy 9:545-567.

Donohue, S.J., R.L. Harrison, and H.E. White (ed.). 1984. A handbook of agronomy. Virginia Coop. Ext. Serv. Publ. 424-100, Blacksburg, VA.

Donohue, S.J., and G.W. Hawkins. 1979. Guide to computer progammed soil test recommendations in Virginia. Virginia Poly. Inst. And State Univ. Ext. Div. Pub. 834.

Donohue, S.J. and S.E. Heckendorn. 1994a. Laboratory procedures:Virginia Tech soil testing and plant analysis laboratory. Virginia Cooperative Ext. Pub. 452-881.

Donohue, S.J. and S.E. Heckendorn. 1994b. Soil test recommendations for Virginia. Virginia Cooperative Extension.

Epstein, E., J.M. Taylor, and R.L. Chaney. 1976. Effects of sewage sludge and sludge compost applied to soil on some soil physical and chemical properties. J. Environ. Qual. 5:422-426.

Furrer, O.J., and W. Stauffer. 1983. Influence of sewage sludge application on physical properties of soils and its contribution to the humus balance. p. 65-76. *In* :G. Catroux et al. (ed.) The influence of sewage sludge application on physical and biological properties of soils. D. Reidel Publishing Co., Boston, MA.

Furrer, O.J., and S.K. Gupta. 1985. Phosphate balance in long-term sewage sludge and pig slurry fertilized field experiment. p. 146-150. *In*: J.H. Williams et al. (ed.) Long-term effects of sewage sludge and farm slurries applications. Elsevier Applied Science Publishers, London.

Gillman, G.P. 1979. A proposed method for the measurement of exchange properties of highly weathered soils. Aust. J. Soil Res. 17:129-139.

Giusquiani, P.L., M. Pagliai, G. Gigliotti, D. Businelli, and A. Benetti. 1995. Urban waste

compost: Effects on physical, chemical, and biological soil properties. J. Environ. Qual. 24:175-182.

Godfrey, M.A. 1980. A Sierra club naturalist's guide to the Piedmont. Sierra Club Books, San Fransisco, CA.

Guidi, G. 1981. Relationships between organic matter of sewage sludge and physio-chemical properties of soil. p. 530-544. *In*: P. L'Hermite and H. Ott (ed.) Characterization, treatment and use of sewage sludge. D.Reidel Publishing Co., Boston, MA.

Guidi, G., and J.E. Hall. 1984. Effects of sewage sludge on the physical and chemical properties of soils. p. 295-306. *In*: P. L'Hermite and H. Ott (ed.) Processing and use of sewage sludge. D. Reidel Publishing Co., Boston, MA.

Guidi, G., M. Paglai, and m. Giachetti. 1983. Modifications of some physical and chemical soil properties following sludge and compost applications. p.122-127. *In*: G. Catroux et al. (ed.) The influence of sewage sludge application on physical and biological properties of soils. D. Reidel Publishing Co., Boston, MA.

Hall, J.E., and E.G. Coker. 1983. Some effects of sewage sludge on soil physical conditions and plant growth. p. 43-64. *In*: G. Catroux et al. (ed.) The influence of sewage sludge application on physical and biological properties of soils. D. Reidel Publishing Co., Boston, MA.

Hinesly, T.D., E.L. Ziegler, and G.L. Barrett. 1979. Residual effects of irrigating corn with digested sewage sludge. J. Environ. Qual. 8: 35-38.

Hohla, G.N., R.L. Jones, and T.D. Hinsesly. 1978. The effect of anaerobically digested sewage sludge on organic fractions of Blount silt loam. J. Environ. Qual. 7:559-563.

Hue, N.V. 1991. Effects of organic acids/anions on P sorption and phytoavailability in soils with different mineralogies. Soil Sci. 152:463-470.

Jackson, M.L. 1979. Soil chemical analysis. Advanced course. Published by M.L. Jackson, Madison, WI.

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

Keeney, D.R., and R.E. Wildung. 1977. Chemical properties of soils. p. 75-97. *In:* L.S. Elliott et al. (ed.) Soils for management of organic wastes and waste waters. Soil Sci. Soc. Am., Madison, WI.

Kiekens, L. 1984. Behavior of heavy metals in soil. p. 126-134. *In:* S. Berglund et al. (ed.) Utilization of sewage sludge on land: Rates of application and long-term effects of metals. D. Reidel Publishing Co., Boston, MA.

King, L.D. 1988. Retention of metals by several soils of the southeastern United States. J. Environ. Qual. 17:239-246.

King, L.D., and H.D. Morris. 1973. Land disposal of liquid sewage sludge: IV. Effect of soil phosphorus, potassium, calcium, magnesium, and sodium. J. Environ. Qual. 2:411-414.

Korcak, R.F., and D.S. Fanning. 1985. Availability of applied heavy metals as a function of type of soil material and metal source. Soil Sci. 140:23-34.

Koskela, I. 1983. Effect of sewage sludge on soil humus content. p. 136-140. *In*: G. Catroux et al. (ed.) The influence of sewage sludge application on physical and biological properties of soils. D. Reidel Publishing Co., Boston, MA.

Latterell, J.J., R.H. Dowdy, and G.E. Ham. 1976. Sludge-borne metal uptake by soybeans as a function of soil cation exchange capacity. Comm. Soil Sci. Plant Anal. 7:465-476.

Lindsay, W.L., and E.C. Moreno. 1960. Phosphate equilibria in soils. Soil Sci. Soc. Am. Proc. 24:177-182.

Loehr, R.C., W.J. Jewell, J.D. Novak, W.W. Clarkson, and G.S. Friedman. 1979. Land application of wastes. Vol II. Van Nostrand Reinhold Co., New York, NY.

Lopez-Hernandez, D., G. Siegert, and J.V. Rodriguez. 1986. Competitive adsorption of phosphate with malate and oxalate by tropical soils. Soil Sci. Soc. Am. J. 50:1460-1462.

Maas, E.V., and G.J. Hoffman. 1977. Crop salt tolerance - current assessment. J. Irrig. Drain. Div., Am. Soc. Civ. Eng. 103:115-134

Madariaga, G.M., and J.S. Angle. 1992. Sludge-borne salt effects on survival of *Bradyrhizobium japonicum*. J. Environ. Qual. 21:276-280.

McBride, M.B. 1994. Environmental chemistry of soils. Oxford Univ. Press, New York, NY.

McLaughlin, M.J., and L. Champion. 1987. Sewage sludge as a phosphorus amendment for sesquioxic soils. Soil Sci. 143:113-117.

McLean, E.O. 1982. Soil pH and lime requirement. *In:* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Agronomy 9:199-224.

McLean, E.O., and J.R. Brown. 1984. Crop response to lime in the Midwestern United States. p. 267-303. *In:* F. Adams (ed.) Soil acidity and liming. Am. Soc. Agron., Madison, WI.

Miller, R.H. 1974. Factors affecting the decomposition of an anaerobically digested sewage sludge in soil. J. Environ. Qual. 3:376-380.

Morel, J.L., and A. Guckert. 1983. Influence of limed sludge on soil organic matter and soil physical properties. p. 25-42. *In:* G. Catroux et al. (ed.) The influence of sewage sludge application on physical and biological properties of soils. D. Reidel Publishing Co., Boston, MA.

Nagarajah, S., A.M. Posner, J.P. Quirk. 1970. Competitive adsorption of phosphate with polygalacturonate and other organic anions on kaolinite and oxide surfaces. Nature 228:83-84.

Nelson, W.L., A. Mehlich, and E. Winters. 1953. The development, evaluation, and use of soil tests for phosphorus availability. Agronomy 4:153-188.

Oberle, S.L., and D.R. Keeney. 1994. Interactions of sewage sludge with soil-crop-water systems. p.17-20. *In:* C.E. Clapp et al. (ed.) Sewage sludge: Land utilization and the environment. Soil Sci. Soc. Am., Madison, WI.

Olsen, S.R., and L.E. Sommers. 1982. Phosphorus. p. 403-430. *In*: A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Chemical and microbiological properties. Amer. Soc. Agron., Madison, WI.

Peterson, A.E., P.E. Speth, R.B. Corey, T.H. Wright, and P.L. Schlect. 1994. Effect of twelve years of liquid digested sludge on the soil phosphorus level. p. 237-247. *In*: C.E. Clapp et al. (ed.) Sewage sludge: Land utilization and the environment. Soil Sci. Soc. Am., Madison, WI.

Petruzzelli, G., G. Guidi, and L. Lubrano. 1986. Modification of heavy metals solubility in soil treated with sewage sludge. p. 478-484. *In*: P.L'Hermite (ed.) Processing and use of organic sludge and liquid agricultural wastes. D. Reidel Publishing Co., Boston, MA.

Rappaport, B.D. 1986. Availability and distribution of heavy metals from sewage sludge in the plant-soil continuum. Ph.D. Diss. p.72-101. Virginia Poly. Inst. and State Univ., Blacksburg, VA.

Rappaport, B.D., J.D. Scott, D.C. Martens, R.B. Reneau, Jr, and T.W. Simpson. 1987. Availability and distribution of heavy metals, nitrogen, and phosphorus from sewage sludge in the plant-soil-water continuum. VPI-VWRRC-BULL 154 5C. Virginia Water Resources Research Center, Virginia Poly. Inst. and State Univ., Blacksburg, VA.

Rappaport, B.D., D.C. Martens, R.B. Reneau, Jr, and T.W. Simpson. 1988. Metal availability in sludge-amended soils with elevated metal limits. J. Environ. Qual. 17:42-47.

Reed, S.T. 1993. Copper adsorption/desorption characteristics on copper amended soils. Ph.D. Diss. p. 6-8. Virginia Poly. Inst. and State Univ., Blacksburg, VA

Rhoades, J.D. 1982. Cation exchange capacity. p. 149-157. *In*: A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed,. Chemical and microbiological properties. Amer. Soc. Agron., Madison, WI.

Rich, C.I. 1961. Cation determination for cation-exchange capacity measurements. Soil Sci. 92:226-231.

Richards, L.A. (ed.) 1969. Diagnosis and improvement of saline and alkali soils. USDA Agric. Handbook No. 60, Washington, DC.

Robertson, W.K. , M.C. Lutrick, and T.L. Yuan. 1982. Heavy applications of liquid-digested sludge on three ultisols: I. Effects on soil chemistry. J. Environ. Qual. 11:278-282.

Sampath, S. 1980. Distribution and plant available sources of copper, iron, manganese, and zinc in soils. Ph.D. diss. Virginia Poly. Inst. and State Univ., Blacksburg, VA (Diss. Abstr. 80-20194).

Sanyal, S.K., and S.K. De Datta. 1991. Chemistry of phosphorus transformations in soil. Adv. Soil Sci. 16:1-120.

Schofield, R.K., and and A.W. Taylor. 1955. The measurement of soil pH. Soil Sci. Soc. Am. Proc. 19:164-167.

Simpson, T.W., S.M. Nagle, and G.D. McCart. 1984. Land application of sewage sludge

for agricultural purposes.

Smith, S.R. 1996. Agricultural recycling of sewage sludge and the environment. CAB International. Wallingford, UK.

Soon, Y.K., T.E. Bates, and J.R. Moyer. 1978. Land application of chemically treated sludge: II. Effects on plant and soil phosphorus, potassium, calcium, and magnesium and soil pH. J. Environ. Qual. 7:269-273.

Sparks, D.L. 1995. Environmental soil chemistry. Academic Press, NY.

Sposito, G., L.J. Lund, A.L. Page, 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.

Steele, R.G.D., and J.H. Torrie. 1980. Principles and procedures of statistics - A biometrical approach. Second Ed., McGraw-Hill, Inc., New York, NY.

Stevenson, F.J. 1982. Humus chemistry. Wiley, New York, NY.

Stevenson, F.J., and Y. Chen. 1991. Stability constants of copper (II)-humate complexes determined by modified potentiometric titration. Soil Sci. Soc. Am. J. 55:1586-1591.

Stewart, B.A., and B.D. Meek. 1977. Soluble salt considerations with waste application. p. 218-232. *In*: L.F. Elliott, et al. (ed.) Soils for management of organic wastes and waste waters. Soil Sci. Soc. of Am., Madison, WI.

Tester, C.F. 1990. Organic amendment effects on physical and chemical properties of a

sandy soil. Soil Sci. Soc. Am. J. 54:827-831.

United States Department of Agriculture (USDA) and Soil Conservation Service (SCS). 1985. Soil survey of Albemarle County, Virginia.

U.S. Environmental Protection Agency. 1983. Process design manual:Land application of municipal sludge. USEPA Rep. EPA-625/1-83-016. U.S. Govt. Printing Office, Washington, DC.

U.S. Environmental Protection Agency. 1993. Standards for use or disposal of sewage sludge. Final Rule, 40 CFR Part 503. U. S. Govt. Printing Office, Washington, DC.

Vlamis, J., and D.E. Williams. 1971. Utilization of municipal organic wastes as agricultural fertilizers. Calif. Agric. 25:7-9.

Walkley, A., and I.A. Black. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 37:29-38.

Woodruff, C.M. 1967. Crop response to lime in the midwestern United States. p. 207-231. *In*: R.W. Pearson and F. Adams (ed.) Soil acidity and liming. Am. Soc. Agron., Madison, WI.

Chapter 3

LONG-TERM EFFECTS OF SLUDGE APPLICATION ON PLANT AVAILABILITY OF COPPER AND ZINC

LITERATURE REVIEW

Stunting of crop growth (Table 18) and a decline in yield at the higher sludge treatments (Tables 20 and 25) were observed in this research. These observations suggested metal phytotoxicity, which was probable with the decrease in soil pH. In order to confirm metal toxicity, we investigated crop symptoms and metal accumulations in plant tissue. The possibility that crop abnormalities were due to other pH related disorders such as Al toxicity was examined. The literature review in this chapter addresses the relationship between soil Cu and plant availability, phytotoxicity, and plant-soil interactions at low pH. Literature on Zn phytotoxicity, a potential cause of the stunting, was also reviewed in the following literature review.

Soil Copper

The total Cu content of uncontaminated soils ranges from 6 to 60 mg Cu kg^{-1} soil (Kabata-Pendias and Pendias, 1984). Levels of soil Cu are much higher in soils which have received applications of sludge, smelting industry waste, and poultry and swine manure (Reed and Martens, 1996). The Cu content of these amendments can lead to phytotoxic soil Cu concentrations. Soil Cu concentrations as high as 3500 mg kg^{-1} in industrially polluted soils and 1500 mg kg^{-1} in agricultural soils have been reported (Kabata-Pendias and Pendias, 1984). Copper deficiencies occur in sandy soils containing low amounts of Cu and in organic soils in which Cu complexes with the functional groups of organic matter (Reed and Martens, 1966).

Numerous forms of Cu exist in soil because Cu is adsorbed by soil components and forms precipitates with a variety of anions (McBride, 1981). The forms of soil Cu include soil solution and exchangeable Cu, Cu weakly bound to specific sites, organically bound Cu, Cu occluded in carbonates and hydrous oxides, and residual Cu in clay lattices (McLaren and Crawford, 1973a,b; 1974). Most of the Cu in soils is insoluble and immobile (Mills and Jones, 1996). Labile forms of Cu available to plants include (Lindsay, 1979):

1. Free and complexed cations in solution,

2. Cations nonspecifically adsorbed (electrostatically held) on cation exchange sites, and

3. Cations specifically adsorbed (covalently held) on surfaces of layer silicate clays, oxides of Fe, Al, and Mn, carbonates, and organic matter.

Soil solution Cu species vary with pH: below 6.9 Cu^{2+} dominates, near 7.0 $CuOH^+$ is common, and above 7.0 $Cu(OH)_2$ is dominate. Other soil solution species include $CuSO_4$ and $CuCO_3$. Concentrations of Cu in soil solution range from 0.003 to 0.135 mg L^{-1} (Kabata-Pendias and Pendias, 1984). Hodgson et al. (1966) reported a range in soil solution Cu from 0.004 to 0.039 mg Cu L^{-1} in calcareous soils. Plant roots absorb Cu as ionic Cu^{2+} or organically complexed Cu^{2+}.

Nonspecific adsorption of Cu occurs when the positive-charged Cu cation is electrostatically attracted to the permanent negative charges arising from isomorphous substitution in phyllosilicates (Sposito, 1981). The ionic bond formed in nonspecific adsorption is easily broken, therefore the nonspecifically adsorbed Cu cation is considered an exchangeable cation. Very little of the labile Cu is supplied by specifically adsorbed Cu because the covalent bond between Cu and the various surfaces is not easily broken. Weathering slowly reverts specifically adsorbed Cu to a labile form (Reed and Martens, 1996). Decomposition of organic matter also adds to the labile pool of Cu. The realization that soil solution Cu is replenished by organically-bound Cu led most soil testing laboratories to replace dilute salt and acid extractants with organic chelating agents, such as EDTA and DTPA, for extraction of "available" soil Cu (Robson and Reuter, 1981).

Occluded Cu does not contribute to the labile pool of soil Cu. A layer of Al, Fe, or Mn hydroxide precipitates over specifically adsorbed Cu prevents dissociation of the Cu into soil solution (Reed and Martens, 1996).

Plant Copper

Copper is absorbed by both active and passive mechanisms, although passive absorption is more likely at toxic concentrations (Kabata-Pendias and Pendias, 1984). Transport of Cu to shoots is reduced by retention in root tissues, especially when Cu is deficient or excessive (Kabata-Pendias and Pendias, 1984). Tissue Cu^{2+} is often associated with the cell walls of root tissue (Kabata-Pendias and Pendias, 1984). Concentrations of Cu in xylem and phloem saps have been correlated with amino acid concentrations (Kabata-Pendias and Pendias, 1984). Copper is complexed with soluble N compounds as it moves through the xylem to leaves, shoots, and flowers (Mills and Jones, 1996).

Approximately half of the active Cu is located in chloroplasts of green tissues (Mills and Jones, 1996). Shoot concentrations of Cu are high in young plants, decreasing as the plant matures (Mills and Jones, 1996). The highest shoot concentrations occur during intensive growth and at luxury Cu levels (Kabata-Pendias and Pendias, 1984). Copper tends to accumulate in the reproductive organs of some plant species (Kabata-Pendias and Pendias, 1984). Most of the Cu in flowers is found in the anthers and ovaries (Mills and Jones, 1996). The highest reported plant Cu concentrations were in the embryo and seed coat of cereal grains (Kabata-Pendias and Pendias, 1984).

Copper is a component of several important enzyme complexes involved in oxidation reactions, electron transport, lignin synthesis, as well as other functions that influence plant metabolism (Mills and Jones, 1996). Copper also functions in the control of water relations, in the control of DNA and RNA production, and in the disease resistance mechanism (Kabata-Pendias and Pendias, 1984). Copper is relatively immobile in plants, therefore deficiency symptoms first occur in young organs.

Sufficiency ranges for Cu in corn are 6 to 20 mg kg^{-1} in ear leaves at silk and 7 to 20 mg kg^{-1} in whole plants at the 3- to 4-leaf stage (Bennett, 1993). The critical concentration for Cu in ear leaves at tassle is 5 mg kg^{-1} (Jones et al., 1990). Donohue et al. (1990) reported that the nutrient sufficiency range for corn (up to 30 cm tall) in Virginia is 3 to 20 mg kg $^{-1}$ based on extensive research conducted throughout the state. Copper deficiency rarely occurs in corn, except in organic soils and at high pH. Deficiency symptoms begin with chlorosis of the youngest leaves, resembling chlorosis in Fe deficient plants (Bennett, 1993). As the deficiency progresses, marginal necrosis of older leaves occurs, resembling K deficiency (Bennett, 1993). The critical concentration for Cu in sorghum seedlings is 2 to 5 mg kg^{-1} (Clark, 1993). Deficiency symptoms in sorghum include interveinal chlorosis of young leaves, and unusual emergence of leaves from the whorl which resembles Ca deficiency (Clark, 1993).

Copper Phytotoxicity

Copper phytotoxicity has been extensively reported (Lexmond and de Haan, 1980). Phytotoxicity has been generally only observed in greenhouse pot studies and in land application of high metal content sludge at very high rates (Smith, 1996). Lexmond and de Haan (1980) conducted a Cu toxicity study and observed the following in corn: decreased dry matter production, increased Cu and Mn levels, and decreased phosphate content. The decrease in phosphate content was attributed to decreased uptake of P as a result of Cu injury to roots. Diagnosis of phytotoxicity in early growth stages is based upon a departure from normal growth (Chang et al., 1992). Growth retardation, leaf chlorosis, necrosis, and branch dieback are early phytotoxicity symptoms (Chang et al., 1992). These early symptoms may continue through plant maturity, with a subsequent reduction in yield. A quantitative relationship between early growth retardation and later yield reductions has not been developed. Chang et al. (1992) made the assumption that 50% or greater early growth retardation will result in significant yield reduction at maturity in development of

their methodology for establishing phytotoxicity criteria.

