

RESPONSE OF CORN TO HIGH LEVELS OF  
CuSO<sub>4</sub> and ZnSO<sub>4</sub> APPLICATIONS

by

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## INTRODUCTION

Copper and Zn deficiencies of crop plants occur in various areas throughout the world (Sparr, 1970; Murphy and Walsh, 1972; Kabata-Pendias and Pendias, 1984). Copper deficiency occurs most commonly in wheat (Triticum aestivum), whereas Zn deficiency occurs most often in corn (Zea mays L.) (Sparr, 1970). The sulfate forms of Cu and Zn are generally used to correct these micronutrient deficiencies in corn (Murphy and Walsh, 1972).

In agricultural practices, Cu and Zn are applied to soils not only as a fertilizer, but also as manures, pesticides, and waste materials such as sewage sludge. High levels of Cu and Zn applications to agricultural soils are considered to pose a potential hazard to plants and animals (Lexmond and deHaan, 1977; U.S. Environmental Protection Agency, 1979). Guidelines have been established for the application of sludges to agricultural land (Sommers and Nelson, 1978). Loading rates for application of heavy metals, including Cu and Zn, to soils have been based on an interpretation of a wide volume of heterogeneous literature. Therefore, the levels of Cu and Zn applications, particular-



ly as sulfate, that will either injure plants or increase Cu and Zn concentrations in edible plant portions to undesirably high levels are still unknown.

There is a need for long-term field research involving high levels of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  applications to agricultural soils. Field research involved with heavy metal applications should consider the fate of metals in soils, changes in concentrations of metals in plants, and effects of metals on crop yields.

The study reported herein was undertaken on a Davidson silty clay soil with specific objectives as follows:

1. to determine corn response to 18 annual applications of various levels of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$ ,
2. to evaluate downward movement of Cu and Zn following 17 annual applications of various levels of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$ , and
3. to investigate the reversion of Cu and Zn to plant unavailable forms following 17 annual applications of various levels of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$ .

## REVIEW OF LITERATURE

### Chemistry of Soil Copper

Geochemistry. Copper in the earth's crust is estimated to vary from 24 to 55 mg/kg (Cox, 1979), while total content of the element in soils is reported to range from 1 to 80 mg/kg (Krauskopf, 1972). This large scale of Cu occurrence in soils indicates that two main factors, parent material and soil formation processes, govern the initial Cu status in soils (Kabata-Pendias and Pendias, 1984).

Copper forms several minerals of which the common primary minerals are simple and complex sulfides such as chalcocite ( $\text{Cu}_2\text{S}$ ), covellite ( $\text{CuS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), and cubanite ( $\text{CuFe}_2\text{S}_3$ ) (Krauskopf, 1972; Cox, 1979). Weathering of Cu containing minerals under oxidizing conditions releases  $\text{Cu}^{2+}$  (Krauskopf, 1972). The released Cu will not precipitate as sulfides since the S present in the weathering minerals is oxidized to sulfate. In the absence of adequate S,  $\text{Cu}^{2+}$  can replace  $\text{Fe}^{2+}$  in primary and secondary silicate minerals (Baker, 1974).

Forms of Soil Copper. Based on solubility, exchange reactions, and chemical form, Viets (1962) proposed five chemical pools of micronutrient cations, such as Cu, in soil. Those five pools are: (a) water soluble, (b) exchangeable cations (c) adsorbed, chelated, or complexed ions, (d) micronutrient cations in secondary clay minerals and insoluble metal oxides, and (e) cations held in primary minerals. For soil Cu, McLaren and Crawford (1973a) presented a similar suite and devised a fractionation scheme using 0.05 M  $\text{CaCl}_2$ , 2.5% acetic acid, 0.1 M  $\text{K}_4\text{P}_2\text{O}_7$ , Tamm's reagent and HF to remove soil solution and exchangeable Cu, specifically bound Cu, organically bound Cu, occluded Cu in soil oxides, and residual Cu mainly in clay lattice structures, respectively. The Cu present in water-soluble, exchangeable, and adsorbed forms is considered as readily available to plants; while Cu associated with primary and secondary soil minerals is relatively unavailable to plants (Viets, 1962).

The amounts of different Cu forms vary considerably in soils. Copper present in soil solution, exchangeable, and specifically bound forms represent a small percentage of the total Cu in most soils (McLaren and Crawford, 1973a; McBride, 1981). The bulk of the Cu is complexed by organic matter, occluded in oxides, and entrapped in primary and secondary minerals.

From the standpoint of uptake by plants, Cu in the soil solution, as ionic and organically complexed species, is of special importance. However, the quantity of this fraction is normally very low and often in the  $\mu\text{g}/\text{kg}$  range (Kabata-Pendias and Pendias, 1984). Hodgson et al. (1965) reported that the amounts of Cu in the soil solutions from A horizons of New York soils varied from 5.0-18.0  $\mu\text{g Cu}/\text{kg}$  and the portion of organically complexed species in solution varied from 79% at soil pH 4.5 to 99.2% at soil pH 9.0. Copper in soil solutions of calcareous Colorado soils ranged from 3.5-39.2  $\mu\text{g Cu}/\text{kg}$  and the amount of the complexed species varied from 96.0% at soil pH 7.6 to 99.8% at soil pH 7.9 (Hodgson et al., 1966).

Adsorption of Soil Copper. Copper ions may be removed from solution by precipitation of the oxide ( $\text{CuO}$ ), the hydroxide [ $\text{Cu}(\text{OH})_2$ ] or the hydroxy carbonate [ $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ] at a high pH (McBride, 1981). However, it is considered that the concentration of Cu in soil solution is too low for such precipitates to control the solubility of soil Cu (McBride, 1978; Cavallaro and McBride, 1978; McBride, 1981; James and Barrow, 1981). Therefore, removal of Cu from solution is not due to reaction with other ions in the solution phase, which is precipitation; rather it is by reaction with atoms on the surface of the solid phase, which is adsorption

(James and Barrow, 1981). McLaren and Crawford (1973b) and Cavallaro and McBride (1978) suggested that Cu adsorption takes place by processes other than by normal cation exchange reactions. These processes are termed 'specific adsorption' which occurs on clay minerals, organic matter, and free oxide.