Chang et al. (1992) developed a phytotoxicity threshold, referred to as PT_{50}, which is the leaf tissue concentration corresponding to 50% growth retardation. Using several sets of data, Chang et al. (1992) determined that the PT_{50} for Cu in corn ranged from 7 mg kg^{-1} in pot experiments to 40 mg kg^{-1} in hydroponic studies. The uptake of metals in hydroponic or pot cultures do not adequately represent uptake from sludge-amended field soil , therefore a PT_{50} for corn grown in the field is needed.

Diagnosis of Cu toxicity cannot be based on visual symptoms. The more common symptoms of Cu toxicity (reduced shoot vigor, poorly developed root systems, and leaf chlorosis) resemble symptoms of other disorders. Chlorosis in Cu toxicity resembles chlorosis in Fe deficiency. Plant and soil analyses are necessary for reliable diagnosis.

Metals may induce phytotoxicity via inhibition of photosynthesis and respiration, alteration of plant water relations, increased permeability of the plasma membrane of root cells, and interference in metabolic enzyme activity (Chang et al., 1992). Plants with high Cu concentrations appear to be more susceptible to some diseases (Kabata-Pendias and Pendias, 1984).

The major mechanism of protection in Cu-tolerant species is exclusion of Cu from the shoots. Once Cu is absorbed by plants, it tends to accumulate in the roots, with little translocation to shoots (Dragun et al., 1976; Jarvis and Whitehead, 1981; Minnich et al., 1987). Most of the root Cu is associated with cell walls (Lonergan, 1981). Excess Cu has a detrimental effect on the root system and, thereby, causes a reduction in lateral root development (Mills and Jones, 1996). When roots become damaged by Cu toxicity, high levels of Cu may enter the shoot (Graham, 1981). The toxicity effect of some heavy metals may be countered by plant Ca, therefore an adequate Ca concentration should be

maintained (Mills and Jones, 1996).

The maximum permissible loading levels of Cr, Cu, Ni, and Zn in current sludge regulations are based upon their most restrictive exposure pathway - the phytotoxicity pathway (USEPA, 1993). The Regional Research Technical Committee W-170, called in to evaluate the procedures used to determine these pollutant levels, believed that the proposed phytotoxicity criteria overestimated the hazard of metals (W-170 Peer Review Committee, 1989). Data to determine the loading limits for the phytotoxicity pathway was obtained from small pot experiments with inorganic metal salts, rather than from sludge-amended field studies. Plants in such pot studies accumulate more metals than sludge-amended field crops (Cunningham et al., 1975 a, b). The committee pointed out that phytotoxicity rarely occurs in agricultural crops grown on sludge-amended soils, even at very high application rates (> 500 t). They also pointed out that Cu and Zn toxicities have not been reported even in sensitive plants grown on sludge-amended soils with a pH > 5.5.

Zinc in Soil and Plants

The total Zn content of uncontaminated surface soils ranges from 17 to 125 mg kg^{-1} soil (Kabata-Pendias and Pendias, 1984). Levels of Zn are higher in soils contaminated by municipal sewage, animal manures, and nonferric metal industry wastes containing Zn. Since Zn is easily adsorbed by soil minerals and complexed by organic matter, it accumulates in the surface horizons of most soils (Kabata-Pendias and Pendias, 1984). Extremely high accumulations of Zn in contaminated surface soils have been reported: up to 7,474 mg kg^{-1} on sludged farmland and up to 66,400 mg kg^{-1} in old mining areas (Kabata-Pendias and Pendias, 1984).

Zinc exists in the same forms in soils as Cu (Reed and Martens, 1996), but occurs in more readily soluble forms (Kabata-Pendias and Pendias, 1984). Several ionic species of

Zn are mobile in soil, with Zn^{2+} the most common among them. The fraction of Zn specifically adsorbed by Fe and Mn oxides is more available to plants than that fraction of Cu (Kabata-Pendias and Pendias, 1984). Soil solution concentrations of Zn range from 0.004 to 0.0270 mg Zn L^{-1} (Kabata-Pendias and Pendias, 1984).

Zinc is primarily taken up as the Zn^{2+} cation and moves through the xylem as an uncomplexed ion (Mills and Jones, 1996). The Zn^+ ion, other complex ions, and Zn chelates may also be absorbed by plants (Kabata-Pendias and Pendias, 1984). However, Halvorsen and Lindsay (1977) concluded that only Zn^{2+} is absorbed by corn roots.

Zinc, found throughout the plant, is mostly present in the root system, where it is preferentially retained (Mills and Jones, 1996), particularly in Zn-contaminated soils. The tops of plants are more likely to accumulate Zn if it is an airborne pollutant (Kabata-Pendias and Pendias, 1984).

Like Cu, Zn is involved in several enzyme systems. Zinc protects proteins from denaturation through its involvement with the carbonic anhydrase enzyme (Mills and Jones, 1996). Ribonucleic acid polymerase is inactivated in the absence of Zn. Zinc also participates in the synthesis of hormones, cytochrome c, and proteins (Kochian, 1993). RNA synthesis, normal development of chloroplast grana, and stabilization of cytoplasmic ribsomes are impaired with Zn deficiencies.

Sufficiency ranges for Zn in corn are 20 to 70 mg kg^{-1} in ear leaves at silk and 20 to 50 mg kg^{-1} in whole plants in the 3- to 4-leaf stage (Bennett, 1993). The critical value for ear leaves at tassle is 15 mg kg^{-1} (Jones et al., 1990). Zinc deficiency is not unusual in corn (Adriano, 1986). Zinc deficiency symptoms in corn begin as a white band at the leaf base extending to the tip. Internodes are shortened, resulting in stunting. New leaves become almost white in cases of severe Zn deficiency, a condition known as "white bud" (Bennett,

1993). The critical value for Zn in sorghum seedlings is 9 to 15 mg kg^{-1} (Clark, 1993). Bleached chlorotic bands on leaves and shortened internodes in Zn deficient sorghum resemble Zn deficiency in corn (Clark, 1993).

Zinc Phytotoxicity

Zinc phytotoxicity seldom occurs (Bennett, 1993), because most plant species are very tolerant of excessive amounts of Zn (Kabata-Pendias and Pendias, 1984). Nevertheless, Zn phytotoxicity has been reported in acid and heavily sludged soils (Kabata-Pendias and Pendias, 1984). Toxicity levels vary with species and growth stage (Kabata-Pendias and Pendias, 1984). Zinc phytotoxicity has been reported in young barley (*Hordeum vulgare*) plants at 300 mg kg^{-1} (Davis et al., 1978). Cereal crops, lettuce, mustard, beet, and spinach are sensitive to excess Zn (Kabata-Pendias and Pendias, 1984; Chaney, 1993). A reduction in root growth and leaf expansion of plants and then chlorosis occurs at levels above 200 mg kg^{-1} (Mills and Jones, 1996). Iron, Mn, and P deficiencies have been induced by high levels of Zn (Mills and Jones, 1996). Other Zn toxicity symptoms include chlorotic and necrotic leaf tips, interveinal chlorosis of young leaves, growth retardation, and root injury (Kabata-Pendias and Pendias, 1984). Injured roots resemble barbed wire.

Plant-Soil Interactions at Low pH

Many mineral nutrition-related factors can cause plant injury at low pH. Soil pH affects the availability of plant nutrients. At low pH levels the availability of N, P, K, Ca, Mg, S, and Mo decreases and the availability of Al, B, Co, Cu, Fe, Mn, and Zn increases (Sparks, 1995). Excess H$^+$ also causes plant damage at low pH levels. Foy (1984) referred to this complex of growth limiting factors as "acid soil toxicity". It has often been misdiagnosed as injury from drought, cold temperatures, herbicides, and plant diseases (Foy, 1984).

Aluminum toxicity is the most limiting growth factor in acidic soils. It may occur at a pH as high as 5.5 in kaolinitic soils (Foy, 1984). Monomeric species of Al are particularly toxic (Sparks, 1995). Symptoms of Al toxicity include stunting (especially during early growth) and poor root development (Mills and Jones, 1996). Aluminum reduces root uptake of P, therefore P deficiency symptoms may appear (Mills and Jones, 1996). Aluminum-induced Ca and Fe deficiencies also occur (Foy, 1984).

Yields can be reduced even though symptoms of Al toxicity are not visible in plant tops (Foy, 1984). Aluminum toxicity is species dependent (Foy, 1984). Corn is considered resistant to Al toxicity (Mills and Jones, 1996), however Evans and Kamprath (1970) observed growth reduction in corn with a solution concentration > 3.6 mg Al L^{-1}. Sorghum is susceptible to Al toxicity (Mills and Jones, 1996), particularly when grown in soils at pH levels < 5.0 (Clark, 1993). Chlorosis on lower leaves, necrosis along leaf margins and at tips, and reduced growth have been reported as Al toxicity symptoms (Clark, 1993). Aluminum toxicity has a more dramatic effect on sorghum roots. Swollen, stubby, brittle, dark roots with reduced elongation have been reported as root toxicity symptoms (Clark, 1993). Dark brown discoloration and lack of root hairs were observed in sorghum roots in an Al toxicity study conducted by Ahlrichs et al. (1991). Differential tolerance to Al toxicity has been reported among corn and sorghum genotypes (Amancio et al., 1991; Galvez and Clark, 1991). Young seedlings are more susceptible to Al toxicity than mature plants (Foy, 1984).

Iron and Zn are seldom, if ever toxic; while H^+, B, Cu, and Mn have occasionally produced toxicity (Bennett, 1993). Manganese toxicity is probably second after Al toxicity in reducing plant growth in acid soils (Foy, 1984). It is usually reported at soil pH values ≤ 5.5. Manganese toxicity symptoms are more visible in plant tops than Al toxicity symptoms, and are often detected at levels that don't reduce vegetative growth (Foy, 1984). Toxicity symptoms include marginal chlorosis and necrosis. A brown discoloration

of roots has been reported in severe toxicity conditions (Foy, 1984). Dark green leaves with reddish purple spots that develop into streaks have been observed in sorghum experiencing Mn toxicity (Clark, 1993).

Excess H^+ damages root membranes, can increase plant requirements for Ca and decrease the uptake of Mg (Foy, 1984). Hydrogen ion toxicity is difficult to determine in acid soils because of the complex of other growth limiting factors at low soil pH levels. It may be dominate in topsoil where organic matter is high , whereas Al toxicity is common in subsoil (Marschner, 1991). At pH < 4.0, Al and Mn toxicity are more likely than H^+ toxicity (Foy, 1984). Iron toxicity has occurred in sorghum grown on acid soils, resulting in light leaves with black lesions at the margins (Clark, 1993).

MATERIALS AND METHODS

Soil Analyses

Soil samples were taken from the 0-to 15-cm surface layer. Mehlich-1 extracting solution ($0.05N$ HCl in $0.025N$ H_2SO_4) was used for determination of P, K, Ca, Mg, Zn, Mn, Cu, Fe, B, and Al (Donohue and Heckendorn, 1994a). Extractable Cu and Zn were also determined by extraction with the diethylenetriaminepentaacetic triethanolamine (DTPA-TEA) solution, (ie., 0.005 M DTPA, 0.01 M $CaCl_2$, and 0.1M TEA buffered at pH 7.3) (Lindsay and Norvell, 1978). Other soil analyses are discussed in Chapter 2.

Plant Analyses

Whole above-ground portions of young corn plants at seedling stage (< 30 cm tall) were sampled. Sorghum ear leaves were sampled at heading, 66 days after planting. The second leaf from the top of the sorghum plant was removed for analysis as recomended by Jones et al.(1990). Corn and sorghum grain were sampled at plant maturity. All plant tissue was dried at 70°C for 16 hours and ground to pass a 20-mesh screen. One-half gram subsamples of plant tissue were digested in a HNO_3-$HClO_4$ acid mixture. Concentrations of Ca, K, Mg, P, S, Cu, Fe, Mn, Ni, Cd, Pb, As, and Zn in ear leaf digests were measured with an ICP. Concentrations of Cu and Zn in grain digests were determined by atomic absorption spectrophotometry.

Height of corn plants was measured at 5 weeks growth in 1993 and at 7 weeks growth in 1994. Plant weight was determined on the basis of g per 8 whole plants. Corn and

sorghum grain and stover yields measured at plant maturity were adjusted to 155 g and 140 g moisture kg $^{-1}$, respectively.

Statistical Analyses

Plant height, weight, yield, and nutrient concentration data were evaluated by LSD mean separation procedures at the 0.05 level of significance (Steele and Torrie, 1980). Mehlich-1 extractable soil nutrient data and DTPA-TEA extractable soil Cu and Zn data were also evaluated by LSD mean separation procedures at the 0.05 level of significance.

RESULTS AND DISCUSSION

Nutrient Content of Soil

Soil levels of P, K, Ca, and Mg were in the High category as determined by soil test calibrations (Donohue and Heckendorn, 1994b). These high nutrient concentrations reflect past fertilizer, lime, and sludge additions. Soil Cu, P, and Zn levels increased with sludge rate during the four-year period from 1992 to 1995 (Tables 12-15). This increase was expected on the basis of the high sludge application rates and the high content of these nutrients in the sludge: 3654 mg Cu, 31.7 g P, and 2982 mg Zn kg^{-1} on a dry weight basis.

Table 12 . Content of Mehlich-1 extractable nutrients 8 years after sludge application on a Davidson clay loam.

Sludge Rate	P	K	Ca	Mg	Fe	Al	Mn	B	Cu	Zn
Mt ha^{-1}	-------	-------	-------	-------	------- mg kg^{-1} -------					
0	17.1f*	108.1a	647.3d	115.9a	12.8e	219.4a	31.7a	0.42b	3.6f	3.7f
42	27.4e	92.4b	718.2d	111.2a	13.0de	203.5b	32.3a	0.42b	17.0e	16.6e
84	41.9d	96.4ab	820.3c	111.4a	14.3cd	208.2ab	31.9a	0.46ab	33.2d	32.7d
126	63.5c	91.1b	943.7b	118.4a	15.4bc	215.7ab	26.5a	0.48ab	51.8c	51.1c
168	73.9b	91.7b	1022.0ab	119.8a	16.1ab	215.3ab	26.4a	0.51a	62.5b	62.3b
210	91.9a	96.0ab	1093.2a	120.3a	17.4a	218.5a	24.7a	0.53a	76.0a	76.7a

* Column means followed by different letters are significantly different at the 0.05 probability level.

Table 13. Content of Mehlich-1 extractable nutrients 9 years after sludge application on a Davidson clay loam.

Sludge Rate	P	K	Ca	Mg	Fe	Al	Mn	B	Cu	Zn
Mt ha^{-1}	-------					mg kg^{-1}	-------			
0	25.4e*	136.7a	538.1d	94.7b	14.3bc	291.2a	83.2a	0.55d	5.2f	6.0f
42	35.6e	113.3b	694.4c	107.2ab	13.6c	258.4b	78.7a	0.62c	20.3e	20.8e
84	53.6d	119.4ab	796.8bc	105.8ab	14.9bc	269.2ab	83.9a	0.65bc	40.6d	40.7d
126	68.6c	112.5b	898.4b	112.5a	15.3ab	272.4ab	74.9a	0.69abc	55.0c	55.1c
168	89.9b	117.3ab	1014.0a	115.9a	15.6ab	274.3ab	78.3a	0.70ab	74.8b	78.3b
210	112.5a	127.1ab	1096.3a	111.7a	16.8a	277.9ab	74.2a	0.73a	92.1a	96.7a

* Column means followed by different letters are significantly different at the 0.05 probability level.

Table 14. Content of Mehlich-1 extractable nutrients 10 years after sludge application on a Davidson clay loam.

Sludge Rate	P	K	Ca	Mg	Fe	Al	Mn	B	Cu	Zn
Mt ha^{-1}	--------					mg kg^{-1}				--------
0	20.1f*	123.5a	491.4d	79.5a	13.2cd	243.3a	98.0b	0.51b	3.9f	4.3f
42	37.3e	101.0b	655.1c	92.4a	12.7d	223.0b	112.8ab	0.60a	20.8e	20.3e
84	61.2d	113.5ab	710.6bc	87.0a	14.4bc	223.7b	122.4a	0.59a	42.0d	41.3d
126	79.3c	100.1b	824.9ab	91.8a	15.0ab	224.3b	96.0b	0.61a	57.0c	57.2c
168	101.5b	111.4ab	886.6a	93.2a	15.0ab	217.4b	99.2b	0.62a	72.4b	72.5b
210	115.0a	111.4ab	930.4a	87.7a	15.9a	224.6b	93.0b	0.65a	84.7a	85.8a

* Column means followed by different letters are significantly different at the 0.05 probaility level.

Table 15. Content of Mehlich-1 extractable nutrients 11 years after sludge application on a Davidson clay loam.

Sludge Rate	P	K	Ca	Mg	Fe	Al	Mn	B	Cu	Zn
Mt ha^{-1}	--- mg kg^{-1} ---									
0	23.2f*	102.1cd	417.3e	61.5b	14.8bc	255.5a	85.7b	0.37c	4.9f	5.7f
42	33.6e	68.3e	573.8d	78.7a	14.4c	225.5b	84.9b	0.45b	21.9e	23.2e
84	49.4d	95.7d	602.1cd	71.9ab	15.7abc	218.6bc	102.2ab	0.45b	41.1d	42.7d
126	68.4c	111.8bc	696.7bc	76.1a	16.5ab	219.3bc	111.3a	0.47ab	62.6c	64.3c
168	78.3b	115.8ab	762.0ab	76.7a	16.5ab	204.9c	92.3ab	0.48ab	73.9b	78.4b
210	92.7a	125.3a	816.5a	75.9a	16.8a	217.3bc	93.1ab	0.52a	90.2a	94.6a

* Column means followed by different letters are significantly different at the 0.05 probability level.

DTPA Extractable Copper and Zinc

Sludge application in 1984 supplied the soil with 153 to 760 kg Cu ha^{-1} and 125 to 620 kg Zn ha^{-1} (Table 5). The maximum cumulative sludge metal application recommended for this soil at that time was 280 kg Cu and 560 kg Zn ha^{-1} (USEPA, 1983). Current sludge regulations for metals are based on sludge metal concentrations (USEPA, 1993). The sludge applied in this study contained 3654 mg Cu and 2982 mg Zn kg^{-1}, below the ceiling concentrations (maximum allowable), but above the pollutant concentration limits (criteria for high quality sludge) (Table 16). Levels of Cu and Zn applied in this study are below the cumulative loading rates, but above the annual loading rates (Table 12).

Table 16. Part 503 sludge concentration limits and loading rates for Cu and Zn.

Pollutant	Ceiling concentration	Pollutant concentration	Annual loading rate	Cumulative loading rate
	------------- mg kg^{-1} -------------		-------------- kg ha^{-1} --------------	
Copper	4300	1500	75	1500
Zinc	7500	2800	140	2800

(USEPA, 1993)

Rappaport (1988) reported that levels of DTPA-extractable Cu in the Ap horizon of the soil under study increased linearly with sludge application rate in 1984 (Figure 1). DTPA-extractable metals reached a maximum of 129 mg Cu and 78 mg Zn kg^{-1} in 1984. Levels of DTPA-extractable Cu also increased linearly with sludge application rate in 1995 (Table 17 and Figure 2). Others have also observed an increase in DTPA extractable Cu and Zn with increasing rates of metal addition (Maclean and Dekker, 1978; Korcak and Fanning, 1985). DTPA extractable Cu and Zn were below the levels observed

in 1984 (Table 17). Rappaport used the DTPA method of Baker and Amacher (1981). Some of the decrease in DTPA extractable metals may be attributed to occlusion over time; i.e., adsorbed metals may have become coated with precipitates of Al and Fe hydrous oxides present in the soil. The DTPA is a chelating agent for assessing plant available micronutrient cations in soil. Occluded metals may not be extracted by the chelate in this solution. DTPA combines with free metal ions in solution, reducing their activities. In response, metal ions are desorbed from soil surfaces or dissolved from labile solid phases to replace the complexed free metal ions in soil solution (Lindsay and Norvell, 1978).

Table 17. DTPA extractable Cu and Zn in a sludge-amended Davidson clay loam.