The sorption of trace elements, such as Cu, by soils and sediments is the subject of an extensive review by Jenne (1977), who discussed the relative abundance and reactivity of the various trace element sinks. He concluded that the important sinks are oxides of iron and manganese, organic matter, sulfides, and carbonates; those of lesser importance are phosphates, iron salts, and clay-size aluminosilicate minerals. McLaren and Crawford (1973b), based on adsorption maxima and bonding energies obtained from the Langmuir adsorption equation for whole soils and soil components, concluded that organic matter and Mn oxides were mainly responsible for Cu sorption by soils. In a study on Cu and Zn sorption-desorption with clay fractions separated from two horizons of an acid soil from New York, Cavallaro and McBride (1984) concluded that microcrystalline and noncrystalline oxides in the clay fraction of this soil, representing < 20% of the clay by weight, provided reactive surfaces for the chemisorption of Cu and Zn. At low pH, adsorption

of these surfaces may be the dominant mechanism of heavy metal immobilization.

It is a common observation that adsorption of Cu increases as the soil pH increases (McBride and Blasiak, 1979; Kuo and Baker, 1980; Harter, 1983). Kuo and Baker (1980) reported that the adsorption maximum for Cu in silty clay loam soils is about pH 6. Similarly, McBride and Blasiak (1979) found that for Mardin silt loam, the minimum amount of Cu in soil solution occurred in the pH range of 6-7. In a study on specific adsorption of Cu on a hydroxy-aluminum-montmorillonite complex, Harsh and Doner (1984) reported that adsorption of Cu increased with pH, and both adsorption and resistance to extraction with 0.25 M  $\text{Ba}(\text{NO}_3)_2$  increased with time. Low pH decreases the adsorption of metals to pH-dependent specific adsorption sites on mineral surfaces and lowers the CEC of soil organic matter (Ellis and Knezek, 1972; Kabata-Pendias and Pendias, 1984). In their extensive review, Stevenson and Alanah Fitch (1981) stated that, among various types of organic substances that play a prominent role in the binding of Cu in soils, humic and fulvic acids play a key role. Humic acids bind Cu more tightly than fulvic acids, and the stability constants of Cu-humate complexes increase with an increase in degree of humification. However, as the stronger binding sites become saturated, an

increasing amount of the Cu will be solubilized through the action of fulvic acids and simple biochemical compounds. Jenne (1968) suggested that soil humus functions in reduction of ferric and manganic oxides and that the occluded Cu is released in available forms during reduction of the oxides.

### Chemistry of Soil Zinc

Geochemistry. The average content of Zn in the earth's crust is estimated to be about 70 mg/kg, while total content of this element in soils varies from 10 to 300 mg/kg (Krauskopf, 1972). Common minerals that contain Zn are sulfides, carbonates, and silicates; and among these minerals, the sulfide mineral sphalerite (ZnS) is the most common (Hodgson, 1963; Krauskopf, 1972).

The solubilization of Zn minerals during weathering produces mobile  $Zn^{2+}$ , especially in acid, oxidizing environments (Kabata-Pendias and Pendias, 1984). In comparison with Cu, Zn migrates farther from its source in soils, rocks, and streams; and therefore, it is known as one of the most mobile of the heavy metals (Krauskopf, 1972). However, Zn is also easily adsorbed by mineral and organic components, and its accumulation in the surface horizons of most soils is recognized (Kabata-Pendias and Pendias, 1984).

Zinc is also known to substitute for  $Mg^{2+}$  in the structure of the clay minerals (Krauskopf, 1972).

Forms of Soil Zinc. The forms of soil Zn are basically the same as those of soil Cu (Viets, 1962; Iyengar et al., 1981). Due to variations in chemistry, the distribution of Zn among the soil fractions can be expected to be different from that of soil Cu. As an example, Cu is held more tightly by humic acid than Zn (Ellis and Knezek, 1972).

Like Cu, the amounts of different Zn forms vary considerably in soils. In their study on the distribution of Zn in 10 Louisiana soils, Sedberry and Reddy (1976) reported that averages of 1.7, 0.9, 2.6, 4.4 and 86.4% of the Zn were in the water-soluble, exchangeable, chelated, organic, and residual mineral fractions, respectively. Iyengar et al. (1981) considered that a portion of the residual mineral Zn in these soils was in association with oxides and hydroxides of Al, Fe, and Mn. Shuman (1979) found that 1 to 7% of the Zn in 10 Georgia soils was in the exchangeable form and that averages of 12 and 20% were in the organic and noncrystalline Fe-oxide forms, respectively. Iyengar et al. (1981) reported that most of the total Zn in 19 Virginia soils, on the average, was present in the Al- and Fe-oxide bound (~25%) and residual mineral (~70%) fractions. The water-soluble plus exchangeable, specifically adsorbed, organically



bound, and Mn-oxide bound fractions averaged 0.4, 3.3, 2.5, and 2.0% of the total Zn, respectively.

The amount of Zn in the soil solution, as ionic and organically complexed species, is generally very low, even in soils that contain a high amount of total Zn (Shuman, 1980). Zinc concentration in soil solution ranges from 4 to 270  $\mu\text{g}/\text{kg}$  (Kabata-Pendias and Pendias, 1984). Hodgson et al. (1965) reported that Zn in soil solution of the A horizon from some New York soils varied from 48 to 180  $\mu\text{g}/\text{kg}$  depending on soil pH and that the percentage of organically complexed species in soil solution ranged from 41% at soil pH 4.1 to 90% at soil pH 8.0. Likewise, the percentage of organically complexed Zn in soil solutions from calcareous Colorado soils varied from 40% at soil pH 7.6 to 99% at soil pH 7.9 (Hodgson et al., 1966).

Adsorption of Soil Zinc. The mechanism that is considered to control the concentration of Zn in soil solution is the adsorption of Zn by clay minerals, hydrous oxides, and organic matter (Ellis and Knezek, 1972). It was indicated that the Zn adsorption was largely specific sorption (Jenne, 1968; Shuman, 1980). There are two different mechanisms of Zn adsorption: one in acid media related to cation exchange sites and the other in alkaline media that is considered to be chemisorption and is highly influenced by organic ligands

(Kabata-Pendias and Pendias, 1984). Once Zn cations are adsorbed they may move into lattice positions in clay minerals (Ellis and Knezek, 1972; Kabata-Pendias and Pendias, 1984).