Sludge Rate	DTPA extractable Cu		DTPA extractable Zn	
	1984	1995	1984	1995
Mt ha $^{-1}$	------------ --------------- mg kg $^{-1}$ ----------------------------			
0	1.4f	3.7f	1.6f	2.8f
42	24.9e	23.1e	19.2e	17.2e
84	53.0d	44.3d	38.9d	33.3d
126	73.4c	64.8c	52.4c	49.6c
168	119.9b	78.7b	73.2b	59.5b
210	129.4a	92.8a	78.2a	69.9a

* Column means followed by different letters are significantly different at the 0.05 probability level.
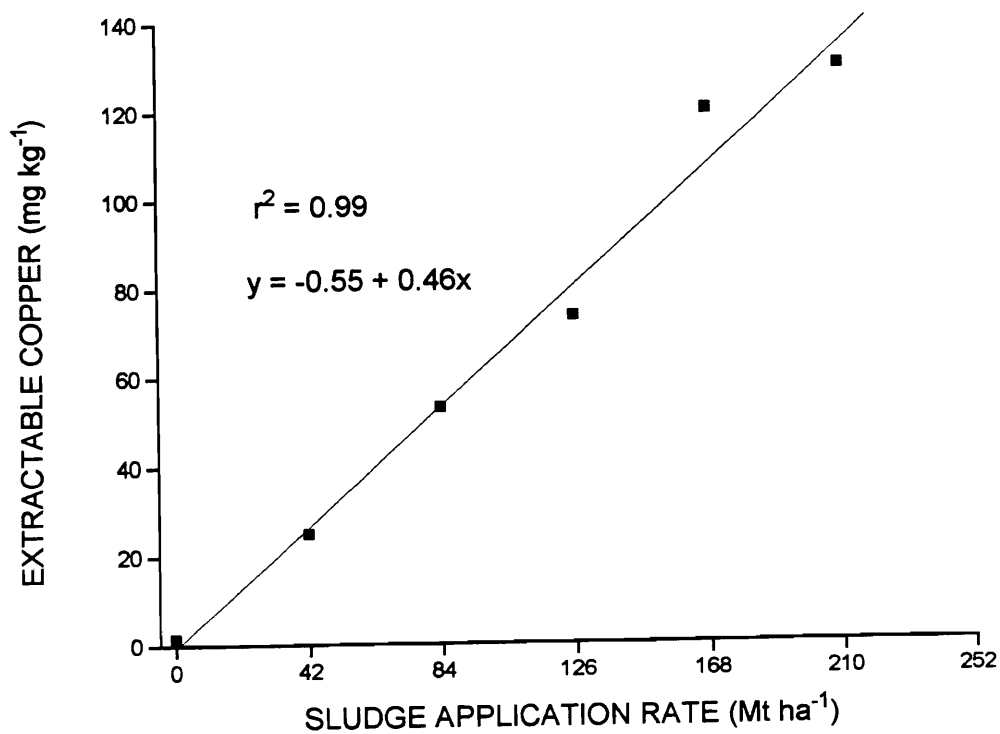
Figure 1. Effect of sludge application on levels of DTPA extractable Cu in a Davidson clay loam one year after application (Rappaport et al., 1988).
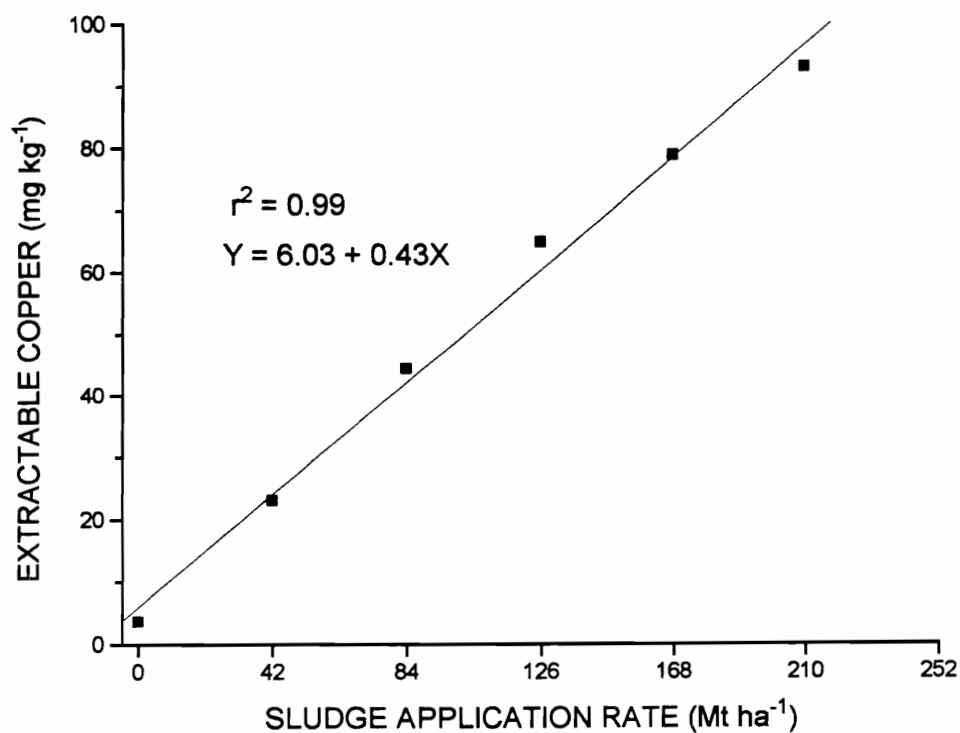
Figure 2. Effects of sludge application on DTPA extractable Cu
in a Davidson clay loam eleven years after
application.

Corn

Corn grain ranked 11th on Virginia's agricultural commodity list in 1994, down from the rank of #9 in 1984 (Purcell, 1996). There has been a dramatic decline in total acreage of corn grain in Virginia which Purcell (1996) attributes to weather problems (particularly drought), national farm policy, and lack of research to generate technology suited to conditions in the state.

Stunting was apparent in early corn growth in the 126 - 210 mt sludge ha^{-1} treatments. The height of young corn plants decreased as sludge rate increased (Table 18). Corn stands in 1994 were poor due to drought (Table 18). Corn plants were removed and the experimental area was replanted to grain sorghum on June 21st.

Table 18. Corn height and weight.

	Corn Height		Corn Weight	
Sludge Rate	1993	1994	1992	1993
Mt ha $^{-1}$	cm at 5 weeks	cm at 7 weeks	------- g per 8 whole plants -----	
0	19.1ab*	33.5bc	10.8a	18.1ab
42	21.2a	46.5a	12.3a	23.9a
84	20.0ab	37.8ab	13.1a	21.5a
126	18.0b	21.8cd	13.5a	18.5a
168	17.7b	18.0d	12.4a	10.7b
210	14.4c	19.3d**	11.5a	11.6b

* Column means followed by different letters are significantly different at the 0.05 probability level.

** 50% of one replication of this treatment were dead.

Corn grain yields in 1992 exceeded the state average yield of 7273 kg ha^{-1} as well as the Orange County, VA average yield (Virginia Agricultural Statistics Service, 1993) (Tables 19 and 20). Record high yields of corn grain in Virginia that year were attributed to timely rains and moderate temperatures throughout most of the growing season (Virginia Agricultural Statistics Service, 1993).

Long periods of dry weather and unusually high temperatures in 1993 were responsible for the large decrease in the average state corn grain yield (Table 19) (Virginia Agricultural Statistics Services, 1994) and the lower yields at the research site (Table 20). The greatest yield limiting factor for corn growth in Virginia is lack of water at critical stages of development (McKenna, 1995). There is a 10% yield reduction if a corn plant at the 12th leaf stage is subjected to 4 days of moisture stress. Four days of moisture stress in a corn plant in the tassle to blister grain stage will reduce yields by 40-50% (McKenna, 1995). Except at the 210 mt ha^{-1} sludge rate, 1993 yields in this study exceeded both state and Orange County average yields. In 1995, yields of all treatments except the highest sludge rate again exceeded state and Orange County yields (Tables 19 and 20).

Table 19. Average corn grain yields in the state of Virginia and in Orange County, VA during the period of 1992 - 1995.

	Average Corn Grain Yield in Virginia	Average Corn Grain Yield in Orange County, VA
Year	------------------------ kg ha^{-1} ----------------------------	
1992	7273	7399
1993	3762	4076
1994	6145	5768
1995	6961	7400

Source: Virginia Agricultural Statistics Service, 1993, 1994, 1995, 1996.

Table 20. Effect of sludge application on corn grain and stover yields.

| Sludge rate | 1992 Yields | | 1993 Yields | | 1995 Yields | |
	Grain	Stover	Grain	Stover	Grain	Stover
Mt ha^{-1}	------------------------------------- kg ha^{-1} -------------------------------------					
0	8503.4bc*	6505.0ab	5524.2ab	4251.5ab	14470.1a	7365.0ab
42	9773.1ab	6505.0ab	7338.1a	5175.0a	13233.3a	8380.8a
84	9657.7ab	6667.6ab	6980.8a	4498.9ab	11914.1a	6805.8ab
126	10157.9a	6927.8a	4369.9b	3690.4b	11831.7a	7196.3ab
168	9119.0abc	6374.9ab	4205.0bc	3380.3bc	10388.8a	5443.3bc
210	8003.2c	4976.3c	2061.3c	2390.6c	5482.9b	3697.0c

*Column means followed by different letters are significantly different at the 0.05 probability level.

In general, yields during all three years decreased with increasing sludge rate (Table 20). The yield decrease in 1995 is depicted in Figure 3. This is in direct contrast to what Rappaport et al. observed in 1984 (Figure 4). This reversal in yield trend may be explained by the decrease in soil pH since that time.
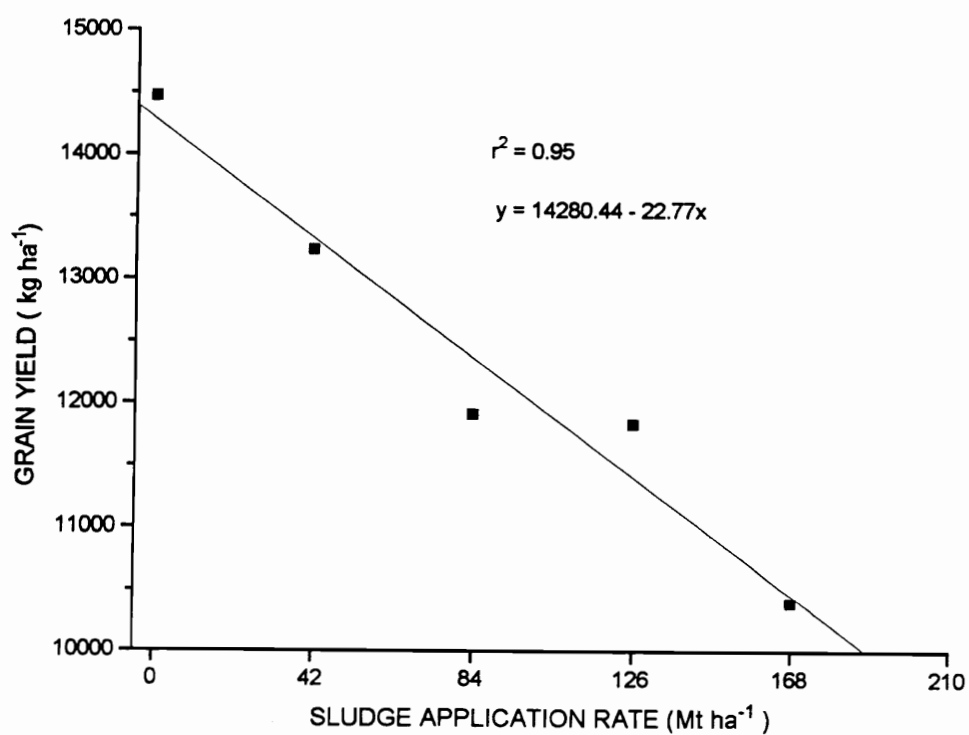
Figure 3. Effect of sludge application on corn grain yields 11 years after sludge application on a Davidson clay loam.
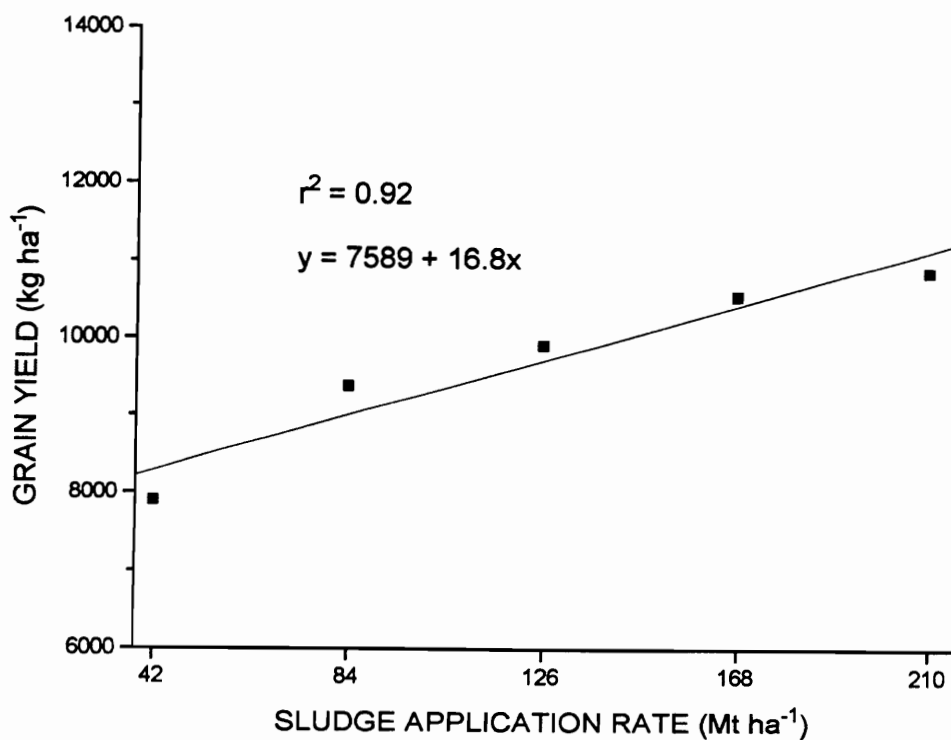
Figure 4. Effect of sludge application on corn grain yields during the
first year of sludge application on a Davidson clay
loam (Rappaport et al., 1988).

Plant tissue concentrations of Ca, Mg, P, and S were within the nutrient sufficiency ranges reported by Mills and Jones (1996) (Tables 21 and 22). Concentrations of K in 1992 plant tissue were slightly below the nutrient sufficiency range (Mills and Jones, 1996) (Table 21 and 22), despite high levels of soil K (Tables 12 to 15). The high levels of Al in the soil (Tables 12 to 15) may have reduced the K content in corn (Mills and Jones, 1996). Potassium deficiency symptoms, which include necrotic spots and marginal burn on older leaves (Robson and Snowball, 1986), were not observed. Plant tissue concentrations of N were slightly below the nutrient sufficiency range in 1993. The uptake of both ammonium and nitrate is reduced at low pH (Reuter and Robinson, 1986). In acidic soils ammonium and hydrogen ions compete for binding sites on plant roots (Reuter and Robinson, 1986). Although the stunting that we observed in this study occurs with a shortage of N, N deficiency symptoms such as yellowing and premature loss of older leaves (Hanway, 1989) were not observed. Reduced uptake of N and K in corn at low soil pH levels was attributed to inhibition of root growth due to Cu toxicity in a study conducted by Lexmond (1980). A reduction in N and K uptake and an inhibition in organic N compound synthesis in corn grown in high Cu solutions in a hydroponics study were observed by Lexmond and van der Worm (1981).

Plant tissue Cu concentrations in 1993 were above the normal range of 5 to 20 mg kg^{-1} (Jones et al., 1990) at the higher sludge rates (Table 22). Corn earleaf Cu concentrations were within the normal range of 3 to15 mg kg^{-1} (Jones et al., 1990) in this study in 1984 (Rappaport, 1988). The increase in Cu concentrations in 1993 can be attributed to increased availability of Cu due to decreased soil pH. The increase may also be due to increases in soil Al, since an association between toxic levels of Al and increased levels of Cu in leaf tissue exists (Mills and Jones, 1996). It should be pointed out that the phytotoxic Cu concentration for field grown crops has not really been established.

Table 21. Nutrient concentration of whole plant tissue (< 30 cm tall) of corn 8 years after sludge amendment on a Davidson clay loam.

Sludge Rate	Ca	K	Mg	N	P	S	Cu	Mn	Zn
Mt ha^{-1}	----------------------------- g kg^{-1} -----------------------------						---------- mg kg^{-1} ----------		
0	6.4c*	22.3a	3.6b	40.6ab	3.9ab	3.6a	17.1b	125.0bc	74.7c
42	6.8bc	20.3a	3.8ab	40.8ab	4.1ab	3.6a	18.5ab	190.0a	103.6bc
84	7.5ab	20.6a	4.1ab	42.5a	4.3a	3.9a	19.7ab	139.6b	126.4ab
126	7.9a	21.1a	4.2a	42.1a	4.3a	3.8a	21.4a	117.2bc	139.2a
168	8.0a	20.6a	4.3a	41.3ab	4.1ab	3.6a	20.0ab	95.9c	138.9a
210	7.9a	21.1a	3.9ab	39.8b	3.7b	3.6a	21.2a	101.4c	146.6a

* Column means followed by different letters are significantly different at the 0.05 probability level.

Table 22. Nutrient concentration of whole plant tissue (< 30 cm tall) of corn 9 years after sludge application on a Davidson clay loam.

Sludge Rate	Ca	K	Mg	N	P	S	Cu	Mn	Zn
Mt ha^{-1}	------------------------ g kg^{-1} ------------------------						---------- mg kg^{-1} ----------		
0	2.8c*	26.7a	2.3b	32.1ab	2.5b	1.9ab	12.7b	246.0b	40.0c
42	3.8b	26.9a	3.3a	33.3a	2.9a	2.1a	15.7b	267.2ab	64.9bc
84	4.0b	26.4a	3.0a	33.4a	2.9a	2.0a	17.7b	238.8b	94.4b
126	4.5a	23.6a	3.2a	31.3bc	2.9a	2.0a	23.9b	254.4ab	111.0ab
168	4.1ab	24.3a	2.9ab	30.6bc	2.7ab	1.8b	40.7a	401.8a	156.0a
210	4.3ab	23.8a	2.9ab	30.2c	2.7ab	1.9ab	37.2a	249.9b	120.3a

* Column means followed by different letters are significantly different at the 0.05 probability level.

Zinc concentrations in plant tissue were above the nutrient sufficiency range (Mills and Jones, 1996) in all treatments in 1992 and in the higher sludge treatments in 1993 (Table 21) . Rappaport et al. (1988) reported corn earleaf Zn concentrations within the normal range in this study in 1984. Plant tissue Mn concentrations in the higher sludge treatments in 1993 exceeded the nutrient sufficiency range (Table 23), but Mn toxicity symptoms as decribed in the literature review were not observed.

In 1992, plant tissue concentrations of As, Cd, Ni, and Pb were determined to ascertain if yield reductions could be attributed to phytotoxicity of these elements. The normal ranges of As, Cd, Ni, and Pb in corn leaves are respectively: 0.01-1.0, 0.05-0.20, 0.1-10.0 , and 0.1-5.0 mg kg $^{-1}$ (dry weight) (Melsted, 1973). The concentrations of these four elements (not shown) were all < 0.1 mg kg $^{-1}$.

Table 23. Nutrient sufficiency ranges for corn (whole plants, < 30 cm tall) and sorghum at bloom stage (66 - 70 days after planting).

	Corn (Mills and Jones, 1996)	Sorghum (Lockman, 1972 a,b)
Element	------------------------ g kg $^{-1}$ ------------------------	
N	35.0-50.0	33.0-40.0
P	3.0-5.0	2.0-3.5
K	25.0-40.0	14.0-17.0
Ca	3.0-7.0	3.0-6.0
Mg	1.5-4.5	2.0-5.0
S	1.5-5.0	no data
	-------------------------mg kg $^{-1}$ ----------------------	
Cu	5.0-20.0	2.0-7.0
Mn	20.0-300.0	8.0-190.0
Zn	20.0-60.0	15.0-30.0

Copper concentrations in grain were within the normal range of 1 to 5 mg kg^{-1} and were not affected by sludge rate (Table 24). Rappaport et al. (1988) also observed normal Cu concentrations in grain in this study in 1984. Other researchers have reported that Cu concentrations in corn grain remained within the normal range following sludge-amendment (Soon et al., 1980; Lutrick et al., 1982). Normal concentrations of grain Zn are 20-100 mg kg^{-1} (Kirkham, 1975). In this study, normal grain Zn concentrations were observed in 1984 (Rappaport et al., 1988) and in 1992 and 1995 (Table 24). A study on the translocation and accumulation of heavy metals in tissues of corn grown on sludge-treated strip-mined soil showed that the lowest accumulation of Cu and Zn in the corn plant occurred in the grain and cob (Garcia et al., 1979). There is very little translocation of Cu from plant roots to plant shoots (Dragun et al., 1976). It is important that Cu and Zn levels in corn grain are suitable for livestock feeding.