The adsorption of Zn increases with increasing soil pH (Shuman, 1975; McBride and Blasiak, 1979; Harter, 1983). Shuman (1975) equilibrated four Georgia soils with solutions containing various levels of Zn (2-128 mg/L) and showed that the amount of Zn adsorbed by the soils increased with an increase in both soil CEC and pH. Working with a Mardin silt loam equilibrated with solutions containing 10-70 mg Zn/L, McBride and Blasiak (1979) found that Zn adsorption increased with increasing pH. Harter (1983) equilibrated two soils with varying amount of  $\text{Ca}(\text{OH})_2$  prior to metal addition, and found that the amount of Zn retained was dependent upon pH, with retention dramatically increasing above pH 7.0 to 7.5.

#### Movement of Applied Copper and Zinc in Soils

Movement of Cu and Zn in soils has generally been considered to be minimal due to their low solubilities (Dowdy and Volk, 1983; Ellis et al., 1983). Copper and Zn movement from the zone of application could occur by diffusion, either as a free ion or as a complex, by mass flow with the water front, or by movement of metal-laden particulates

through open channels in soil (Dowdy and Volk, 1983). From these mechanisms, mass flow is considered the principle means by which Cu, Zn and other heavy metals move appreciable distances within soils.

Laboratory Studies. Copper has been shown to move downward only in soils with a sandy texture. Jones and Belling (1967) applied radioactive Cu ( $^{64}\text{Cu}$ ) on the surface of columns packed with topsoils of varying properties and then leached the columns with deionized water equivalent to one year of rainfall. They found that movement of Cu (1-3 cm) was detected only in sandy soils of low cation exchange capacity. Sommers et al. (1979) studied the movement of Cu and some other metals through intact 50-cm core of five Indiana soils ranging in textures from a sand to a silty clay loam and in surface pH from 4.7 to 6.3. They found that essentially all added metals were retained within the zone of incorporation, even on the sand texture with a pH of 4.9. They incorporated a digested sludge containing 540 mg Zn, 2170 mg Cu, 540 mg Pb, 740 mg Ni, and 480 mg Cd/kg into the upper 7.5 cm soil layer at a rate equivalent to 22.4 t/ha and leached the columns monthly with ~3.2 cm of distilled water over a 1-year period.

Zinc was reported to be more mobile than Cu (Gilkes et al., 1975). They applied 1-g samples of commercial granu-

lated Cu-Zn phosphate (0.66% Cu and 0.52% Zn) to the surface of a yellow podzolic soil (90% sand and 8% clay) which was packed in columns. Each column received 90 leaches of 1 cm of water. They found that a very small portion of the Cu was leached to a depth of 20 mm by 60 leaches, while Zn in the leachate from the soil columns increased during the first 30 leaches and then gradually declined. Similar to Cu, it was noted that downward movement of applied Zn occurred in soils of lighter texture (Singh, 1974). He compared  $^{65}\text{Zn}$  movement in a sandy and a loamy soil. Zinc moved 12 cm in the sandy soil and 8 cm in the loamy soil after the soils received 30 cm of water, and proportionally larger amounts of Zn moved to a lower depth in both soils when the rate of water application was increased to 120 cm.

Experimental results from many column studies have shown that, when Cu and Zn were applied with sewage sludge, they practically remained within the zone of incorporation (Emmerich et al., 1982; Sommers et al., 1979; Giordano and Mortedt, 1976). Dowdy and Volk (1983) suggested that mobility of trace metals, including Cu and Zn, applied as inorganic salts was greater under excessive leaching when the metals were applied with sewage sludge.

Field Studies. Little downward movement of Cu was reported to occur in organic soils. Lundbland et al. (1949)

applied Cu as  $\text{CuSO}_4$  to a peat soil in Sweden at rates of 0, 25, and 250 kg/ha. After six years of application, downward movement of Cu was not detected in the soil that received 25 kg  $\text{CuSO}_4$ /ha; while approximately 0.2% of the applied Cu was detected at depths lower than five cm in the soil that received 250 kg  $\text{CuSO}_4$ /ha. They also applied Cu as  $\text{CuSO}_4$  to a mineral soil at the same rates as those for the peat soil. They found that downward movement of Cu in the mineral soil was slightly greater than in the peat soil.

In their study on the effect of soil type on mobility of Zn in the soil, Barrows et al. (1960) concluded that the movement of Zn through the soils could not be explained on the basis of any one chemical or physical soil property, but rather by a combination of soil properties. They added  $\text{ZnSO}_4$  to tung (Aleurites fordii) trees at levels of 0, 28.4, 56.8, and 113.5 g/tree on four soils (one fine sand, two fine sandy loams, and one loamy fine sand). They found that the depth of Zn movement varied from none to 61 cm in these soils.

Most of the recent field studies on the movement of Cu and Zn in soils are with application of the metals as sewage sludge. Numerous observations reviewed by Dowdy and Volk (1983) showed retention of about 95% of Cu and Zn in the 0 to 30-cm depth after application of sewage sludge to soil.

Zinc was considered to be more mobile than Cu. Kelling et al. (1977) determined the extractable metals in soils, which had been treated with sewage sludge, and found somewhat increased levels of Cu, Cd, and Ni at the 15 to 30-cm depth, but indicated that the increase was related to tillage incorporation. The Zn concentration was found to increase at depths greater than 30 cm and, therefore, they concluded that some downward movement of Zn did occur.

In summary, although some studies have indicated downward movement of Cu and Zn to layers below either the soil surface or the depth of incorporation, it appears that the magnitude of their movement is very small. Downward movement of Cu and Zn most likely will occur with large applications to a sandy, acid, low organic matter soil that receives high rainfall or irrigation. Leaching of Zn in soil appears to be relatively greater than that of Cu.

#### Plant Uptake of Copper and Zinc from Soil

##### Soil Properties Affecting Copper and Zinc Uptakes.

Soil Cu and Zn must be in an available form before either can be taken up by plants. In relation to soil properties, the availability of either soil Cu or Zn depends on the soil pH, texture, and organic matter content (Kabata-Pendias and Pendias, 1984).