Table 24. Effect of sludge application on copper and zinc concentrations in corn grain.

	Grain Copper Concentration		Grain Zinc Concentration	
Sludge Rate	1992	1995	1992	1995
Mt ha^{-1}	---------------------------- mg kg^{-1} ----------------------------			
0	2.7a*	2.3b	20.6a	13.9b
42	2.6a	2.5b	21.9a	15.8ab
84	2.3a	2.8ab	19.4a	20.1a
126	1.9a	3.1a	15.0a	20.4a
168	2.1a	2.6ab	17.5a	17.0ab
210	2.2a	2.9a	18.8a	17.7ab

* Column means followed by different letters are significantly different at the 0.05 probability level.

Sorghum

Grain sorghum ranked 26th on Virginia's agricultural commodity list in 1994 (Purcell, 1996). Although only about 4,000 hectares have been planted in the state in recent years, grain sorghum could become more important as the state becomes more feedgrain deficient (Purcell, 1996). It is similar to corn in feeding value. It tends to be produced in southern Virginia and planted on acreage where corn does not perform well due to limited rainfall and/or low moisture retention of soil.

The sorghum plant has been referred to as a "crop camel" because it remains practically dormant during periods of drought (Martin et al., 1976). Sorghum can withstand drought better than corn because it has more secondary roots, a smaller leaf area per plant, and its leaves and stalks wilt and dry slower than those of corn (Martin et al., 1976). Dekalb 41Y grain sorghum was planted on the research site on June 21, 1994 to replace drought-affected corn.

Sorghum grain yields were low and, like corn, decreased with sludge application rate (Table 25 and Figure 5). Sorghum grain yield should be 80 - 90% of an adapted hybrid corn yield (Donohue et al., 1984). The average state corn grain yield in 1994 was 6145 kg ha -1 (Virginia Agricultural Statistics Service, 1995). Sorghum grain yields at the 168 and 210 mt ha^{-1} sludge rates were 46 and 35 % respectively, of the state average corn yield (Tables 19 and 25). The highest reported sorghum grain yield in Virginia in 1994 was 10,660 kg ha^{-1}; 6300 kg ha^{-1} was considered to be a good yield that year (Brann, 1995).
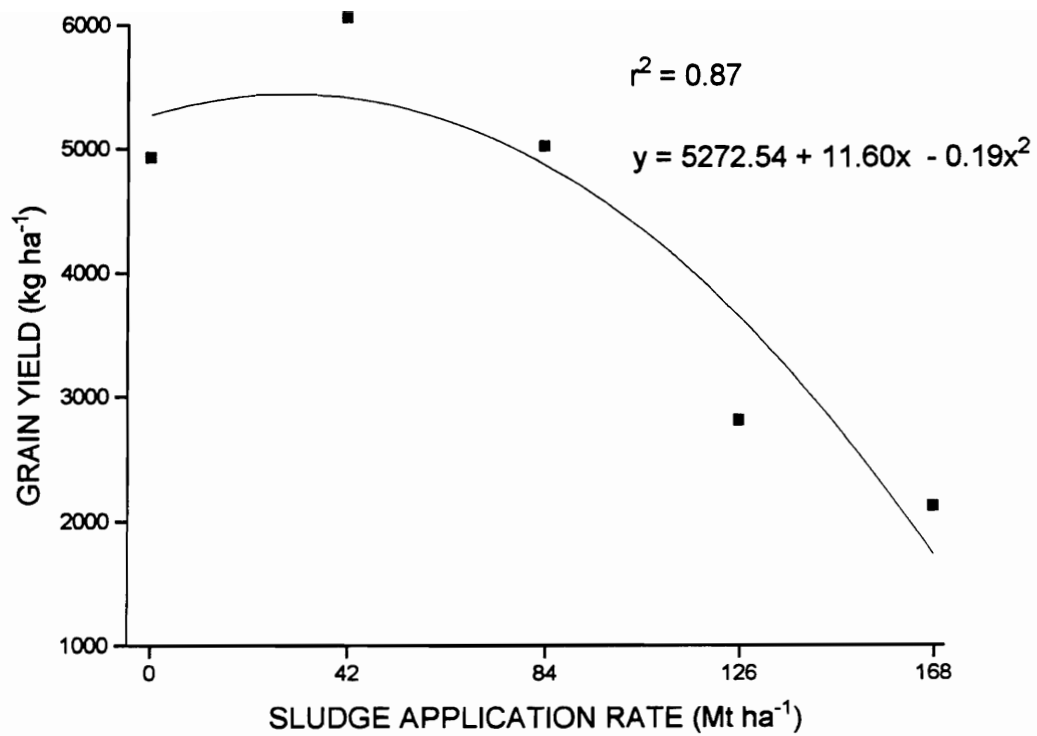
Figure 5. Effect of sludge application on sorghum grain yields 10 years after application (1994) on a Davidson clay loam.

Table 25. Effect of sludge application on sorghum grain and stover yields.

Sludge Application Rate	Sorghum Grain Yield	Sorghum Stover Yield
Mt ha^{-1}	----------------- kg ha^{-1} -----------------	
0	4927.5a*	5567.6abc
42	6056.6a	6578.0a
84	5018.1a	5931.3ab
126	2808.8b	4679.1bcd
168	2118.8b	4045.1cd
210	2146.6b	3254.4d

* Column means followed by different letters are significantly different at the 0.05 probability level.

Nutrient concentrations in sorghum ear leaves were similar to those found in corn: low in K, and high in Cu and Zn (Table 26). Copper and Zn were much lower in sorghum leaves than in corn leaves, an observation also made by Lutrick et al. (1982) in a sludge study conducted on three Ultisols. Potassium levels were below the nutrient sufficiency range and Cu and Zn levels exceeded the nutrient sufficiency ranges (Tables 23 and 26). Manganese concentrations in sorghum leaves, however, did not exceed the sufficiency range (Tables 23 and 26). Grain concentrations of Cu were similar in corn and sorghum, but Zn concentrations were much lower in sorghum (Tables 24 and 27).

Table 26. Nutrient concentration of leaf tissue of sorghum grown ten years after sludge application on a Davidson clay loam.

Sludge Rate	Ca	K	Mg	P	S	Cu	Mn	Zn
Mt ha^{-1}	-------- g kg^{-1} --------					-------- mg kg^{-1} --------		
0	3.0a	11.9a	1.6a	2.8a	1.8b	11.4a	147.4b	27.3c
42	3.1a	12.0a	1.6a	2.8a	1.8b	10.7b	201.3a	39.6b
84	3.2a	12.3a	1.7a	3.1a	1.9ab	13.1a	125.4bc	51.1a
126	2.7a	12.1a	1.6a	3.0a	1.9ab	14.3a	87.6cd	45.0ab
168	3.0a	10.8a	1.8a	3.2a	2.0a	13.9a	72.9d	48.9a

* Column means followed by different letters are significantly different at the 0.05 probability level.

Table 27. Effect of sludge application on copper and zinc concentrations in sorghum grain.

Sludge Application Rate	Grain Copper Concentration	Grain Zinc Concentration
Mt ha $^{-1}$	----------------------- mg kg $^{-1}$ ----------------------------	
0	2.6a*	6.5a
42	3.0a	9.1a
84	2.6a	9.3a
126	3.0a	8.7a
168	1.9a	7.4a
210	3.5a	9.5a

* Column means followed by the same letter are not significantly different at the 0.05 probability level.

Assessment of Phytotoxicity

The author concludes that pH-induced phytotoxicity reduced yields of corn and sorghum at the higher sludge rates applied in this study. Most likely a combination of Al, Cu, Mn, and Zn phytotoxicity contributed to early crop stunting and subsequent yield reductions. Competition of Al^{3+}, Zn^{2+}, Cu^{2+}, and Mn^{2+} ions, all of which occur in higher concentrations at low pH, probably occurred at absorption sites of the roots. The yield decrease was sludge-related since yields decreased with increasing sludge rates. It is possible that the Cu and Zn supplied by the sludge were involved in the yield decrease. Phytotoxic responses of Cu and Zn were once thought to be additive, but later research suggests that the metals act independently in their toxicity (Beckett and Davis, 1982; Davis and Carlton-Smith, 1984; Mitchell et al., 1978). Chaney (1993) asserts that Zn phytotoxicity occurs far more often than Cu phytotoxicity in strongly acidic soils. British sewage sludge loading rates have been based on the assumption that Cu is twice as toxic

as Zn, but Maclean and Dekker (1978) questioned that assumption after they found that sewage sludge eliminated the toxic effect of Cu on corn in pot experiments. The effectiveness of sewage sludge in reducing metal toxic effects was also observed by Chaney (1973) and attributed to strong binding of metals to organic matter. However, organic matter decomposes and can gradually release phytotoxic amounts of metals. Zinc competitively inhibits the uptake of Cu, and vice versa (Mills and Jones, 1991). Small changes in Zn leaf concentration can dramatically affect crop yields (Smith, 1996). Cunningham et al. (1975c) investigated metal phytotoxicity in corn which received Cu and Zn as inorganic salts or amended sludge. They observed the lowest yields with the high Zn treatments. If Cu and Zn toxicity contributed to yield reductions in this study, as suspected, it would be difficult to ascertain which metal played the larger role.

Metal phytotoxicity has occurred in field grown crops when large dressings of highly contaminated sludges have been applied (Smith, 1996). Yield reductions of corn, sorghum-sudangrass (*Sorghum bicolor* L. Moench X S. *sudanese* P. Stapf.), and soybean (*Glycine max* L.) were attributed to Zn and Ni phytotoxicity from repeated sewage sludge applications on a sandy loam (Berti and Jacobs, 1996). They applied sewage sludge at rates ranging from 240 to 870 Mt ha^{-1}, which supplied up to 1,870 kg Cu and 11, 300 kg Zn ha^{-1}. Soil pH levels were maintained between 6.9 and 7.6, which reduced metal phytotoxicity. Yields of all three crops were reduced on one or more sludge treatments, although corn phytotoxicity abated for 5 of the 11 years during the study. Copper phytotoxicity was not a problem in their study because high soil pH levels kept plant Cu concentrations within the normal range. Soil loadings of Zn appeared to be of greater environmental concern than Cu.

It should be noted that Cu and Zn loading rates in this study were well below the phytotoxicity threshholds suggested by Chang et al.(1992). Few, if any, studies have examined Cu and Zn phytotoxicity in corn and sorghum grown under field conditions on

sludge-amended soils with low pH levels. Sludge researchers have attributed decreased availability of Cu and Zn and a reduction in their toxic effects to the maintenance of soil pH values $\geq$ 6.5 (Keeney and Walsh, 1975; Mortvedt and Giordano, 1975; Soon et al., 1980). Raising the pH of field soil increases soil binding of Cu and Zn, and thereby reduces the amount of the plant available Cu and Zn ions (Lexmond and van der Vorm, 1981; Marschner, 1993). Lexmond (1980) observed that the reduction in Cu phytoxicity in corn when the soil pH was raised was less than he predicted. He concluded that the increase in pH increased the toxicity of Cu^{2+} ions in soil solution. Lexmond and van der Vorm (1981) observed this intensification of Cu toxicity with increased pH in a study with hydroponically grown corn. They explained the increased Cu toxicity by the decreased proton concentrations at higher pH, which decreased proton competition with Cu on root sites.

"Acid soil toxicity", as previously described, was carefully considered as the cause of yield reduction. The yields on the control and lower sludge treatments were well above state and Orange County averages, which indicates that the crops were not performing poorly at the low soil pH. Soil pH levels in the control treatment were lower than in the sludge treatments (Table 6). Although "acid soil toxicity" cannot be discarded as a factor in the observed yield reductions, it does not entirely explain the yield decrease.

The reduction in crop growth observed in the high-sludge treatments in this study is indicative of both Cu and Zn toxicity. The concentrations of Cu and Zn in plant tissue, which were higher in the high-sludge treatments, corresponded to the higher amounts of soil Cu and Zn in those treatments. Chang et al. (1992) suggest that leaf tissue may not be the appropriate indicator tissue for Cu phytotoxicity. They pointed out that the specific plant tissue where the toxic action of metals occurs has not been pinpointed and suggested that roots might be an appropriate indicator of metal phytotoxicity. Lexmond and van der Vorm (1981) were able to observe root morphology and growth in a hydroponics study

on the effect of pH on Cu phytotoxicity in corn. As they increased the Cu supply, the Cu content of both roots and shoots increased, with the increase in root Cu more pronounced. A reduction in root surface area and a reduction in the number and length of secondary and tertiary roots were observed at 3.1 μM Cu at pH 4.7. They concluded that the toxic effect of Cu primarily manifested itself by a reduction in root growth. Garcia et al. (1979) also observed a greater accumulation of Cu and Zn in root tissue of corn grown on sludge-amended soil. Copper concentrations in their corn roots, leaves, upper stems, lower stems, husks, cobs, and kernels were 39.6-52.0, 10.3-13.1, 11.0-15.4, 13.0-15.1, 5.3-6.8, 2.8-3.5,and 1.8-2.1 mg kg^{-1} (dry weight), respectively. Zinc concentrations in their corn roots, leaves, upper stems, lower stems, husks, cobs, and kernels were 71.0-74.6, 72.4-84.8, 26.6-95.3, 24.3-43.7, 48.7-34.5, 38.1-33.9, and 27.2-30.4 mg kg^{-1} (dry weight), respectively. It is difficult to remove roots from soil for observation, particularly in the clay subsoil of the soil under study. Observation and analysis of roots in this study would be helpful in diagnosing Al, Cu, Mn, and Zn phytotoxicity and is recommended before termination of the field study.

Conclusions

A sludge-related decrease in corn and sorghum yields occurred every year, 8 to 10 years following sludge application, on a Davidson clay loam. Yield decreases at the higher sludge rates were attributed to a combination of Al, Mn, Cu, and Zn phytotoxicity induced by low soil pH levels. Sludges are an important long-term source of Cu and Zn in agricultural soils. As previously pointed out, phytotoxicity was selected as the most limiting route of environmental exposure in land application of sludge-applied Cu and Zn in the development of the recent Part 503 sludge regulations.

Soil management practices strongly affect the phytotoxicity of Cu and Zn, particularly maintenance of soil pH. The author recommends that in addition to meeting ceiling concentrations and pollutant concentration limits as outlined in current sludge regulations, former USEPA guidelines should be followed as regards the maintenance of soil pH $\geq$ 6.5. Monitoring of soil pH is necessary because various factors such as acidic rainfall and nitrogen fertilization can increase soil acidity and necessitate corrective measures.

Virginia is becoming increasingly deficient in feedgrain production, threatening the economic viability of the state's livestock and dairy sectors (Purcell, 1996). It has been estimated that Virginia's average corn grain yields would have to increase 564 kg ha $^{-1}$ to be competitive on a statewide basis (Purcell, 1996). Improvement in soil moisture retention would improve yields, therefore addition of organic matter via sludge application could assist the state with that competitive increase.

REFERENCES

Adriano, D.C. 1986. Trace elements in the terrestrial environment. Springer-Verlag, New York.

Alrichs, J.L., R.R. Duncan, G. Ejeta, P.R. Hill, V.C. Baligar, R.J. Wright, and W.W. Hanna. 1991. Pearl millet and sorghum tolerance to aluminum in acid soil. p. 947-951. *In*: R.J. Wright et al. (ed.) Plant-soil interactions at low pH. Kluwer Academic Publishers. Norwell, MA.

Amancio, S., A. Lopes, H. Santos, M. Rodrigues, and A. Teixeira. 1991. Behavior of inbred and hybrid maize lines in the presence of aluminum as evaluated by some physiological and biochemical parameters. p. 795-803. *In:* R.J. Wright et al. (ed.) Plant-soil interactions at low pH. Kluwer Academic Publishers .Norwell, MA.

Baker, D.E., and M.C. Amacher. 1982. Nickel, copper, zinc, and cadmium. p. 323-336. *In*: A.L. Page et al., (ed.) Methods of soil analysis. Am. Soc. Agron., Madison, WI.

Beckett, P.H.T., and P. Brindley. 1982. Heavy metals in sludge - are their toxic effects additive? Water Pollution Control 81:112-119.

Bennett, W.F. 1993. Plant nutrient utilization and diagnostic plant symptoms. p. 1-7. *In*: W.F. Bennett (ed.) Nutrient deficiencies and toxicities in crop plants. American Phytopathological Soc., St. Paul, MN.

Bertie, W.R., and L.W. Jacobs. 1996. Heavy metals in the environment. Chemistry and phytotoxicity of soil trace elements from repeated sewage sludge applications. J. Environ. Qual. 25:1025-1032.

Brann, D. E. 1995. Personal communication. Extension grain specialist. Virginia
Polytechnic Institute and State University, Blacksburg, VA.

Chaney, R.L. 1973. Crop and food chain effects of toxic elements in sludges and effluents.
p. 129-141. *In*: Recycling municipal sludges and effluents on land. Nat. Assoc. St.
Univ. and Land-Grant Coll., Washington, D.C.

Chaney, R.L. 1993. Zinc phytotoxicity. p. 135-150. *In*: A.D. Robson (ed.) Zinc in soils
and plants. Kluwer Academic Publishers, Norwell, MA.

Chang, A.C., T.C. Granato, and A.L. Page. 1992. A methodology for establishing
phytotoxicity criteria for chromium, copper, nickel, and zinc in agricultural land
application of municipal sewage sludges. J. Environ. Qual. 21:521-536.

Clark, R.B. 1993. Sorghum. p. 21-26. *In*: W.F. Bennett (ed.) Nutrient deficiencies and
toxicities in crop plants. Am. Phytopathological Soc., St. Paul, MN.

Cunningham, J.D., J.A. Ryan, and D.R. Keeney. 1975a. Phytotoxicity in and metal uptake
from soil treated with metal-amended sewage sludge. J. Environ. Qual. 4:455-460.

Cunningham. J.D., J.A. Ryan, and D.R. Keeney. 1975b. Phytotoxicity and metal uptake of
metal added to soils as inorganic salts or in sewage sludge. J. Environ. Qual. 4:460-
462.

Cunningham, J.D., J.A. Ryan, and D.R. Keeney. 1975c. Metal-amended sewage sludge.
J. Environ. Qual. 4:455-459.

Davis, R.D., P.H.T. Beckett, and E. Wollan. 1978. Critical levels of twenty potentially

toxic elements in young spring barley. Plant Soil 49:395.

Davis, R.D., and C.H. Carlton Smith. 1984. An investigation into the phytotoxicity of zinc, copper, and nickel using sewage sludge of controlled metal content. Environmental Pollution 8: 163-185.

Donohue, S.J., G.K. Evanylo, and D.W. Aho. 1990. Sampling instructions and nutrient sufficiency ranges for plant tissue analysis. Virginia Cooperative Ext. Pub. 452-211. Blacksburg, VA.

Donohue, S.J., R.L. Harrison, and H.E. White. (ed.) 1984. A handbook of agronomy. Virginia Cooperative Ext. Pub. 424-100. Blacksburg, VA.

Donohue, S.J., and S.E. Heckendorn. 1994a. Laboratory procedures: Virginia Tech soil testing and plant analysis laboratory, Virginia Cooperative Ext. Pub. 452-881.

Donohue, S.J., and S.E. Heckendorn. 1994b. Soil test recommendations for Virginia. Virginia Cooperative Extension, Virginia Tech, Blacksburg, VA.

Dragun, J., D.E. Baker, and M.L. Risius. 1976. Growth and elemental accumulation by two single-cross corn hybrids as affected by copper in solution. Agron. J. 68:466-470.

Evans, C.E., and E.J. Kamprath. 1970. Lime response as related to percent Al saturation, solution Al and organic matter response. Soil Sci. Soc. Am. Proc. 34:893-896.

Fox, C.D. 1984. Physiological effects of hydrogen, aluminum, and manganese toxicities in acid soils. p. 57-97. *In*: F. Adams (ed.) Soil acidity and liming. Am. Soc. Agron., Madison, WI.

Galvez, L., and R.B. Clark. 1991. Nitrate and ammonium uptake and solution pH changes for Al-tolerant and Al-sensitive sorghum (*Sorghum bicolor*) genotypes grown with and without aluminum. p. 805-814. In: R.J. Wright et al. (ed.) Plant-soil interactions at low pH. Kluwer Academic Publishers, Norwell, MA.

Garcia, W.J., C.W. Blessin, H.W. Sanford, and G.E. Inglett. 1979. Translocation and accumulation of seven heavy metals in tissues of corn plants grown on sludge-treated strip-mined soil. J. Agric. Food Chem. 27:1088-1094.

Graham, R.D. 1981. Absorption of copper by plant roots. p. 141-163. *In*: J.F. Lonergan et al. (ed.) Copper in soils and plants. Academic Press, Australia.

Halvorsen, A.D., and W.L. Lindsay. 1977. The critical Zn^{2+} concentration for corn and the nonabsorption of chelated zinc. Soil Sci. Soc. Am. J. 41:531.

Hanway, J.J. 1989. Maize. p. 67-72. *In*:Detecting mineral nutrient deficiencies in tropical and temperate crops. Westview Press, Inc., Boulder, CO.

Hodgson, J.F., W.L. Lindsay, and J.F. Trierweiler. 1966. Micronutrient cation complexing in soil solution: II. Complexing of zinc and copper in displaced solution from calcareous soils. Soil Sci. Am. Proc. 30:723-726.

Jarvis, S.C., and D.C. Whitehead. 1981. The influence of some soil and plant factors on the concentration of copper in perennial ryegrass. Plant Soil 60:275-286.

Jones, J.B., Jr., H.V. Eck, and R. Voss. 1990 . Plant analysis as an aid in fertilizing corn and grain sorghum. p. 521-548. *In*: R. L. Westerman (ed.) Soil testing and plant analysis. Soil Sci. Soc. Am., Madison, WI.

Kabota-Pendias, A., and H. Pendias. 1984. Trace elements in soils and plants. CRC Press, Inc., Boca Raton, FL.

Keeney, D.R., and L.M. Walsh. 1975. Heavy metal availability in sewage-sludge amended soils. p. 379-401. *In*: T. C. Hutchinson (ed.) Proc. Int. Conf. Heavy Metals in the Environ. Vol. 2. 25-31 Oct. 1975, Ontario, Canada.

Kirkham, M.B. 1975. Trace elements in corn grain on long-term sludge disposal sites. Environ. Sci. Technol. 9:765-768.

Kochian, L.V. 1993. Zinc absorption from hydroponic solutions by plant roots. p. 45- 57. *In*: A.D. Robson (ed.) Zinc in soils and plants. Kluwer Academic Publishers, Norwell, MA.

Korcak, R.F., and D.S. Fanning. 1985. Availability of applied heavy metals as a function of type of soil material and metal source. Soil Sci. 140: 23-34.

Lexmond, Th. M. 1980. The effect of soil pH on copper toxicity to forage maize grown under field conditions. Neth. J. Agric. Sci. 28:164-183.

Lexmond, Th.M., and F.A.M. de Haan. 1980. Toxicity of copper. p. 410-419. *In*: J.K.R. Gasser (ed.) Effluents from livestock. Applied science Publishers, Ltd., London.

Lexmond,Th.M., and P.D.J. van der Vorm. 1981. The effect of pH on copper toxicity to hydroponically grown maize. Neth. J. Agric. Sci. 29: 217-238.

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley and Sons, New York, NY.

Lindsay, W.L., and W.A. Norvell. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci. Soc. Am. J. 42:421-428.

Lockman, R.B. 1972a. Mineral composition of grain sorghum plant samples. Part 1. Comparative analysis with corn at various stages of growth and under different environments. Commun. Soil Sci. Plant Anal. 3:271-282.

Lockman, R.B. 1972b. Mineral composition of grain sorghum plant samples. Part 3. Suggested and sufficient limits at various stages of growth. Commun. Soil Si. Plant Anal. 3:295-304.

Lonergan, J.F. 1981. Distribution and movement of copper in plants. p. 165-188. *In:* (ed.) Copper in soils and plants. Academic Press, Australia.

Lutrick, M.C., W.K. Robertson, and J.A. Cornell. 1982. Heavy applications of liquid-digested sludge on three Ultisols: II. Effects on mineral uptake and crop yield. J. Environ. Qual. 11: 283-287.

Maclean, A.J., and Dekker, A.J. 1978. Availability of zinc, copper, and nickel to plants grown in sewage-treated soils. Can. J. Soil Sci. 58: 381-389.

Marschner, H. 1991. Mechanisms of adaptation of plants to acid soils. p. 683-702. *In:* R.J. Wright et al. (ed.) Plant-soil interactions at low pH. Kluwer Academic Press, Norwell, MA.

Marschner, H. 1993. Zinc uptake from soils. p. 59-77. *In:* A.D. Robson (ed.) Zinc in soils and plants. Kluwer Academic Publishers, Norwell, MA.

Martin, J.H., W.H. Leonard, and D.L. Stamp. 1976. Principles of field crop production. Macmillan Publishing Co., New York, NY.

McBride, M.B. 1981. Forms and distribution of copper in solid and solution phases of soil. p. 25-45. *In*: J.F. Lonergan et al. (ed.) Copper in soils and plants. Academic Press, Australia.

McKenna, J.R. 1995. Personal communication. Associate Professor. Virginia Poly. Inst. and State Univ., Blacksburg, VA.

McLaren, R.G., and D.V. Crawford. 1973a. Studies on soil copper. I. The fractionation of copper in soils. J. Soil Sci. 24:172-181.

McLaren, R.G., and D.V. Crawford. 1973b. Studies on soil copper. II. The specific adsorption of copper by soils. J. Soil Sci. 24: 443-452.

McLaren, R.G., and D.V. Crawford. 1974. Studies on soil copper. III. Isotopically exchangeable copper in soils. J. Soil Sci. 25: 111-119.

Melsted, S.W. 1973. Soil-plant relationships - some practical considerations in waste management. *IN*: Proceedings joint conference on recycling municipal sludges and effluents in land.Univ. Of Illinois, Urbana, IL.

Mitchell, G.A., F.T. Bingham, and A.L. Page. 1978. Yield and metal composition of lettuce and wheat grown on soils amended with sewage sludge enriched with cadmium, copper, nickel, and zinc. J. Environ. Qual.7: 165-171.

Mills, H.A., and J.B. Jones, Jr. 1996. Plant analysis handbook II. MicroMacro Publishing,

Athens, GA.

Minnich, M.M., M.B. McBride, and R.L. Chaney. 1987. Copper activity in soil solution: II. Relation to copper accumulation in young snapbeans. Soil Sci. Soc. Am. J. 51:573-578.

Mortvedt, J.J., and P.M. Giordano. 1975. Response of corn to zinc and chromium in municipal wastes applied to soil. J. Environ. Qual. 4: 170-174.

Purcell, W. 1996. The economic position of Virginia agriculture: Mid 1990s. Special Report March 1996. Virginia's Rural Economic Analysis Program. Virginia Polytechnic Institute and State University, Blacksburg, VA.

Rappaport, B.D., D.C. Martens, R.B. Reneau, Jr., and T.W. Simpson.1988. Metal availability in sludge-amended soils with elevated metal levels. J. Environ. Qual. 17:42-47.

Reed, S.T., and D.C. Martens. 1996. Copper and Zinc. p. 703-722. *In*: Methods of Soil Analysis. Part 3. Chemical Methods - SSSA Book seies no. 5, Soil Sci. Soc. Am. And Am. Soc. Agron., Madison, WI.

Reuter, D.J. and J.B. Robinson. (ed.) 1986. Plant analysis: an interpretation manual. Inkata Press, Sydney and Melbourne, Australia.

Robson, A.D., and D.J. Reuter. 1981. Diagnosis of copper deficiency and toxicity. p. 287-312. *In:* J.F. Lonergan et al. (ed.) Copper in soils and plants. Academic Press, Australia.

Robson, A.D., and K. Snowball. 1986. Nutrient deficiency and toxicity symptoms. p. 13-19. *In:* D.J. Reuter and J.B. Robinson (ed.). Plant analysis: an interpretation manual. Inkata Press, Melbourne and Sydney, Australia.

Smith, S.R. 1996. Agricultural recycling of sewage sludge and the environment. CAB International, Wallingford, UK.

Soon, Y.K., T.E. Bates, and J.R. Moyer. 1980. Land application of chemically treated sewage sludge: III. Effects on soil and plant heavy metal content. J. Environ. Qual. 9: 497-504.

Sparks, D.L. 1995. Environmental soil chemistry. Academic Press, NY.

Sposito, G. 1981. The operational definition of the zero point of charge in soils. Soil Sci. Soc. Am. J. 45:292-297.

Soon, Y.K., T.E. Bates, and J.R. Moyer. 1980. Land application of chemically treated sewage sludge: III. Effects on soil and plant heavy metal content. J. Environ. Qual. 9:497-504.

Steele, R.G.D., and J.H. Torrie. 1980. Principles and procedures of statistics - A biometrical approach. Second Ed., McGraw-Hill, Inc., New York, NY.

U.S. Environmental Protection Agency. 1983. Process design manual for land application of municipal sludge. USEPA Rep. EPA-625/1-83-016. U. S. Gov. Print. Office, Washington, DC.

U.S. Environmental Protection Agency. 1993. Standards for use or disposal of sewage

sludge. Final Rule, 40 CFR Part 503. U.S. Gov. Print. Office, Washington, DC.

Virginia Agricultural Statistics Service. 1993. Virginia agricultural statistics:1992 annual bulletin. Bulletin No. 64. Virginia Agricultural Statistics Service, Richmond, VA.

Virginia Agricultural Statistics Service. 1994. Virginia agricultural statistics:1993 annual bulletin. Bulletin No. 64. Virginia Agricultural Statistics Service, Richmond, VA.

Virginia Agricultural Statistics Service. 1995. Virginia agricultural statistics:1994 annual bulletin. Bulletin No. 64. Virginia Agricultural Statistics Service, Richmond, VA.

Virginia Agricultural Statistics Service. 1996. Virginia agricultural statistics:1995 annual bulletin. Bulletin No. 64. Virginia Agricultural Statistics Service, Richmond, VA.

W-170 Peer Review Committee. 1989. Peer review of standards for the disposal of sewage sludge (USEPA Proposed Rule 40 CFR Part 503) USDA-CSRS W-170 Regional Research Committee. USDA, Washington, DC.

Chapter 4

COPPER ADSORPTION ON A SLUDGE-AMENDED DAVIDSON CLAY LOAM

LITERATURE REVIEW

Adsorption of Cu in soils is influenced by the clay mineralogy and organic matter content of the soil and the Cu concentration, pH, and ionic strength of the soil solution. In this study, the long-term effects of sludge amendment on Cu adsorption were investigated. The effect of pH on Cu adsorption was considered important to this study because of the low soil pH levels that were investigated. The effect of ionic strength on Cu adsorption was researched as well.

The edges of layer silicate clays provide adsorption sites for heavy metals, but to a lesser extent than oxides of Fe, Al, and Mn (McBride, 1994). Adsorption of Cu on hydrous oxides of Al, Fe, and Mn has been reported for some time (Ellis and Knezek, 1972). It has been proposed that metal availability is controlled mainly by interactions with Fe and Mn hydroxides (Jenne, 1968). King (1988) determined that metal retention in several southeastern United States soils was related to Fe oxide content. A selective adsorption of heavy metals to the oxygen and hydroxyl surface groups of Fe oxides occurs

because they readily form hydroxy species (Bell et al., 1991). The specific adsorption of metal cations in soil clays increases with pH (McBride, 1994). Copper has a higher affinity for Fe oxides than Zn and a greater affinity for Al oxides than other heavy metals (McBride,1989).

The role of soil organic matter on heavy metal retention has been widely studied. Soil organic matter consists mainly of humic and fulvic acids, which are involved in complexation with heavy metals. The sorption of Cu on humic acids ranges from 48 to 160 mg Cu g^{-1} (Stevenson and Fitch, 1981). Copper complexes of fulvic acids are more soluble than those of humic acids (Stevenson and Fitch, 1981). Temminghoff et al. (1994) reported that at low pH (4.4) Cu was predominately bound by the fulvic fraction of the soil and at pH 5.7 by the humic fraction of the soil.

Soil organic matter contains many different types of functional groups, such as carboxylic, phenolic, amine, and carbonyl groups, that are involved in metal adsorption. Generally Cu is considered to undergo an inner-sphere complexation with functional groups of organic matter (McBride, 1994). Copper has a greater ability to form complexes with organic matter than other heavy metals (McBride, 1994). Trivalent cations of Al and Fe form stronger complexes with organic matter than Cu and can reduce Cu adsorption through competition for binding sites (Stevenson and Fitch, 1981). The desorption of Cu from organic matter is several orders of magnitude slower than adsorption (McBride, 1994).

The Langmuir equation was chosen to model the adsorption data in this research. The equation was developed in 1918 to describe the adsorption of gasses on a clean solid (Langmuir, 1918). Soil scientists began using the equation in the 1950s (Fried and Shapiro, 1956; Olsen and Watanabe, 1957) and by the mid 1970s it was extensively used to model adsorption in soils. The Langmuir equation has been popular because it provides

a theoretical adsorption maximum and a coefficient theoretically related to bonding energy. The limitations of the Langmuir equation for soil scientists, many of which had been overlooked, began to appear in publications in the late 1970s and early 1980s (Griffin and Au, 1977; Harter and Smith, 1981; Veith and Sposito, 1977; and Sposito, 1982).These limitations include:

1. It cannot apply to sorption phenomena governed by a solubility product,

2. It describes precipitation data as well as it does adsorption data, and

3. Ions in solution are not independent in their action.

Despite these limitations, the equation has been used by a large number of soil scientists with apparent success, with adsorption maxima approximating actual adsorption (Harter and Smith, 1981).

MATERIALS AND METHODS

The batch-adsorption or static-equilibrium technique was used to assess the capacity of the soil to adsorb Cu. This technique involves mixing a determined mass of adsorbent with an aqueous solution containing known concentrations of solute for a determined period of time. The solution is analyzed after it is separated from the adsorbent to determine the amount of solute adsorbed. The difference between solute concentration before contact with the adsorbent and after mixing (the equilibrium concentration) is assumed to be the amount of solute adsorbed. Guidelines made by the USEPA for conducting this procedure were consulted (Roy et al., 1991). Two methods of the batch-adsorption technique were used for comparison: the constant soil:solution ratio method and the variable soil:solution ratio method (Roy et al., 1991). The data generated was used to construct equilibrium adsorption isotherms. The effects of soil pH and ionic strength on Cu adsorption were investigated in this research.

Adsorbent Preparation

Description of the soil used in this study, a Davidson clay loam, can be found in Chapter 2. Soil from the 0, 42, and 210 Mg dry sludge ha^{-1} treatments were utilized in the adsorption studies. We obtained 1.02 kg soil per field plot from the 0-to 15-cm depth of the surface horizon. Soil from the four replication plots of each treatment were combined, yielding a total of 4.1 kg soil per treatment. The soil was air-dried rather than oven-dried to minimize changes that can occur from oven-drying. Such changes include increases in pH (Van Lierop and Mackenzie, 1977; Raveh and Avnimelech, 1978), hydrophobicity (Debano and Hamilton, 1976), and both cation and anion exchange capacity (Harada and Wada, 1974). The soil was ground to pass a 2-mm sieve.

Solute Preparation

Copper adsorption was determined using a range of 0 to 100 μg ml $^{-1}$ Cu in the constant soil:solution ratio method and a single concentration of 100 ug ml $^{-1}$ Cu in the variable soil:solution ratio method. Copper was supplied as $Cu(ClO_4)_2$. A background electrolyte, 0.02 M $NaClO_4$, was added to the $Cu(ClO_4)_2$ solution to reduce the formation of ion pairs. Both synergistic and antagonistic effects have been observed with the use of background electrolytes in some soil-solute systems (Roy et al., 1991). The effect of the background electrolyte on Cu adsorption was investigated in an ionic strength study in this research.

Methods of Mixing and Phase Separation

The mechanical devise used to agitate the solid-liquid mixture during the equilibration period was a reciprocating water bath shaker (Precision Model 50). The mixture was agitated at 29 rpm at $25 \pm 0.5°C$. Tubes were placed in a horizontal position to permit adequate mixing. Solid and liquid phases were separated by centrifugation

Analyses of Equilibrated Solutions

After centrifugation, the pH of the equilibrated solution was measured. The electrical conductivity of the equilibrium solution was also measured using a conductivity meter with a cell constant of 0.609. The ionic strength of equilibrated soil-solution can be estimated by the equation

$$I = 0.0127 \times EC \quad \text{(Griffin and Jurinak, 1973)}$$

where I = ionic strength in mol L^{-1}, and

EC = electrical conductivity in dS m $^{-1}$.

The USEPA Technical Resource Document for batch-type procedures emphasizes that failure to measure and report pH and EC data can make adsorption data difficult to interpret (Roy et al., 1991). The supernatant was then filtered through Whatman # 42 filter paper and analyzed by atomic absorption spectrophotometry.

Determination of Soil:Solution Ratio

Measurable, statistically significant differences in equilibrium concentrations are required for construction of adsorption isotherms. The selection of a soil:solution ratio that permits sufficient adsorption of the solute for such measurable differences is necessary. If the soil:solution ratio is too high, small differences in concentration between large amounts of solute will be measured. If the ratio is too low, small differences in concentration between small amounts of solute will be measured (Roy et al., 1991).

The soil:solution ratio for this study was determined by the procedure recommended by the USEPA for ionic solutes for the batch-type adsorption technique (Roy et al., 1991). In this procedure a series of soil:solution ratios ranging from 1:4 to 1:500 are tested and evaluated for solute adsorption. The soil:solution ratio is considered to be the oven-dry equivalent mass of adsorbent (g) per volume (ml) of solution. Two replications of soil from treatments receiving 0 (control) and 210 (high-sludge) Mt dry sludge ha^{-1} were used in this procedure. The moisture content of air-dried soil was calculated with 10-g subsamples dried at 105°C for 24 hours. The air-dry soil mass equivalent to the desired mass of oven-dried soil was then determined for each of the ratios (Table 28) using the following equation:

$$A = M_s [1 + (M/100)]$$

where   A = air dry soil mass (g),

M_s = mass of oven-dried soil desired (g), and

M = percent moisture.

The volume of solution containing the solute was 80 ml, a decision based on the availability of 100-ml polypropylene centrifuge tubes for use in this study.

Table 28. Soil-solution ratios evaluated in determination of an appropriate soil:solution ratio for Cu adsorption studies on a sludge-amended Davidson clay loam.

Sludge Rate	Soil-Solution Ratio	Air-dry Soil Weight	Oven-dry Soil Equivalent	Solution Volume
Mt ha^{-1}	g ml^{-1}	------------------ g -----------------		ml
0	1:4	20.41	20.00	80
	1:5	16.33	16.00	80
	1:10	8.16	8.00	80
	1:20	4.08	4.00	80
	1:40	2.04	2.00	80
	1:60	1.36	1.33	80
	1:100	0.82	0.80	80
	1:200	0.41	0.40	80
	1:500	0.16	0.16	80
210	1:4	20.53	20.00	80
	1:5	16.43	16.00	80
	1:10	8.21	8.00	80
	1:20	4.11	4.00	80
	1:40	2.05	2.00	80
	1:60	1.37	1.33	80
	1:100	0.82	0.80	80
	1:200	0.41	0.40	80
	1:500	0.16	0.16	80

Four replications of each treatment were used for isotherm data. Eighty ml of a Cu $(ClO_4)_2$ /$NaClO_4$ solution containing 100 μg ml^{-1} Cu was added to the weighed soil. This procedure recommends that the highest solute concentration that will be utilized in the adsorption studies be used to determine the soil:solution ratio. We selected 100 μg ml^{-1} Cu based on a study conducted by Zhu et al. (1991). In that study, up to 100 μg ml^{-1} Cu was used to determine Cu adsorption on a clay loam amended with Cu-enriched hog manure. The adsorption maxima for that soil was 69.0 μg g^{-1}.

The soil:solution mixture was continuously agitated for 24 hours at 25° C, centrifuged, filtered, and analyzed as previously described. Adsorbed Cu was calculated by subtracting the equilibrium concentration from the initial concentration. The USEPA recommends the use of a soil:solution ratio that produces a value of 10% to 30% adsorption (Roy et al., 1991). They assert that adsorption in this range provides statistically acceptable data for the construction of adsorption isotherms. The percent of solute adsorberd was calculated using the equation

$$\%A = \frac{(Co - C)}{Co} \; X \; 100 \quad \text{(Roy et al., 1991)}$$

where %A = percent adsorbed,

   Co = initial solute concentration (μg ml^{-1}), and

   C = solute concentration after contact with the adsorbent.

The amount of Cu adsorbed by the control and highest sludge treatment soils is presented in Table 29. The pH and electrical conductivity of the equilibrium solutions were measured (Table 30 and 31). A soil:solution ratio of 1:100, which generated between 10% and 30% adsorption for both treatment soils, was selected (Table 28). This ratio was used to determine equilibration time and construct constant soil:solution isotherms.

Table 29. Copper adsorption on control and high-sludge treatment soils at various soil:solution ratios.