An increase in soil pH tends to decrease the plant availability of Cu, except in organic soils where the reverse may be true (Hodgson, 1963). Soil texture is of importance in determining the amount of Cu needed by Cu-responsive crops (Baker, 1974). He estimated that 6.72 kg Cu/ha/year could be applied for 5 to 10 years on some sandy soils and for 60 or more years on soils with a high cation exchange capacity. Hodgson (1963) stated that soils high in organic matter have a high Cu fixing capacity. Up to 224 kg CuSO<sub>4</sub>/ha are required to correct Cu deficiencies on some muck soils.

The plant availability of soil Zn varies inversely with soil pH (Hodgson, 1963; Giordano and Mortvedt, 1980). Due to this relationship, Zn deficiency is most prevalent on calcareous soils of pH 7.4 or higher (Giordano and Mortvedt, 1980). Liming acid soils, especially those which are coarse textured, may induce Zn deficiency. Soil organic matter contains an important reserve of available Zn for crops. For this reason, Zn deficiency has been associated with irrigated soils from which topsoil has been removed by land leveling (Giordano and Mortvedt, 1980).

Copper and Zn reach plant roots by diffusion, mass flow, and root interception (Wilkinson, 1972). Movement of Cu to a plant root can be accounted for by convection (mass

flow) and aided by root interception (Ellis et al., 1983). According to studies by Oliver and Barber (1966), diffusion accounted for less than 5% of the total Cu absorbed by the plant. On the other hand, diffusion was the principle means of Zn movement to the root surface. This was confirmed by other studies (Ellis et al., 1983; Giordano and Mortvedt, 1980). It was noted that, although total Cu levels in soil solution are similar to those of Zn for many soils, total Cu uptake by plants is an order of magnitude lower than for Zn (Ellis et al., 1983).

Normal Ranges in Plant Tissue. The ranges of 5-20 mg Cu/kg and 25-150 mg Zn/kg in mature plant leaf tissue have been reported to be sufficient for plant growth (Jones, 1972). Plants are considered to contain inadequate Cu or Zn if their mature leaves contain <4 mg Cu/kg or <20 mg Zn/kg. Excessive or toxic concentrations of Cu and Zn would be >20 and >400 mg/kg for mature leaves, respectively. Critical Cu and Zn concentrations for corn (Zea mays L.) were reported to be 5 mg Cu/kg and 15 mg Zn/kg in earleaves at the early-silk growth stage (Jones and Eck, 1973). A sufficiency range of 1-5 mg Cu/kg in corn grain at plant maturity was also reported. Kabata-Pendias and Pendias (1984) listed a mean Zn content of about 25-36 mg/kg in corn grain depending on the sources they cited.



Differential Response of Plant Genotypes. The uptake of Cu and Zn by plants differs among species and among varieties within a species (Brown et al., 1972). In his study on responses of genotypes to Cu, Nambiar (1976) found that in the absence of applied Cu only one genotype out of nine genotypes of various cereal crops produced grain; but when 0.1 mg Cu was applied per pot, five of the nine genotypes produced some grain. He also indicated that the sensitivity to Cu differed in various genotypes and those with relatively higher yield potentials were less sensitive to Cu deficiency than ones with lower yield potentials.

Rao et al. (1977) studied three soybean [Glycine max (L.) Merr.] cultivars that differed in the capacity to absorb Zn. In addition to total uptake differences, the distribution of Zn in plant parts varied among the cultivars. Working with corn hybrids, Terman et al. (1975) suggested that differences in the absorption of Zn or other nutrients by corn hybrids are influenced through genetic effects on growth rates and yield potentials.

Differences in Accumulation in Plant Parts. Plants tend to accumulate more Cu and Zn in their root system than in their aerial parts (Loneragan, 1981; Tiffin, 1972). This was also reported to occur in corn (Dragun et al., 1976). They used a split root procedure for growing corn seedlings

in receptacles containing 100 g Hagerstown silt loam and nutrient solutions containing from 0.01 to 0.64 mg Cu/L. After four weeks, Cu concentrations in the corn shoots and roots were 12.8 and 99.3 mg/kg when grown in the 0.01 mg Cu/L solution and 13.0 and 1008.6 mg/kg when grown in the 0.64 mg Cu/L solution, respectively. In the case of Zn that was added initially to the soil at a rate of 6.0 mg/L, the Zn concentration in the corn tops varied from 22.8-40.3 mg/kg and in the roots from 43.0-134 mg/kg.

Copper is considered to have low mobility relative to other elements in plants and most of this metal appears to remain in root and leaf tissues until they senesce (Kabata-Pendias and Pendias, 1984). On the other hand, Zn is considered to have intermediate to high mobility in plants. With luxury levels of soil Zn, this element may be translocated from the roots and accumulated by the plant shoots (Kabata-Pendias and Pendias, 1984).

Interactions with Other Elements. It has been observed that either Cu or Zn may undergo interactions with other elements within plant tissues and also in external root media, especially in the uptake-transport processes (Olsen, 1972; Kabata-Pendias and Pendias, 1984). Among many observed interactions, those of either Cu or Zn with P and Fe have been the subject of many studies. Interaction with P

is antagonistic in character and is known to induce Cu or Zn deficiency (Olsen, 1972). This antagonism appears to be based, to a great extent, on chemical reactions in the root media. Synergism between P and Zn was also observed in some plants (Kabata-Pendias and Pendias, 1984).

Copper- or Zn-Fe antagonism may result in a decrease in Fe concentration in plants and leads to Fe chlorosis (Kabata-Pendias and Pendias, 1984; Giordano and Mortvedt, 1980). Iron reduces Cu absorption from soil solutions, especially on peat soils. The toxic effects of Cu can be decreased by additions of Fe, but the adverse effect of high Cu has never been completely overcome by Fe (Olsen, 1972). The Zn-Fe antagonism may occur via competition between  $Zn^{++}$  and  $Fe^{++}$  in the uptake processes and through interference in chelation processes during the uptake and translocation of Fe from the roots to tops (Olsen, 1972; Kabata-Pendias and Pendias, 1984). Also, Fe decreases Zn absorption and the toxicity of Zn that was absorbed.