Soil:Solution Ratio	Replication	Percent Cu Adsorbed	
		Control Soil	High-Sludge Soil
1:4	A	95.2	99.1
	B	95.1	99.1
1:5	A	92.4	98.6
	B	92.4	98.7
1:10	A	76.6	94.9
	B	76.3	94.7
1:20	A	54.5	80.1
	B	55.1	79.3
1:40	A	34.5	54.5
	B	33.4	55.1
1:60	A	25.8	41.2
	B	26.4	41.5
1:100	**A**	**17.7**	**27.8**
	B	**17.0**	**28.1**
1:200	A	12.5	16.9
	B	10.5	17.7
1:500	A	6.5	9.6
	B	7.2	10.6

Table 30. Levels of pH measured in equilibrated solutions used in determination of a soil:solution ratio for Cu adsorption studies.

Soil:Solution Ratio	pH of Equilibrated Solution			
	Control Soil		High-sludge Soil	
	Replication A	Replication B	Replication A	Replication B
1:4	4.47	4.41	4.95	4.93
1:5	4.41	4.41	4.88	4.91
1:10	4.31	4.33	4.72	4.73
1:20	4.29	4.30	4.55	4.53
1:40	4.29	4.31	4.44	4.46
1:60	4.29	4.29	4.40	4.41
1:100	4.28	4.28	4.37	4.38
1:200	4.32	4.33	4.40	4.39
1:500	4.42	4.42	4.41	4.41
Blank	4.71	4.71	4.62	4.61

Table 31. Electrical conductivity measurements of equilibrated solutions used in determination of a soil:solution ratio for Cu adsorption studies.

Soil:Solution Ratio	Electrical Conductivity of Equilibrated Solution (dS m^{-1})			
	Control Soil		High-Sludge Soil	
	Replication A	Replication B	Replication A	Replication B
1:4	2.68	2.74	2.74	2.78
1:5	2.65	2.67	2.71	2.71
1:10	2.64	2.62	2.65	2.65
1:20	2.61	2.54	2.62	2.62
1:40	2.57	2.52	2.60	2.58
1:60	2.55	2.52	2.57	2.58
1:100	2.58	2.58	2.58	2.58
1:200	2.54	2.54	2.54	2.56
1:500	2.54	2.54	2.53	2.51
Blank	2.59	2.60	2.60	2.58

Determination of Equilibrium Time

The equilibration time in batch-adsorption experiments is reached when the concentrations of products and reactants no longer change with respect to time (Roy et al., 1991). This experimental variable needs to be determined for any system before generating data for adsorption isotherms. Adsorption is usually a fast process and it is difficult to determine over time whether adsorption, penetration, or preciptation of an ionic solute is occurring with soil adsorbents (Roy et al., 1991). The USEPA (1982; 1991) recommends that the equilibration time should be the minimum amount of time required for $\leq 5\%$ change in solution concentration per 24 hour time interval. Six agitation intervals were evaluated to determine equilibration time: 0.5, 1, 4, 12, 24, 48, and 72 hours. The change in solute concentrations was determined using a 1:100 soil:solution ratio in the manner described previously for determining soil:solution ratio. The rate of change in the solute concentrations at the various agitation intervals was calculated with the following:

$$\%_\Delta C = \frac{(C_1 - C_2)}{C_1} \; X \; 100$$

where $\%_\Delta C$ = percent change,

C_1 = concentration of the solute before agitation, and

C_2 = concentration of the solute after agitation for a given time interval.

The rate of change in the solute concentration for soils from the 0 (control), 42 (low-sludge), and 210 (high-sludge) Mg dry sludge ha^{-1} treatments were determined using two

replications (Table 32). The minimum time required for $\leq$ 5% change in solute concentration was one hour (Table 32). However, an equilibration period of 24 hours was chosen for the following reasons: similar Cu adsorption studies have used 24 hours (Zhu et al., 1991; Reed, 1993), only a few μg Cu ml^{-1} difference in equilibrium solute concentration were observed between 1 hour and 24 hour agitation intervals, the rate of change of the solute concentration at 24 hours for all treatments was < 5%, and it was convenient. The pH and electrical conductivity of the equilibrated solutions were measured (Table 33 and 34).

Table 32. Rate of change in solute concentrations of equilibrated solutions at various agitation intervals.

	Equilibrium Solute Concentration			Change in Solute Concentration		
Agitation Time	Control	Low Sludge	High Sludge	Control	Low Sludge	High Sludge
h	---------------- μg ml^{-1} ----------------			--------------------%--------------------		
0.0	100.0	100.0	100.0	-------	-------	-------
0.5	86.5	82.5	80.1	13.5	17.2	19.9
1.0	87.8	84.5	80.3	0.6	- 0.1	3.8
4.0	87.5	83.0	77.7	0.3	1.8	0.0
12.0	85.5	81.4	77.2	2.3	1.9	0.6
24.0	84.3	80.6	75.6	1.4	1.0	2.1
48.0	85.8	80.8	75.1	-1.7	-0.2	0.7
72.0	86.0	80.8	73.7	-0.2	0.0	1.9

Table 33. Levels of pH in equilibrated solutions used in determination of an equilibration time for Cu adsorption studies.

Agitation time (h)	Average pH of Equilibrated Solution		
	Control	Low-Sludge	High-Sludge
0.5	4.19	4.36	4.32
1.0	4.16	4.31	4.31
4.0	4.15	4.29	4.32
12.0	4.19	4.39	4.35
24.0	4.20	4.39	4.35
48.0	4.19	4.34	4.35
72.0	4.19	4.34	4.34

Table 34. Electrical conductivity of equilibrated solutions used in determination of equilibration time for Cu adsorption studies.

Agitation Time (h)	Electrical Conductivity of Equilibrated Solution (dS m^{-1})		
	Control	Low-Sludge	High-Sludge
0.5	2.46	2.50	2.51
1.0	2.50	2.51	2.52
4.0	2.48	2.47	2.46
12.0	2.36	2.50	2.48
24.0	2.44	2.64	2.58
48.0	2.45	2.64	2.72
72.0	2.42	2.41	2.42

Constant and Variable Soil:Solution Ratio Methods

Two experimental methods were used to generate batch-adsorption data: the constant soil:solution ratio method and the variable soil:solution ratio method. The two methods were compared in the determination of long-term effects of sludge amendment on Cu adsorption. An isotherm produced by variable soil:solution ratios is considered to be more environmentally conservative and is referred to as an environmentally conservative isotherm (ECI) (Roy et al., 1991). An isotherm produced by the constant soil:solution ratio method is referred to as a constant soil:solution ratio isotherm (CSI).

In the constant soil:solution method, the amount of adsorbent is kept constant and solutions with progressively decreasing solute concentrations are mixed with the adsorbent. This has been the most common method used in batch-adsorption studies. In the variable soil:solution method, the solute concentration is held constant and increasing amounts of adsorbent are mixed with the solute solutions. The USEPA recommends the ECI as the method of choice for batch-adsorption studies (Roy et al., 1991)

A soil:solution ratio of 1:100 and Cu concentrations ranging from 0 to 100 μg Cu ml^{-1} were used in the constant soil:solution method. A Cu concentration of 100 μg Cu ml^{-1} and soil:solution ratios of 1:4, 1:10, 1:20, 1:40, 1:60, 1:100, 1:200, and 1:500 were used in the variable soil:solution method.

Construction of Adsorption Isotherms

The USEPA guidelines for construction of both CSI and ECI isotherms (Roy et al., 1991) were used in this research. Six data points were used to construct the ECI - a minimum of 5 data points are recommended. Soil:solution ratios which generated < 10% adsorption of the solute were not used for the ECI, as recommended. A

soil:solution ratio of 1:100, which generated between 10% and 30% solute adsorption, was used to construct the CSI, as recommended.

The amount of solute adsorbed by the adsorbent was calculated with the following equation:

$$x/m = \underline{C_o - C} \ (V) \qquad \text{(Roy et al., 1991)}$$
$$m$$

where   x/m = amount of solute adsorbed per unit mass of adsorbent in $\mu g \ g^{-1}$,

m = mass of adsorbent (oven-dried basis) in g,

C_o = initial solute concentration before contact with adsorbent in $\mu g \ ml^{-1}$,

C = equilibrium solute concentration after contact with adsorbent, and

V = volume of solute solution in ml.

In the construction of the isotherms, the equilibrium concentration (C) was plotted on the x axis and the amount of adsorbed solute (x/m) was plotted on the y axis. The linear form of the Langmuir equation was used to model the adsorption data:

$$\frac{C}{x/m} = \frac{1}{V_m b} + \frac{C}{V_m}$$

where   C = the equilibrium concentration of Cu in solution,

x/m = Cu adsorbed per unit mass of soil (μg Cu g^{-1} soil),

V_m = the adsorption capacity (adsorption maximum), and

b = the coefficient related to the bonding energy.

pH Study

The pH of the soil was altered to ascertain the effect of pH on Cu adsorption on the Davidson clay loam. Soil from the 0, 42, and 210 Mg dry sludge ha^{-1} treatments were used in this study. One hundred g subsamples of soil were amended with $Ca(OH)_2$ at rates of 896, 1792, 2688, 3584, and 5040 kg ha^{-1} and $AlSO_4$ at rates of 1344 and 5376 kg S ha^{-1}. The soils were wet with deionized distilled water and allowed to dry continuously over a period of four weeks.

Ionic Strength Study

The concentration of the background electrolyte, $NaClO_4$, was varied in this study to determine the effects of ionic strength on Cu adsorption on the Davidson clay loam. Soil from the 0, 42, and 210 Mg dry sludge ha^{-1} treatments were used. Background electrolyte concentrations of 0, 0.02, and 0.05 M were compared.

RESULTS AND DISCUSSION

Adsorption is a very complicated process. There is a continuum between low surface coverage where surface complexation dominates (adsorption) and high surface coverage where precipitation dominates (Sparks, 1995). Precipitation may be reflected in the adsorption isotherms generated in this study. Sparks (1995) states that one cannot differentiate between adsorption and precipitation using adsorption isotherms. The Langmuir equation used to model adsorption in this study describes precipitation as well as it describes adsorption (Veith and Sposito, 1977). The adsorption isotherms presented herein should provide a good estimate of Cu retention in the soil because Cu is tightly bound through inner-sphere comlexation in adsorption and Cu precipitates are very insoluble. Adsorption maxima obtained with the Langmuir equation are considered applicable for soil scientists (Harter and Baker, 1977). The adsorption maxima presented herein should have practical significance in determining Cu loading rates for sludge application, particularly under low soil pH conditions.

Long-Term Effects of Sludge Amendment on Copper Adsorption

Long-term effects of sludge-amendment were observed in the adsorption study. Adsorption of Cu increased with an increase in sludge rate (Figures 6 and 7). This increase is attributed to the higher soil organic matter levels in the sludge treatments (Table 8). Organic matter is a very important sorbent for metals in soil because of its high specific surface and high CEC. The specific surface of soil organic matter can be as great as 800-900 $m^2 g^{-1}$ (Sparks, 1995) and it has been estimated that up to 80% of soil CEC is due to organic matter (Stevenson, 1982). Zhu et al. (1991) reported that soils amended with Cu-enriched hog manure had increased Cu sorptive capabilities, which was attributed
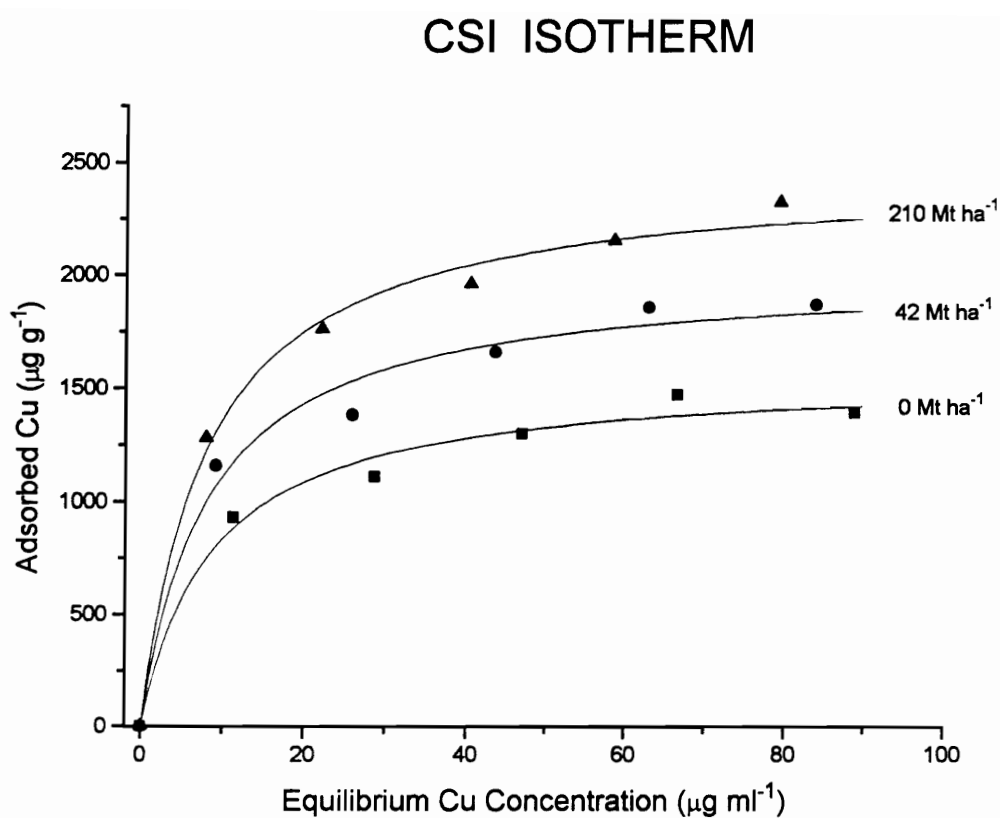
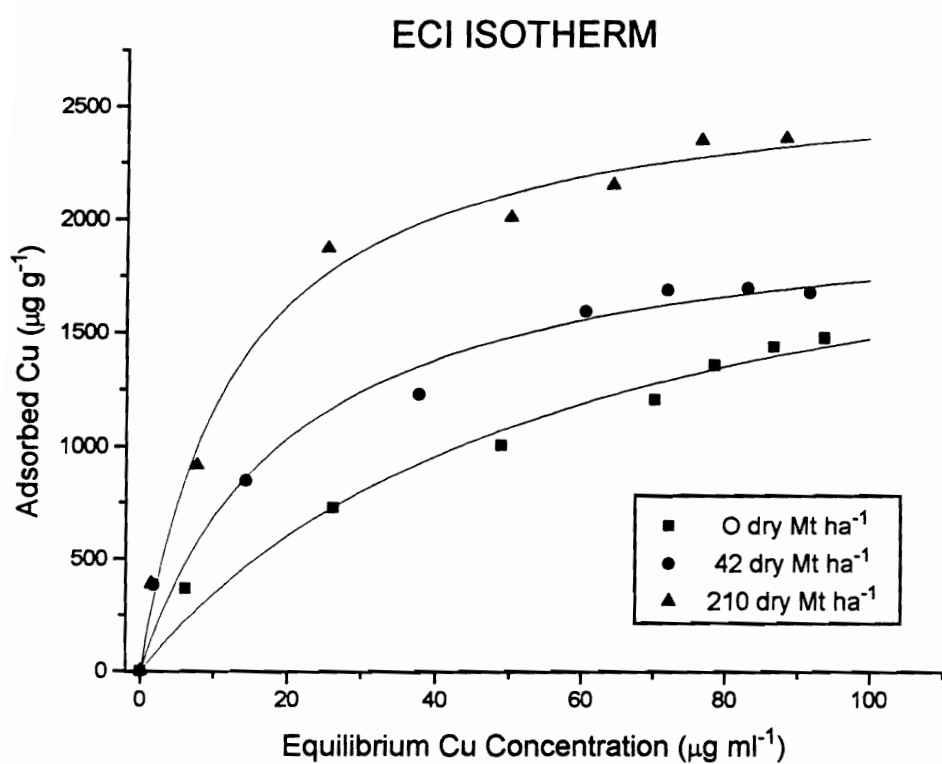Figure 6. Long-term effect of sludge amendment on Cu adsorption (CSI method).

Figure 7. Long-term effect of sludge amendment on Cu
adsorption (ECI method).

to higher organic matter levels in manure-amended soils. Karapanagiotis et al. (1991) reported that addition of sludge organic matter enhanced Cu retention in a sludge-amended soil and that Cu was bound stronger than Zn with organic substances.

Copper adsorption varied between the constant soil:solution ratio (CSI) and variable soil:solution ratio (ECI) methods used to evaluate long-term sludge effects on Cu adsorption (Figures 6 and 7). The ECI method did not, as expected from USEPA recommendations (Roy et al., 1991), yield the most environmentally conservative estimate of the soil's capacity to adsorb Cu. The adsorption maxima obtained with the ECI isotherm were higher in all treatments than those obtained with the CSI isotherm (Table 35), particularly in the unamended control treatment. However, the equilibrium concentrations of Cu with a 1:100 soil:solution ratio and 100 μg ml^{-1} solute concentration were similar between the two methods (Table 36). The adsorption maxima for the unamended control soils obtained by both methods (Table 35) reveal that the Davidson clay loam has a high adsorption capacity for Cu. The retention of metals by several soils of the southeastern United States, including a Davidson soil, was studied by King (1988). He found that the Davidson soil was superior to the organic soils in metal retention and explained his findings by a strong relation between Fe oxide content and metal retention. Electrical conductivity and pH measurements of the equilibrated solutions in the CSI and ECI methods are presented in Tables 36-40.

Table 35. Copper adsorption maxima obtained from the Langmuir model by the CSI and ECI methods.

Sludge rate	CSI Method		ECI Method	
Mt ha^{-1}	μg Cu g^{-1}	kg Cu ha^{-1}	μg Cu g^{-1}	kg Cu ha^{-1}
0	1554.8	3482.7	2302.4	5157.3
42	2009.5	4501.3	2083.6	4667.3
210	2450.4	5488.9	2662.1	5963.1

Table 36. Comparison of equilibrium Cu concentrations (μg ml^{-1}) between CSI and ECI methods (1:100 soil:solution ratio and 100 μg ml^{-1} solute concentration).

Method	Control	Low-Sludge	High-Sludge
CSI	89.8	85.3	79.7
ECI	86.7	83.1	76.6

Table 37. Levels of pH in equilibrated solutions used in the CSI method.

Concentration of Solute (Cu)	Equilibrium pH		
μg ml^{-1}	Control	Low-Sludge	High-Sludge
0	5.27	5.72	5.68
20	4.46	4.78	4.76
40	4.62	4.63	4.69
60	4.62	4.54	4.57
80	4.94	4.49	4.49
100	4.92	4.44	4.42

Table 38. Electrical conductivity in equilibrated solutions used in the CSI method.

Concentration of Solute (Cu)	Equilibrium Electrical Conductivity (dS m^{-1})		
μg ml^{-1}	Control	Low-Sludge	High-Sludge
0	2.05	2.20	2.23
20	2.17	2.21	2.19
40	2.20	2.27	2.20
60	2.40	2.37	2.44
80	2.47	2.52	2.50
100	2.51	2.55	2.60

Table 39. Levels of pH in equilibrated solutions used in the ECI method.

Soil:Solution Ratio	Equilibrium pH		
	Control	Low-Sludge	High-Sludge
1:4	3.93	4.01	4.12
1:10	3.80	3.92	3.99
1:20	3.83	3.94	3.91
1:40	3.85	3.91	3.93
1:60	3.85	3.94	3.93
1:100	4.02	4.06	4.02
1:200	3.95	4.03	4.03
1:500	4.00	3.96	4.02

Table 40. Electrical conductivity of equilibrated solutions used in the ECI method.

Soil:Solution Ratio	Equilibrium Electrical Conductivity (dS m^{-1})		
	Control	Low-Sludge	High-Sludge
1:4	2.75	2.71	2.91
1:10	2.73	2.71	2.76
1:20	2.72	2.72	2.71
1:40	2.73	2.72	2.75
1:60	2.67	2.63	2.65
1:100	2.63	2.63	2.51
1:200	2.73	2.70	2.70
1:500	2.78	2.78	2.80

Effect of pH on Copper Adsorption

An increase in Cu adsorption was observed with increased pH in all of the treatments (Figures 8-10). This pH effect on Cu adsorption has been observed by others (Kishk and Hassan, 1973; Forbes, 1976; McBride and Blasiak, 1979; Kuo and Baker, 1980; Sanders, 1982; Reed, 1993). As the soil pH increases, the negative charge increases due to deprotonation or dissociation of H$^+$ from functional groups of organic matter and from edges of kaolinite surfaces (Sparks, 1995). Kishk and Hassan (1973) investigated sorption of Cu by clay minerals as a function of pH and reported that kaolinite retained more Cu than its CEC at pH values above 5.0. The mineralogy of the Ap horizon of the soil under study is dominated by kaolinite and the organic matter levels in all of the treatments are in the high to very high range, therefore there should have been a considerable increase in negative charge with increased pH. The variable charge of the Fe oxides, which also adsorb Cu, contributed to the increased Cu adsorption with increased pH. Sanders (1982)

also observed an increase in Cu adsorption with increasing pH. He reported that the proportion of Cu present as cupric ion decreased with pH increase. The cupric ion is generally assumed to be the most plant available species of Cu, therefore it plays an important role in Cu phytotoxicity.

Regardless of pH, Cu adsorption increased with sludge rate. A comparison of Cu adsorption between the treatments is depicted at a pH range of 4.5-4.9 in Figure 11. Electrical conductivity and pH measurements of the equilibrated solutions in the pH study are presented in Tables 41-46.
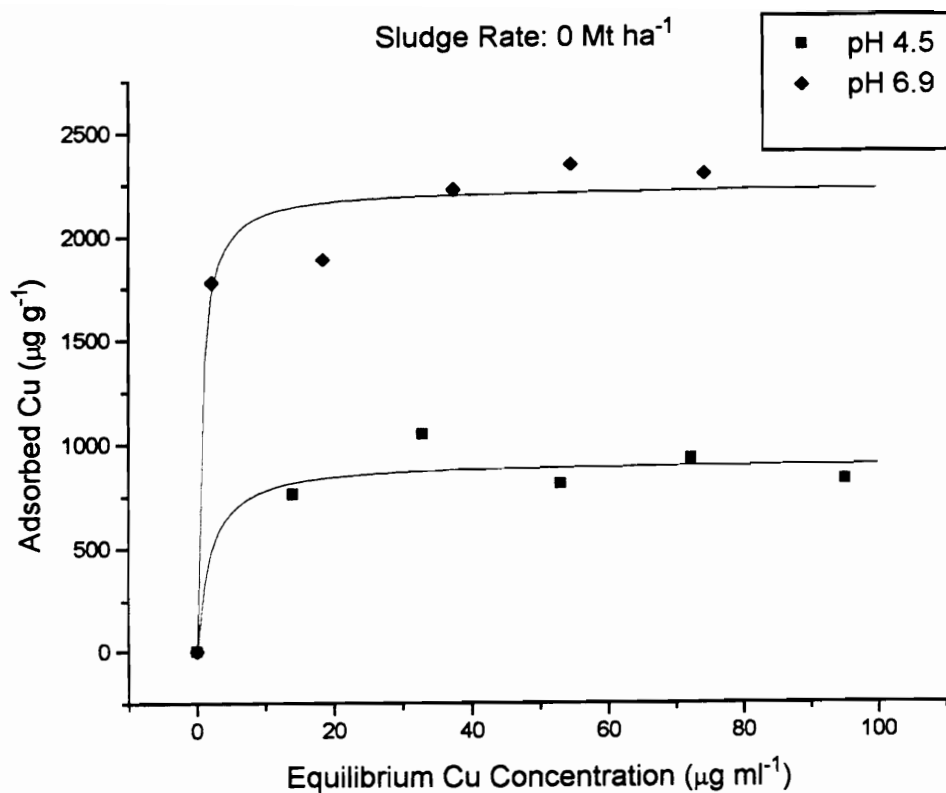
Figure 8. Effect of pH on Cu adsorption in the control treatment.
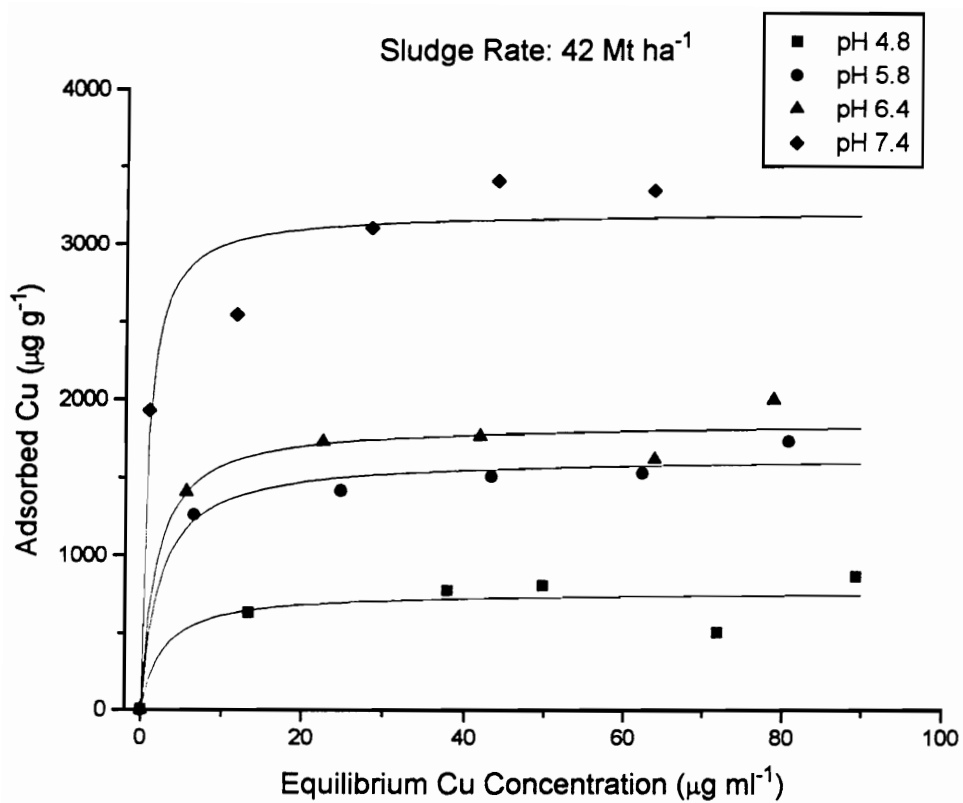
Figure 9. Effect of pH on Cu adsorption in the low-sludge
treatment.
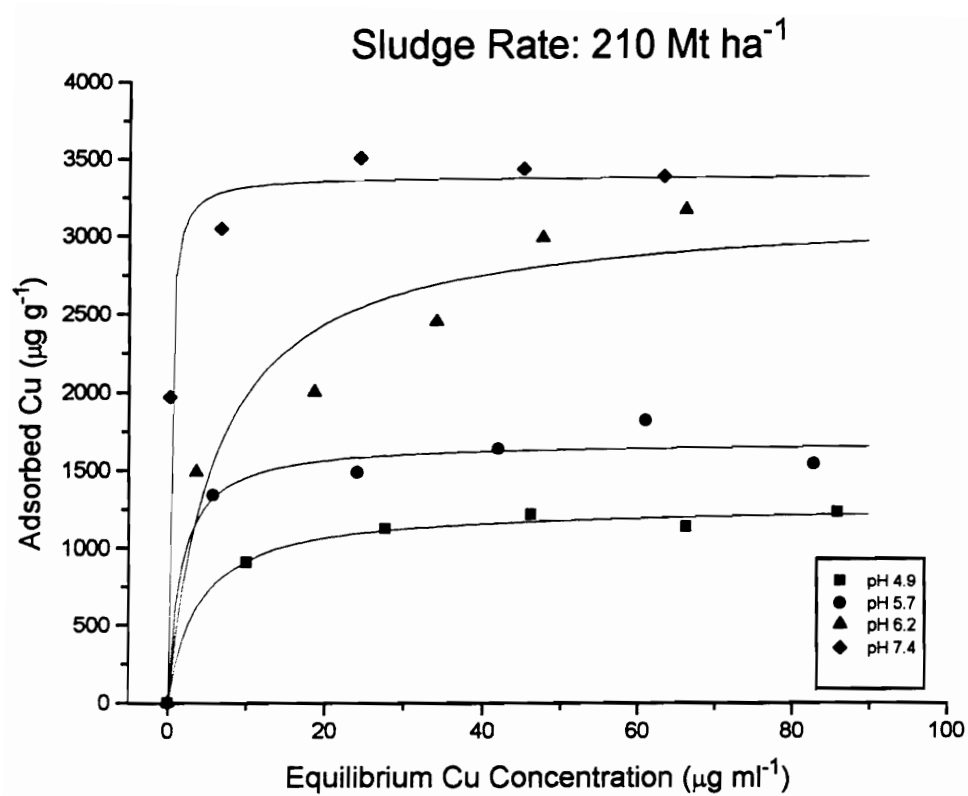
Figure 10. Effect of pH on Cu adsorption in the high-sludge treatment.

pH 4.5-4.9
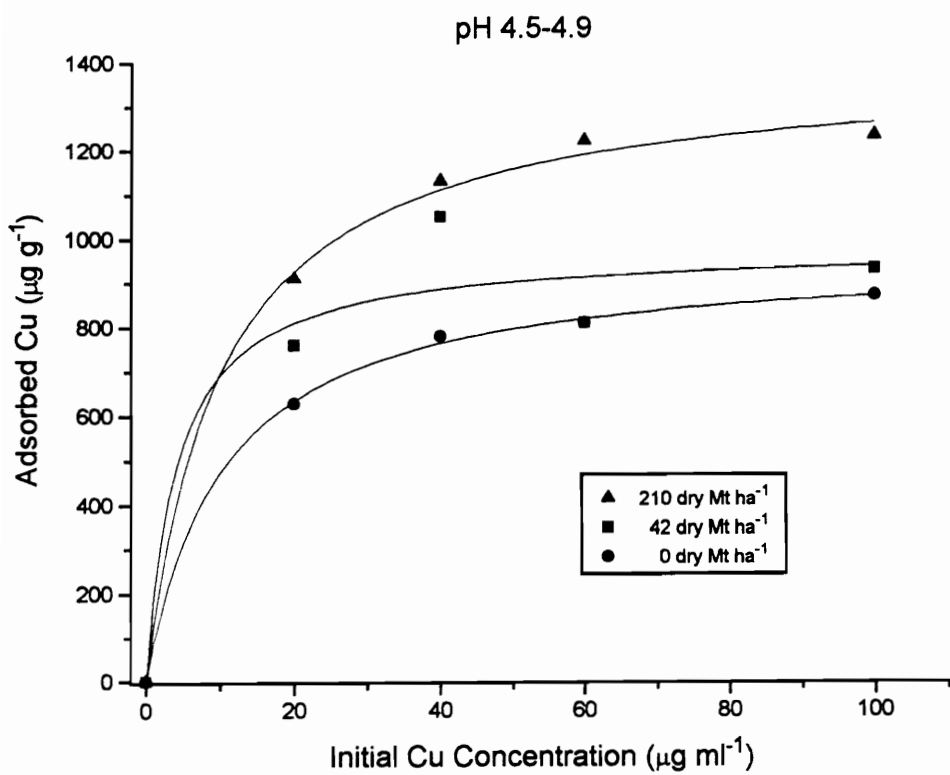
Figure 11. Effect of pH on Cu adsorption in the pH range of 4.5 to 4.9.

Table 41. Electrical conductivity of equilibrated solutions of amended control treatments in pH adsorption study.

Solute (Cu) Concentration	Equilibrium Electrical Conductivity (dS m^{-1})					
	Amendment /(kg ha^{-1})					
μg ml^{-1}	Ca(OH)$_2$/896	Ca(OH)$_2$/1792	Ca(OH)$_2$/3584	Ca(OH)$_2$/5040	Al$_2$(SO4)$_3$/1344	Al$_2$(SO4)$_3$/5376
0	1.94	2.02	2.15	2.16	2.22	2.18
20	1.98	2.03	2.18	2.21	2.25	2.24
40	2.07	2.08	2.29	2.30	2.29	2.36
60	2.17	2.13	2.32	2.34	2.37	2.43
80	2.18	2.20	2.38	2.39	2.41	2.52
100	2.26	2.25	2.47	2.44	2.46	2.59

Table 42. Levels of pH in equilibrated solutions of amended control treatments in pH adsorption study.

| Solute (Cu) Concentration | Equilibrium pH | | | | | |
| | Amendment /(kg ha^{-1}) | | | | | |
μg ml^{-1}	Ca(OH)$_2$/896	Ca(OH)$_2$/1792	Ca(OH)$_2$/3584	Ca(OH)$_2$/5040	Al$_2$(SO4)$_3$/1344	Al$_2$(SO4)$_3$/5376
0	5.66	5.82	6.34	6.90	4.82	4.79
20	4.83	4.81	5.11	5.63	4.46	4.49
40	4.68	4.66	4.82	5.14	4.36	4.44
60	4.58	4.60	4.77	5.00	4.29	4.33
80	4.51	4.52	4.71	4.89	4.26	4.28
100	4.50	4.49	4.66	4.82	4.20	4.26

Table 43. Electrical conductivity of equilibrated solutions of low-sludge treatments in pH adsorption study.

| Solute (Cu) Concentration | Equilibrium Electrical Conductivity (dS m^{-1}) | | | | |
| | Amendment/kg ha^{-1} | | | | |
μg ml^{-1}	Ca(OH)$_2$/2688	Ca(OH)$_2$/3584	Ca(OH)$_2$/5040	Al$_2$(SO4)$_3$/1344	Al$_2$(SO4)$_3$/5376
0	2.11	2.23	2.13	2.16	2.20
20	2.18	2.28	2.15	2.21	2.25
40	2.30	2.25	2.19	2.25	2.31
60	2.35	2.35	2.27	2.35	2.39
80	2.51	2.40	2.34	2.50	2.53
100	2.56	2.50	2.40	2.54	2.59

Table 44. Levels of pH in equilibrated solutions of amended low-sludge treatments in pH adsorption study.

| Solute (Cu) Concentration | Equilibrium pH | | | | | |
| | Amendment/kg ha^{-1} | | | | | |
μg ml^{-1}	Ca(OH)$_2$/2688	Ca(OH)$_2$/3584	Ca(OH)$_2$/5040	Al$_2$(SO4)$_3$/1344	Al$_2$(SO4)$_3$/5376
0	5.90	6.13	7.26	5.37	4.87
20	5.00	5.19	6.03	4.62	4.51
40	4.73	4.83	5.25	4.48	4.38
60	4.54	4.77	5.09	4.39	4.39
80	4.55	4.68	4.96	4.36	4.28
100	4.54	4.63	4.90	4.34	4.28

Table 45. Electrical conductivity of equilibrated solutions of high-sludge treatments in pH adsorption study.

Solute (Cu) Concentration	Equilibrium Electrical Conductivity (dS m^{-1}) Amendment/kg ha^{-1}					
μg ml^{-1}	Ca(OH)$_2$/896	Ca(OH)$_2$/3584	Ca(OH)$_2$/5040	Al$_2$(SO4)$_3$/1344	Al$_2$(SO4)$_3$/5376
0	2.14	2.16	2.18	2.17	2.11
20	2.21	2.19	2.26	2.24	2.14
40	2.32	2.24	2.31	2.36	2.29
60	2.40	2.34	2.32	2.43	2.33
80	2.50	2.42	2.36	2.56	2.43
100	2.57	2.48	2.41	2.62	2.48

Table 46. Levels of pH in equilibrated solutions of amended high-sludge treatments in pH adsorption study.

Solute (Cu) Concentration	Equilibrium pH					
	Amendment/kg ha^{-1}					
$\mu g\ ml^{-1}$	$Ca(OH)_2$/896	$Ca(OH)_2$/3584	$Ca(OH)_2$/5040	$Al_2(SO4)_3$/1344	$Al_2(SO4)_3$/5376
0	5.87	6.13	7.32	5.45	4.97
20	5.08	5.32	6.40	4.86	4.56
40	4.73	4.88	5.53	4.55	4.39
60	4.62	4.79	5.23	4.49	4.37
80	4.53	4.79	5.09	4.41	4.36
100	4.42	4.68	5.02	4.35	4.30

Effect of Ionic Strength on Copper Adsorption

A reduction in Cu adsorption ocurred with an increase in ionic strength using $NaClO_4$ as a background electrolyte (Figures 11-13). Garcia-Miragaya and Page (1976,1977) reported a decrease in Cd adsorption by montmorillonite with increasing ionic strength using either $NaClO_4$, NaCl, or Na_2SO_4. They attributed the decreased adsorption to competition of Na^+ and Cd^{2+} for exchange sites and a decrease in Cd^{2+} activity in solution with the increase in ionic strength. The inhibitory effects of added Ca, Mg, and K on Cu and Zn adsorption were investigated by Zhu and Alva (1993). They observed a decrease in Cu and Zn adsorption with an increase in exchangeable cation concentration. They concluded that the major factor reducing Cu adsorption was ion competition. They also observed that the inhibitory effects of cations on Cu and Zn adsorption were greater in lower pH soils. With the low soil pH levels in this study, the effect of ionic strength on Cu adsorption was probably greater than would have been observed if soil pH had been maintained at levels commonly used for corn and sorghum production. Electrical conductivity and pH measurements of the equilibrated solutions in the ionic strength study are presented in Tables 47-49.
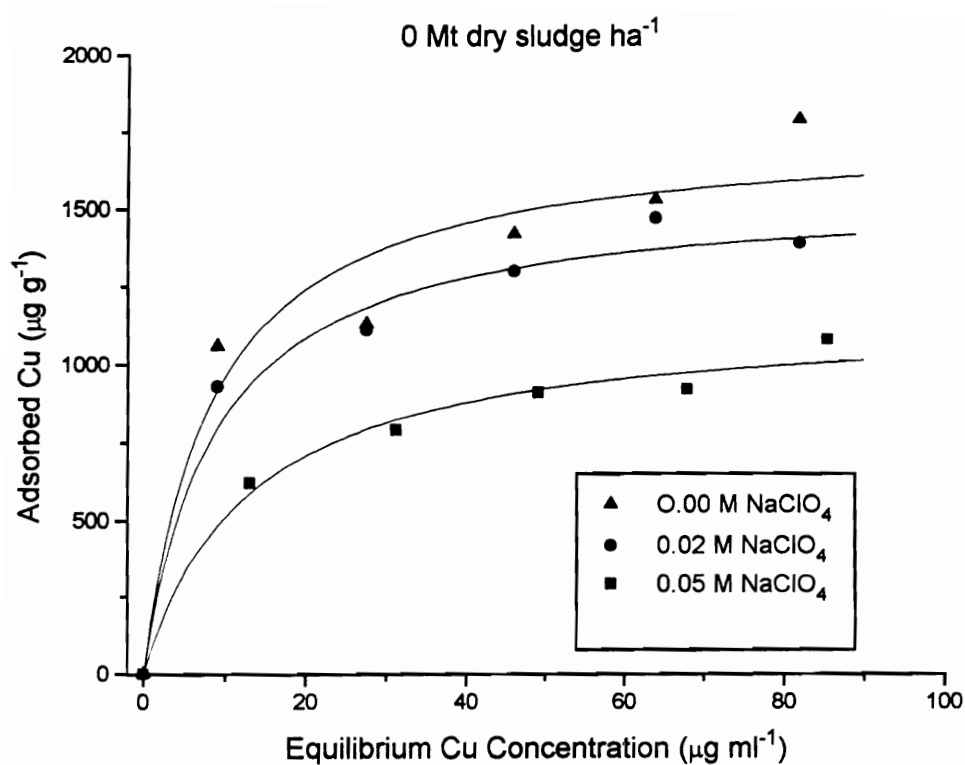
Figure 12. Effect of ionic strength on Cu adsorption in the control treatment.