Interactions between Cu and Zn have been commonly observed (Olsen, 1972; Graham, 1981). The interactions may occur either in soils or in the process of plant uptake. In their study on Zn and Cu sorption and interaction in four California soils, Kurdi and Doner (1983) found that sorbed Cu was only slightly affected by Zn additions; however, Zn

sorption was greatly affected by the Cu additions. They indicated that these phenomena demonstrate the inability of Zn to compete strongly with Cu for the sorption sites. Graham (1981) stated that Cu and Zn apparently are absorbed by roots via the same mechanism and, therefore, the uptake of one element is competitively inhibited by the other. The significant effect of this interaction in plant uptake is usually observed in an environment of low supply of either Cu or Zn (Olsen, 1972).

#### Response of Corn to Cu and Zn Applications

Copper and Zn Applied to Soils as Wastes. There are concerns about effects of long-term applications of sludges and manures with high heavy metal contents on the food chain and on crop production (Logan and Chaney, 1983). Guidelines for the application of sludges to agricultural land have been established (Sommers and Nelson, 1978). The soil pH of the disposal site must be 6.5 or more to prevent metal toxicity. Maximum sludge loading rates for Cd, Cu, Ni, Pb, and Zn are based on soil CEC (Table 1). There have been many studies on corn response relative to soil Cu and Zn contents from sludge application.

Field research was conducted on a Warsaw silt loam to study the effects of long-term applications of sewage sludge

Table 1. Total amount of sludge metals allowed on agricultural land.

Metal	Soil Cation Exchange Capacity cmol (+)/kg		
	0-5	5-15	>15
-----Maximum Amount of Metal (kg/ha)-----			
Pb	560	1120	2240
Zn	280	560	1120
Cu	140	280	560
Ni	140	280	560
Cd	5.6	11	22

on soil Cu and Zn status and on corn tissue Cu and Zn concentrations (Kirkham, 1975). This soil had received 35 annual applications from 1930-1965 of an estimated 28 t municipal sludge/ha. The top 61 cm of the amended soil contained 4.4 t Cu and 10.7 t Zn/ha in 1973. Total Cu in the top 30 cm of the amended soil was increased by 792 mg Cu/kg, while total Zn was increased by 1,907 mg Zn/kg. Corn grown on the soil in 1973 contained 12, 40, and 617 mg Cu/kg and 79, 196 and 1,349 mg Zn/kg in grain, leaves, and roots, respectively. Corn on control plots contained 8, 10, and 85 mg Cu/kg and 12, 67, and 236 mg Zn/kg in grain, leaves, and roots, respectively.

Corn response to a single application of anaerobically digested sewage sludge was investigated by Ritter and Eastburn (1978) on a Metapeake silt loam (pH = 5.8, 2.3% OM, CEC = 9.5 cmol(+)/kg). The highest rate of sludge application supplied 26.3 kg Cu and 87.6 kg Zn/ha. They found that the sludge application did not increase the Cu content of corn seedlings, ear leaves, or grain. The same results were obtained for Zn, except that the Zn concentration in ear leaves was increased by 19 mg/kg on plots with the highest rate of application. Sheaffer et al. (1979) studied corn response to a single application of anaerobically digested sewage sludge but at a much higher rate of application. They

worked with a Sassafras sandy loam (pH = 5.6, 1.3% OM, CEC = 5.62 cmol(+)/kg) amended with a 0, 56, and 112 t sludge/ha on a dry weight basis. The highest rate of application supplied 246.4 kg Cu and 492.8 kg Zn/ha. Both rates of sludge application increased Cu and Zn concentrations in corn seedlings, ear leaves, grain, and stover. But the increase of Cu in grain was not significant at 0.05 level of probability.

Response of corn to sludge application that supplied a total of 1,290 kg Zn/ha over a period of five years was studied by Hinesly et al. (1979) on a Blount silt loam. Corn was grown during the last two years of sludge application and four years following sludge application. They reported that sludge applications did not affect corn yields in comparison with control plots. During the final year, the 1,290 kg Zn/ha from sludge application increased the Zn concentrations in corn ear leaves and grain by 103 and 14 mg Zn/kg, respectively. But four years after sludge application, Zn concentration in ear leaves was increased by only 22 mg Zn/kg and Zn concentration was not increased in corn grain.

Kirleis et al. (1982) investigated the effect of sewage sludge application on the composition of corn grain and fractions obtained by dry-milling. Corn 'Beck's 65X' was

grown on soil amended with 56 to 448 t sewage sludge/ha from three treatment plants. Corn grain yields were not adversely affected by sewage sludge applications. Also, Cu and Zn contents of the grain were not increased by the sewage sludge treatments.

Corn response to three annual applications of Cu-enriched hog manure on Groseclose silt loam (clayey, mixed, mesic Typic Hapludult) was investigated by Kornegay et al. (1976). They incorporated manure from hogs fed diets with 0 and 307 mg Cu/kg of supplemental  $\text{CuSO}_4$  into the soil. Three annual applications supplied an average of 24 kg Cu/ha/year. The manure applications increased Cu concentrations in corn ear leaves, but did not affect either corn-grain yields or Cu concentrations.

A study on the effects of Cu-enriched hog manure applications on Cu availability, form, and mobility in one Alfisol and two Ultisols was conducted by Mullins et al. (1982b). Five field treatments applied to the three soils annually for three years were 33.6 and 67.2 t/ha of wet manure from hogs on high-Cu diets, Cu levels as  $\text{CuSO}_4$  equivalent to that in the manure, and a control. The highest manure rate supplied from 55.6 to 65.6 kg Cu/ha in the soils over the three years. Application of these levels of Cu as either  $\text{CuSO}_4$  or Cu-enriched hog manure did not decrease corn



grain yields on the three soils. In some cases, the Cu applications caused relatively small increases in Cu concentrations in corn ear leaves and grain.

Copper and Zn Applied to Soils as Inorganic Salts.

There are few data in the literature from field study on corn response to Cu and Zn applications as inorganic salts. Some studies have been conducted to determine the effects of relatively large applications of these micronutrients on other crops, such as snapbean (Phaseolus vulgaris L.) and soybean (Glycine max L. Merr.).