42 Mt dry sludge ha^{-1}

Adsorbed Cu (μg g^{-1})

Equilibrium Cu Concentration (μg ml^{-1})

▲ 0.00 M NaClO$_4$
● 0.02 M NaClO$_4$
■ 0.05 M NaClO$_4$
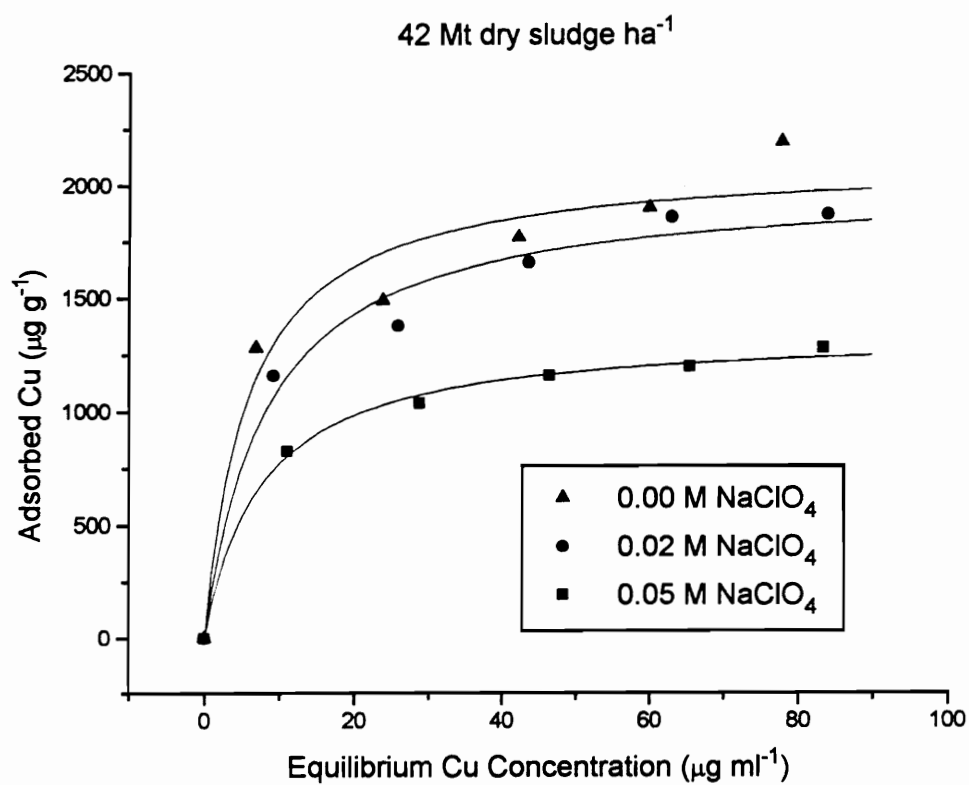
Figure 13. Effect of ionic strength on Cu adsorption in the low-sludge treatment.
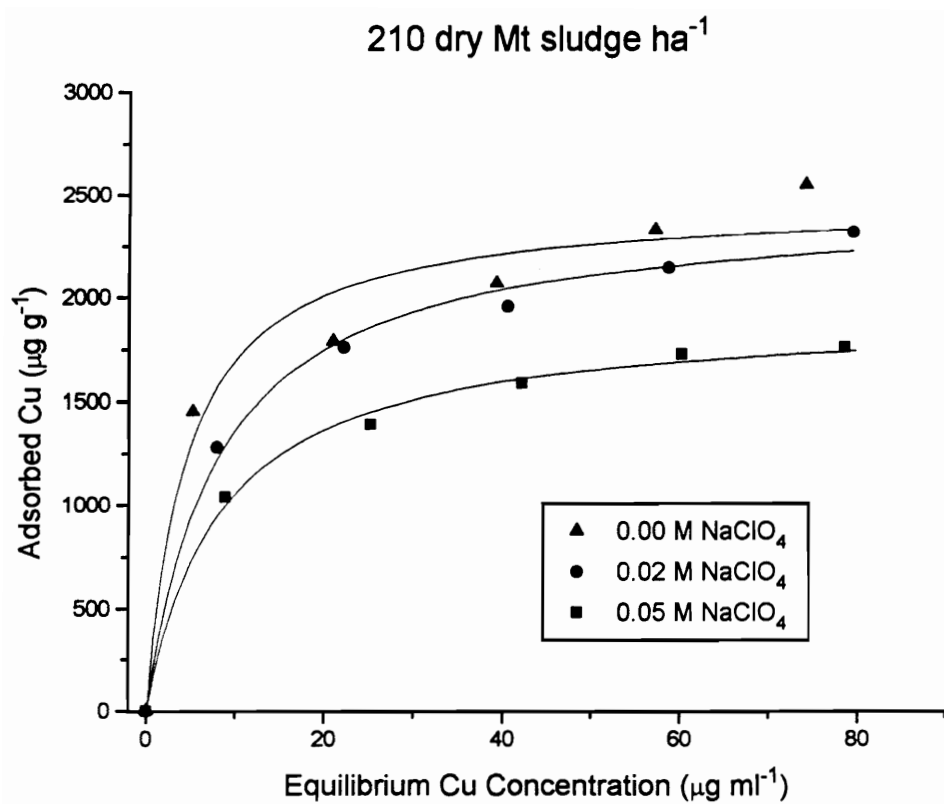
210 dry Mt sludge ha^{-1}

Figure 14. Effect of ionic strength on Cu adsorption in the high-sludge treatment.

Table 47. Electrical conductivity and pH measurements in equilibrated control treatment in ionic strength study.

Solute (Cu) Concentration	Equilibrium pH			Equilibrium Electrical Conductivity (dS m^{-1})		
μg ml^{-1}	0.00 M NaClO$_4$	0.02 M NaClO$_4$	0.05 M NaClO$_4$	0.00 M NaClO$_4$	0.02 M NaClO$_4$	0.05 M NaClO$_4$
0	5.64	5.27	5.12	0.01	2.05	4.90
20	4.70	4.46	4.64	0.10	2.17	5.22
40	4.55	4.62	4.54	0.18	2.20	5.39
60	4.46	4.62	4.49	0.26	2.40	5.50
80	4.40	4.94	4.43	0.34	2.47	5.70
100	4.35	4.92	4.40	0.41	2.51	5.70

Table 48. Electrical conductivity and pH measurements in equilibrated mid-sludge treatment in ionic strength study.

Solute (Cu) Concentration $\mu g\ ml^{-1}$	Equilibrium pH			Equilibrium Electrical Conductivity ($dS\ m^{-1}$)		
	0.00 M NaClO$_4$	0.02 M NaClO$_4$	0.05 M NaClO$_4$	0.00 M NaClO$_4$	0.02 M NaClO$_4$	0.05 M NaClO$_4$
0	6.09	5.72	5.57	0.01	2.20	5.24
20	4.85	4.78	4.79	0.09	2.21	5.30
40	4.64	4.62	4.65	0.17	2.27	5.48
60	4.55	4.53	4.58	0.23	2.37	5.40
80	4.48	4.48	4.50	0.31	2.52	5.58
100	4.45	4.43	4.45	0.37	2.55	5.60

Table 49. Electrical conductivity and pH measurements in equilibrated high-sludge treatment in ionic strength study.

Solute (Cu) Concentration	Equilibrium pH			Equilibrium Electrical Conductivity (dS m^{-1})		
μg ml^{-1}	0.00 M NaClO$_4$	0.02 M NaClO$_4$	0.05 M NaClO$_4$	0.00 M NaClO$_4$	0.02 M NaClO$_4$	0.05 M NaClO$_4$
0	6.01	5.67	5.50	0.02	2.23	5.29
20	4.94	4.78	4.85	0.10	2.19	5.38
40	4.70	4.69	4.67	0.16	2.20	5.42
60	4.57	4.56	4.58	0.24	2.44	5.77
80	4.48	4.49	4.51	0.31	2.50	5.50
100	4.45	4.43	4.48	0.38	2.60	5.50

CONCLUSIONS

Copper adsorption was greater in the sludge-amended soils than in the control. The adsorption capacity of the soil was apparently increased by the organic matter supplied by the sludge. Beckett et al. (1983) also reported an increase in metal binding capacity as a result of sludge application. A major portion of sludge organic matter is relatively persistent (Terry et al., 1979). In a study by Sposito et al. (1982), the fulvic acid fraction of soil which had received repeated sludge applications was more typical of sludge-derived material than soil-derived material. At high application rates, the sludge matrix is involved in trace element binding (Logan et al., 1997).

Copper adsorption increased with pH in all of the treatments. Regardless of pH , Cu adsorption remained highest in the high-sludge treatment. Temminghoff et al. (1994) observed that Cu binding to soil humic and fulvic fractions increased as pH increased. Negative charges on kaolinite edges arise at alkaline pH levels as adsorbed protons are removed (White and Zelazny, 1988). Kishk and Hassan (1973) studied the adsorption of Cu by different clay minerals as a function of pH and concluded that the increase in pH-dependent charge of kaolinite contributed to increased Cu adsorption at high pH levels. Copper ions are adsorbed by Fe, Al, and Mn oxides and hydroxides, which also have pH-dependent charges (James and Barrow, 1981). Copper adsorption decreased with ionic strength. Increases in ionic strength decrease the activity of free Cu^{2+} ions (Zhu and Alva, 1993).

REFERENCES

Beckett, P.H.T., E. Warr, and R.D. Davis. 1983. Cu and Zn in soils treated with sewage sludge: Their extractability to reagents compared with their availability to plants. Plant Soil 70:3-14.

Bell, P.F., B.R. James, and R.L. Chaney. 1991. Heavy metal extractability in long-term sewage sludge and metal salt-amended soils. J. Environ. Qual. 20:481-486.

Debano, L.F., S.M. Savage, and D.A. Hamilton. 1976. The transfer of heat and and hydrophobic substances during burning. Soil Sci. Soc. Am. J. 40:779-782.

Ellis, B.G., and B.D. Knezek. 1972. Adsorption reactions of micronutrients in soils. p. 59-78. *In*: Mortvedt et al. (ed.) Micronutrients in agriculture. SSSA, Madison, WI.

Forbes, E.A., A.M. Posner, and J.P. Quirk. 1976. The specific adsorption of divalent Cd, Co, Cu, Pb, and Zn on goethite. J. Soil Sci. 27:154-166.

Fried, M., and R.E. Shapiro. 1856. Phosphate supply pattern of various soils. Soil Sci. Soc. Am. Proc. 20:471-475.

Garcia-Miragaya, J., and A.L. Page. 1976. Influence of ionic strength and inorganic complex formation on the sorption of trace amounts of Cd by Montmorillonite. Soil Sci. Soc. Am. J. 40:658-663.

Garcia-Miragaya, J., and A.L. Page. 1977. Influence of exchangeable cation on the sorption of trace amounts of cadmium by montmorillonite. Soil Sci. Soc. Am. J. 41:718-721.

Griffin, R.A., and A. K. Au. 1977. Lead adsorption by montmorillonite using a competitive Langmuir equation. Soil Sci. Soc. Am. J. 41:830-882.

Griffin, R.A., and J.J. Jurinak. 1973. Estimation of activity coefficients from the electrical conductivity of natural aquatic systems and soil extracts. Soil Sci.116:26-30.

Harada, Y., and K. Wada. 1974. Effects of previous drying on the measured cation and anion exchange capacities of Andosols. p. 248-256. Tenth International Congress of Soil Science Transactions.

Harter, R.D., and D.E. Baker. 1977. Applications and misapplications of the Langmuir equation to soil adsorption phenomena. Soil Sci. Soc. Am. J. 41: 1077-1080.

Harter, R.D., and G.Smith. 1981. Langmuir equation and alternate methods of studying "adsorption" reactions in soils. p. 167-182. *In*: R.H. Dowdy et al. (ed.) Chemistry in the soil environment.Am. Soc. Agron., Madison, WI.

James, R.O., and N.J. Barrow. 1981. Copper reactions with inorganic components of soils including uptake by oxide and silicate minerals. p. 47-68. *IN*: Lonergan et al. (ed.) Copper in soils and plants. Academic Press, Australia.

Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides. *In*: R.F. Gould (ed.) Trace inorganics in water. Advances in Soil Chemistry Series. Am. Chem. Soc., Washington, DC.

Karapangagiotis, N.K., R.M. Sterritt, and J.N. Lester. Heavy metal complexation in sludge-amended soil. The role of organic matter in metal retention. Environ. Tech.

12:1107-1116.

King, L.D. 1988. Retention of metals by several soils of the southeastern United States. J. Environ. Qual. 17:239-246.

Kishk, F.M., and M.N. Hassan. 1973. Sorption and desorption of copper by and from clay minerals. Plant Soil 39:497-505.

Kuo, S., and A.S. Baker. 1980. Sorption of copper, zinc, and cadmium by some acid soils. Soil Sci. Soc. Am. J. 44:969-974.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum. J. Am. Chem. Soc. 40:1361-1403.

Logan, T.J., B.J. Lindsay, L.E. Goins, and J.A. Ryan. 1997. Field assessment of sludge metal bioavailability to crops: Sludge rate response. J. Environ. Qual. 26:534-550.

McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils. p. 1-56. *In*: B.A. Stewart (ed.) Advances in soil science. Vol. 10. Springer-Verlag, New York, NY.

McBride, M.B. 1994. Environmental chemistry of soils. Oxford University Press, New York, NY.

McBride, M.B., and J.J. Blasiak. 1979. Zinc and copper solubility as a function of pH in an acid soil. Soil Sci. Soc. Am. J. 43:866-870.

Olsen, S.R., and FS. Watanabe. 1957. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. Soil Sci. Soc. Am. Proc.

21:144-149.

Raveh, A., and Y. Avnimelech. 1978. The effect of drying on the colloidal properties and stability of humic compounds. Plant Soil 50:545-552.

Reed, S.T. Copper adsorption/desorption characteristics on copper amended soils. P.79-108. Ph.D. Diss. P.72-101. Virginia Poly. Inst. and State Univ., Blacksburg, VA.

Roy, W.R., I.G. Krapac, S.F.J. Chou, and R.A. Griffin. 1991. Technical Resource Document. Batch-type procedures for estimating soil adsorption of chemicals. EPA/530-SW-87-006-F. USEPA, Washington, D.C.

Sanders, J.R. 1982. The effect of pH upon the copper and cupric ion concentrations in soil solutions. J. Soil Sci. 33:679-689.

Sparks, D.L., 1995. Environmental soil chemistry. Academic Press, San Diego, CA.

Sposito, G. 1982. On the use of the Langmuir equation in the interpretation of "adsorption" phenomena. II. The "two surface" Langmuir equations. Soil Sci. Soc. Am. J. 46:1147-1152.

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.

Stevenson, F.J. 1982. Humus chemistry. Wiley, New York, NY.

Stevenson, F.J., and A. Fitch. 1981. Reactions with organic matter. p. 69-95. *In:* J.F.

Lonergan et al. (ed.) Copper in soils and plants. Academic Press, Australia.

Temminghoff, E.J.M., S.E.A.T.M. van der Zee, and M.G. Keizer. 1994. The influence of pH on the desorption and speciation of copper in a sandy soil. Soil Sci. 158:398-408.

Terry, R.E., D.W. Nelson, and L.E. Sommers. 1979. Decomposition of anaerobically sewage sludge as affected by soil environmental conditions. J. Environ. Qual. 8:342-347.

Tyler, L.D., and M.B. McBride. 1982. Mobility and extractability of cadmium, copper, nickel, and zinc in organic and mineral soil columns. Soil Sci. 134:198-205.

Van Lierop, W., and A.F. Mackenzie. 1977. Soil pH measurement and its application to organic soils. Can. J. Soil Sci. 57:55-64.

Veith, J.A., and G. Sposito. 1977. On the use of the Langmuir equation in the interpretation of "adsorption" phenomena. Soil Sci. Soc. Am. J. 41:697-702.

White, G.N., and L.W. Zelazny. 1988. Analysis and implications of the edge structure of dioctahedral phyllosilicates. Clays and Clay Minerals 36:141-146.

Zhu, B., and A.K. Alva. 1993. Differential adsorption of trace metals by soils as influenced by exchangeable cations and ionic strength. Soil Sci. 155:61-66.

Zhu, Yin-Mei, D.F. Berry, and D.C. Martens. 1991. Copper availability in two soils amended with eleven annual applications of copper-enriched hog manure. Commun. Soil Sci. Plant Anal. 22:769-783.

Chapter 5

OVERALL CONCLUSIONS AND RECOMMENDATIONS

This study was a continuation of research conducted by Rappaport et al. (1988) in 1984, in which a single application of heavily contaminated sewage sludge applied at rates up to 210 mt ha^{-1} supplied up to 760 Cu and 620 kg Zn ha^{-1} on a Davidson clay loam. The levels of sludge-applied Cu and Zn exceeded USEPA guidelines at that time, which were based on the maintenance of soil pH at $\geq$ 6.5 (USEPA, 1983). The 1984 application levels of Cu and Zn are below current cumulative loading rates; however, they exceed annual loading rates (USEPA, 1993). The concentrations of Cu and Zn in the sludge (3653 and 2982 mg kg^{-1}, respectively) would not meet current criteria for high quality sludge and therefore the sludge would have restrictive requirements and management practices. Soil pH levels at the experimental site were not maintained at the recommended pH of $\geq$ 6.5 and decreased to levels capable of inducing metal phytotoxicity.

Field and laboratory studies were conducted from 1992 -1995 with the following objectives: 1) to determine the long-term effects of the sludge application on Cu availability and adsorption, 2) to ascertain pH effects on Cu adsorption on the soil, and 3) to evaluate corn and sorghum response to metal toxicity following sludge application. The long-term effects of sludge amendment on Zn availability, soil organic matter, CEC,

soluble salts, and Mehlich-1 extractable P were also investigated during the course of the field study. Effects of pH and ionic strength on Cu adsorption were investigated in a laboratory study. The major conclusions from this research are summarized as follows:

1. Sludge amendment had a long-term effect on soil organic matter. High soil organic matter levels persisted in the sludge treatments 11 years after sludge application, with levels at the high sludge rate almost double those of the unamended control. An increase in CEC was observed with sludge rate, which was attributed to the higher amounts of organic matter in the sludge treatments.

2. Soluble salt levels were unaffected by sludge rate and were well below levels reported to reduce corn and sorghum yields.

3. Mehlich-1 extractable P increased with level of sludge application, reflecting the high level of P supplied by the sludge (6657 kg ha $^{-1}$) and the relatively slow reversion of P to insoluble forms in the soil.

4. There was a linear increase in DTPA-extractable Cu and Zn with sludge application rate, a trend also observed by Rappaport et al. (1988) in the year following sludge application.

5. Stunting was apparent in early corn growth where higher levls of sludge were applied to the soil.

6. Copper concentrations in corn and sorghum tissue were above the normal range on the sludge treatments. Zinc tissue concentrations exceeded the toxic concentration of 100 mg kg $^{-1}$ on sludge treatments. The elevated levels of Cu and Zn in plant tissue were attributed to increased availability under acidic soil conditions.

7. Corn and sorghum yields decreased with sludge rate, in direct contrast to what Rappaport et al. (1988) observed in 1984. A combination of Al, Cu, Zn, and Mn phytotoxicity was probably responsible for the yield decrease.

8. Levels of Cu and Zn in corn and sorghum seed were within the normal range on the sludge-amended soil and were suitable for livestock feed.

9. Copper adsorption increased with sludge rate. It also increased with pH due to an increase in negative charge from deprotonation of hydroxyl groups on organic matter, kaolinite edges, and Al and Fe hydroxides in the soil. Copper adsorption decreased with ionic strength, most likely the result of decreased activity of Cu ions.

Long-term benefits of sludge application included increases in available P, CEC, and organic matter. The most important benefit was an increase in organic matter, which improves water retention and infiltration in soil. This is an important benefit in Virginia, where water is the most limiting factor for crop growth. It is apparent from both the field and laboratory studies that careful management of sludge-amended soils is necessary to reduce the availability of sludge-applied Cu and Zn and therefore prevent metal toxicity.

Recommendations for Future Research

The experimental site will be valuable in furthur long-term research on sludge amendment. The author makes the following recommendations for future research:

1. Crop root tissue should be analysed to determine levels of Al, Cu, Zn, and Mn, which are suspected of causing phytotoxicity.

2. Soil pH levels should be increased to determine if crop yields will improve in the sludge

treatments.

3. Crops other than corn should be grown on the experimental site because most of the past sludge research has utilized corn.

References

Rappaport, B.D., D.C. Martens, R.B. Reneau, Jr., and T.W. Simpson. 1988. Metal availability in sludge-amended soils with elevated metal levels. J. Environ. Qual. 17:42-47.

U.S. Environmental Protection Agency. 1983. Process design manual for land application of municipal sludge. USEPA Rep. EPA-625/1-83-016. U.S. Gov. Print. Office, Washington, DC.

U.S. Environmental Protection Agency. 1993. Standards for use and disposal of sewage sludge. Final Rule, 40 CFR Part 503. U.S. Gov. Print. Office, Washington, DC.

VITA

The author was born in Roanoke, Virginia on January 10, 1955. She is the daughter of Oscar William Anderson and Virginia Woody Anderson. She received an Associate in Applied Science Degree in Horticulture from Virginia Western Community College in June 1984. While enrolled there, she managed the college greenhouse and also was employed by Bent Mountain Greenhouses. In September of 1984, she enrolled in the B.S. program in Horticulture at Virginia Polytechnic Institute and State University. In 1986 she participated in an agricultural internship in Zambia, where she worked on a commercial farm. She received her B.S. in July, 1987. She remained at VPI & SU, where she received a M.S. degree in Crop and Soil Environmental Sciences in December, 1990. She enrolled in the Ph.D. program in the same department in 1991. While completing this degree she was an instructor at New River Community College in Dublin, Virginia and an Assistant Professor at Bluefield State College in Bluefield, West Virginia. The author has one son, Jedidiah David, who was born on April 10, 1988.