Walsh et al. (1972b) found that a single application of Zn as  $ZnSO_4$ , equivalent to 81 years of fungicide application (363 kg Zn/ha), decreased snapbean yield on a Plainfield loamy sand (mixed, mesic Typic Udipsamment) during the first growing season, but did not affect yield during the second growing season. Yield of corn, which was grown during the fourth growing season following  $ZnSO_4$  application, was not affected by Zn application. However, the Zn concentration in corn leaves was increased by 139.4 mg Zn/kg. In a study on snapbean response to Cu, Walsh et al. (1972a) found that a single application of Cu as  $CuSO_4$ , equivalent to 27 years of fungicide application (486 kg Cu/ha), decreased snapbean yields on the Plainfield loamy sand during two successive growing seasons. Martens et al. (1974) reported that six

annual applications of up to 8.4 kg Cu and 11.1 kg Zn/ha as sulfates did not adversely affect soybean growth on a Davidson clay loam (clayey, kaolinitic, thermic Rhodic Paleudult) and a Marlboro fine sandy loam (clayey, kaolinitic, thermic Typic Paleudult).

A field study on corn response to Cu and Zn as sulfates was conducted by Brown and McCormick (1971). Copper and Zn were applied to Mexico (pH = 7.1, 2.5% OM, CEC = 16.8 cmol(+)/kg) and Marshall (pH = 6.5, 3% OM, CEC = 17.5 cmol(+)/kg) soils at rates of 11.2 kg Cu/ha, and 11.2 and 22.4 kg Zn/ha. Yields of corn grain were not affected on the soils by the Cu and Zn treatments. The Zn treatments increased Zn concentrations in corn ear leaves.

A study that was the predecessor of the study reported in this thesis was conducted by Mullins et al. (1982a). They found that neither corn grain nor silage yields were affected by 15 years of applications of various levels of Cu and Zn sulfates, which provided a cumulative total of 171.7 kg Cu/ha and/or 290.4 kg Zn/ha. Copper concentrations in ear leaves sampled at the early silk growth stage generally were not affected by the Cu applications, whereas Zn concentrations in the ear leaves varied directly with levels of Zn application. Similarly, the Cu concentrations in corn grain were unaffected by the Cu applications, but the Zn concen-

traits in corn grain were increased by the Zn applications.

## MATERIALS AND METHODS

A long-term field experiment was conducted to evaluate corn (Zea mays L.) response to applications of Cu and Zn sulfates. The field experiment was initiated in 1967 and continued through 1984 on a Davidson silty clay soil (clayey, kaolinitic, thermic Rhodic Paleudult) located in Orange, Virginia. Corn was grown on the experimental area each year, except in 1972, when soybeans [Glycine max L. Merr.] were grown on the site.

### Field Experimentation

Five treatments applied to the soil annually during the 18-year period from 1967 through 1984 consisted of various levels of Cu and Zn sulfates, either alone or together, and a control (Table 2). The treatments were arranged in a randomized complete block design with four replications and with a plot size of 5.0 and 7.6 m.

Boron, Mg, N, P, and K as Na borate, MgO,  $\text{NH}_4\text{NO}_3$ , triple superphosphate, and KCl, respectively, were applied to the experimental area at levels to prevent these deficiencies. The entire experimental area received 1.1 kg B, 168

Table 2. Total Cu and Zn applied to the Davidson soil as sulfates during the 17th and 18th years of the long-term field experiment.

Treatment number	Cumulative micronutrient application			
	1983		1984	
	Cu	Zn	Cu	Zn
	-----kg/ha-----			
1	0.0	0.0	0.0	0.0
2	0.0	560.1	0.0	695.4
3	142.8	188.5	151.2	199.8
4	279.9	0.0	334.0	0.0
5	279.9	560.1	334.0	695.4

kg Mg, 263 kg N, 39 kg P and 74 kg K/ha. The Cu and Zn sulfates for the treatments were broadcast on the soil surface on April 3, 1984 and disked into the soil to a depth of approximately 12 cm. 'Pioneer 3192' corn was grown on the experimental area at a population of 57,400 plants/ha. Weeds were controlled on the experimental area by herbicide application. A total of 9.8 cm of supplemental water was applied to the experimental area by irrigation. Corn grain and stalk (earless shoot) yields were determined for each plot of the field experiment at plant maturity. The grain yields were reported at 15.5% moisture whereas stalk yields were reported on a dry weight basis.

#### Corn Tissue Analysis

Plant tissue samples consisted of ten ear leaves/plot sampled at the early silk growth stage and of grain shelled from 10 ears/plot at plant maturity. The ear leaf and grain samples were dried at 70 C for 48 h and ground to pass a 20-mesh screen in preparation for Cu and Zn analyses. One-g subsamples of the ear leaf tissue were dry-ashed at 450 C for 2 h. The ash was equilibrated with successive 10-, 10- and 5- mL portions of 0.5 M HCl for 1 h and filtered through Whatman no. 42 filter paper. Copper and Zn in the combined filtrate were determined by atomic absorption spectrophoto-

metry. One-g subsamples of grain were digested in a  $\text{HNO}_3\text{-HClO}_4$ , diluted to 35 mL with water, and filtered through Whatman no. 42 filter paper. Copper and Zn in the filtrate were determined by atomic absorption spectrophotometry.

### Soil Analyses

Before application of the treatments, soil samples were collected on April 3, 1984 for soil characterization, DTPA-extractable Cu and Zn, and Cu and Zn fractionation analyses. The 0- to 20-cm soil layer (Ap horizon) was sampled from all plots, and the 25- to 33-cm soil layer was sampled from four replications of selected treatments. Ten soil cores/plot were collected using a sampling probe with a 1.9-cm diameter. Soil samples were air dried and ground to pass a 10-mesh sieve.

Soil Characterization Analyses. Soil characterization analyses were completed on Ap horizon samples from the four replicates of the control treatment. Soil pH was determined with a glass electrode using a 1:1 soil-to-water ratio and a 1-h equilibration period. Organic matter was determined by a dichromic acid ( $\text{H}_2\text{Cr}_2\text{O}_7$ ) oxidation technique (Walkley and Black, 1934), free Fe by a dithionite-citrate-bicarbonate procedure (Mehra and Jackson, 1960), CEC by a 0.5 M Ca ace-

tate (pH 7.0) saturation and 0.5 M Mg acetate (pH 7.0) displacement procedure, and particle-size distribution by a pipet method (Kilmer and Alexander, 1949).

Mineralogical analysis of the silt and clay fractions was conducted after organic matter and free Fe oxides removal. Organic matter was removed from the sample with  $H_2O_2$  buffered in M NaOAc (pH 5.0) and free Fe oxides with citrate-bicarbonate-dithionite. The sample was dispersed with 0.5 M  $Na_2CO_3$  and the sand fraction removed by wet sieving on a 300-mesh sieve. Silt was separated from the clay fraction by centrifugation.

The clay fraction was flocculated with solid NaCl and washed twice with distilled water. Approximately one-half of the clay was K-saturated and the remainder was Mg-saturated by repeated washings with 1 M KCl and 0.5 M  $MgCl_2$  solutions, respectively. Oriented X-ray diffraction mounts of the K- and Mg-saturated clay were made by a millipore filter technique. Water was removed from an aliquot of clay suspension by suction with a 0.47  $\mu$  filter. The Mg-saturated clay sample was also glycerol solvated with a 20% glycerol solution. The clay was then transferred to a glass slide and allowed to dry. X-ray diffractograms were obtained using  $CuK\alpha$  radiation. Analyses were performed on both samples at room temperature (25 C) and after heating to 110 C for 4



h. For the K-saturated mount, X-ray analyses were completed with two additional 4-h heat treatments at 300 and 550 C, respectively. Percentages of the minerals in the clay fraction were estimated by visual comparison of relative peak intensities with standard minerals.

A random powder mount was made of the dried silt, and X-ray analysis was performed at 25 C. Quantification of mineral species was performed by the aforementioned peak intensity comparisons for clay fraction.

DTPA-extractable Cu and Zn Analyses. To evaluate downward movement of applied Cu and Zn, DTPA-extractable Cu and Zn were determined in samples from the two depths. The DTPA-extractable Cu and Zn were determined by the procedure devised by Lindsay and Norvell (1978). Ten g of air-dry soil was extracted in duplicate with 20 mL of DTPA extracting solution (0.005 M DTPA, 0.1 M triethanolamine, and 0.01 M  $\text{CaCl}_2$ , with a pH of 7.3). The extraction was performed by shaking the suspension for 2 h on a reciprocating shaker at a rate of 120 cycles/min. The suspension was centrifuged for 10 min at 2,000 rpm and filtered through Whatman no. 42 filter paper. Copper and Zn in the extract were determined by atomic absorption spectrophotometry.

Copper and Zn Fractionation Analyses. A sequential extraction procedure was used to determine soil solution and

exchangeable, specifically adsorbed, organically bound, free oxide bound, and residual Cu and Zn fractions in the Ap horizon samples. The sequential extraction procedure used was a modified version of the McLaren and Crawford (1973a) fractionation scheme. Table 3 lists the soil fractions, their extractants and abbreviations.

Soil-solution and exchangeable Cu and Zn (Ca-Cu and Ca-Zn) were extracted by shaking 5 g of air-dry soil (<2mm) in 50 mL of 0.25 M CaCl<sub>2</sub> for 24 h on a reciprocating shaker at 120 cycles/minute. The suspension was centrifuged at 2000 rpm for 10 min, and the supernatant was decanted and saved for Cu and Zn analyses.

Specifically adsorbed Cu and Zn (AAC-Cu and AAC-Zn) were extracted by adding 50 mL of 2.5% acetic acid to the residue from above and then by shaking the suspension for 24 h. The solution was decanted after the sample was centrifuged at 2000 rpm for 10 min. The decant was saved for Cu and Zn analyses, and the remaining soil residue was discarded.

Organically bound Cu and Zn (PYR-Cu and PYR-Zn) were extracted by shaking a 0.5-g sample of air-dry soil with 50 mL of 0.1 M K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> for 16 h. The suspension was centrifuged at 2000 rpm for 10 min and the supernatant was saved for Cu and Zn analyses. The PYR-Cu and PYR-Zn were calculated by

Table 3. Sequential soil Cu and Zn fractionation scheme used to fractionate Ap horizon samples of the Davidson soil after 17 annual Cu and Zn applications.

Form	Extractant	Abbreviation
Soil solution and exchangeable	0.25 M CaCl <sub>2</sub>	Ca-Cu/Zn
Specifically adsorbed	2.5% acetic acid	AAC-Cu/Zn
Organically bound	0.1 M potassium pyrophosphate	PYR-Cu/Zn
Free oxide bound	0.1 M oxalic acid, 0.175 M NH <sub>4</sub> <sup>+</sup> -oxalate, pH 3.25	OX-Cu/Zn
Residual	[total Cu/Zn]-[sum of other fractions]	RES-Cu/Zn

subtraction of Ca- and AAC-Cu or Zn from the 0.1 M  $K_4P_2O_7$ -extractable Cu or Zn, respectively.

The residue from the soil used for extraction of organically bound Cu and Zn was washed with 50 mL of deionized water. To determine free oxide-bound Cu and Zn (OX-Cu and OX-Zn), the washed residue was transferred to a 100-mL beaker with 25 mL of 0.1 M oxalic acid-0.175 M  $NH_4^+$ -oxalate solution at pH 3.25 (Tamm's reagent). The beaker was covered with saran wrap (having one pin hole) to prevent evaporation and the soil hydroxides and oxides were extracted by placing the beaker in a hot water bath and agitating under uv light for 3 h at a rate of 250 rpm (Miller, 1981). The suspension was transferred to a centrifuge tube, centrifuged at 1000 rpm for 5 min, and the supernatant was saved for Cu and Zn analyses. The residue was washed with 15 mL of Tamm's reagent, centrifuged at 1000 rpm for 5 min, and the wash was combined with the initial extract.

To determine residual Cu and Zn (RES-Cu and RES-Zn), total Cu and Zn analyses were conducted by the procedures described by Bernus (1968). Samples of 0.5-g oven-dry (105 C, <100-mesh) soil were placed in teflon bombs containing 1 mL of aqua regia and 10 mL of HF. The bombs were assembled in metal containers and heated at 110 C for three h. The cooled digests were transferred into a 50-mL volumetric

flask containing 1.4 g boric acid and 5 mL of deionized water. Complete transfer of the digests to the flask was accomplished with deionized water. The solutions were diluted to a 50-mL volume with deionized water, transferred to a centrifuge tube, and centrifuged at 2000 rpm for 5 minutes. The supernatants were saved for Cu and Zn analyses. RES-Cu or RES-Zn was calculated by subtracting the sum of other fractions from the total Cu or Zn, respectively.

Copper and Zn in the various solutions, from the above fractionation scheme, were determined by atomic absorption spectrophotometry.

#### Statistical Analyses

Corn yield, Cu and Zn concentrations in corn tissue, DTPA-extractable Cu and Zn, and Cu and Zn fractionation data were evaluated by analyses of variance (Anova). Mean separations were performed by linear contrasts when the F-value of the Anova was significant at the 0.05 probability level. These analyses were performed on an IBM 3081 computer utilizing SAS programs (SAS Institute, Inc., 1982).

## RESULTS AND DISCUSSION

A long-term field experiment was conducted to determine the response of corn to 18 annual  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  applications which provided a cumulative total of 334.0 kg Cu and 695.4 kg Zn/ha. Corn response to the applied Cu and Zn were evaluated from the measurements of corn-grain and -stalk (earless shoot) yields and of Cu and Zn concentrations in corn tissue. Downward movement and reversion of Cu and Zn in soil following 17 annual  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  applications that provided a cumulative total of 279.9 kg Cu and 560.1 kg Zn/ha were also investigated.

### Soil Properties

The soil used in this long-term field study was a Davidson silty clay soil located in the Piedmont region of Virginia (Tables 4 and 5). This is a highly weathered soil. The Ap horizon of the soil contained mainly kaolinite and 14-A intergrade clay minerals and had a low organic matter content, moderate CEC, and very high free Fe content. The pH of the soil of 6.3 was very close to 6.5, which has been suggested for soils used for applications of heavy metals (Sommers and Nelson, 1978).

Table 4. Properties of the Davidson soil used to evaluate Cu and Zn uptakes by corn plants where these micronutrients were applied annually for 18 years.

Soil property	Value
Soil pH	6.3
Organic matter, g/kg	15
Free iron, g/kg	59
Cation exchange capacity, cmol(+)/kg	11.2

Table 5. Physical and mineralogical properties of the Davidson soil used to evaluate Cu and Zn uptakes by corn plants where these micronutrients were applied annually for 18 years.

Particle size analysis*				Mineralogy**	
Sand	Silt	Clay	Texture	Silt	Clay
-----g/100g-----					
9	41	50	Silty Clay	Q(85), M(10) F(5)	K(40), I(30) Q(10), M(10) G(5), F(5)

\*Sampling depth was 0-20 cm

\*\*K = kaolinite; I = intergrade; Q = quartz; M = mica; F = feldspar; G = gibbsite. Approximate percentages of each mineral are in parentheses.



### Corn Yields

Corn-grain yields were not decreased by 18 annual applications of various levels of Cu and Zn in 1984 (Table 6). Likewise, corn-stalk yields were unaffected by the Cu and Zn applications. The overall corn yield that was relatively high was attributable to irrigation and to adequate nutrients.

In relation to Cu and Zn application as sewage sludge, the highest levels of applied Cu and Zn in this experiment (Table 2) exceed the limitations given by Sommers and Nelson (1978) (Table 1). Therefore, the non-significant effects of the treatments on corn yields (Table 6) indicate that the data with sewage sludge may not be directly applicable for determination of tolerable Cu and Zn loading rates from soluble inorganic sources. This was expected because plants absorb different amounts of Cu and Zn from soluble inorganic sources than from sewage sludge (Cunningham et al., 1975).

### Copper and Zn Concentrations in Corn Tissue

Eighteen annual applications of various levels of Cu and Zn, which provided a cumulative total of up to 334.0 kg Cu/ha, did not affect Cu concentrations in corn grain (Table 7). Copper concentration in ear leaves was increased by the highest level of Cu application, but was not affected by the

Table 6. Grain and stalk yields after 18 annual applications of various levels of Cu and Zn to the Davidson soil.

Treatment number	Total micronutrient application		Corn yield	
	Cu	Zn	Grain	Stalk
	-----kg/ha-----			
1	0.0	0.0	12,100	8,738
2	0.0	695.4	11,506	8,517
3	151.2	199.8	12,062	8,970
4	334.0	0.0	12,082	8,239
5	334.0	695.4	11,981	8,297
Analysis of variance:			----- F value -----	
			1.47ns	1.20ns

ns Not significant at the 0.05 level of probability.

Table 7. Copper concentrations in corn tissue after 18 annual applications of various levels of Cu and Zn to the Davidson soil.

Treatment number	Total micronutrient application		Copper concentration in corn tissue	
	Cu	Zn	Grain	Ear leaf
	-----kg/ha-----		----- mg Cu/kg-----	
1	0.0	0.0	2.2	19.9
2	0.0	695.4	2.3	20.4
3	151.2	199.8	2.0	21.0
4	334.0	0.0	2.0	21.4
5	334.0	695.4	2.3	21.7
Analysis of variance:			----- F value -----	
Linear contrasts:			0.71ns	3.57*
Treat. 1, 2 vs 3			--	2.99ns
Treat. 3 vs 4, 5			--	1.46ns
Treat. 1, 2 vs 4, 5			--	12.94**
Treat. 4 vs 5			--	0.44ns

\*\*Significant at the 0.01 level of probability.

\*Significant at the 0.05 level of probability.

ns Not significant at the 0.05 level of probability

moderate level of Cu application (Table 7). Linear contrast for treatment 4 versus treatment 5 showed that applied Zn did not interact with Cu uptake by corn.

The Zn concentration in corn grain was increased only by the highest level of Zn application, which provided a cumulative total of 695.4 kg Zn/ha (Table 8). Concentrations of Zn in ear leaves varied directly with cumulative levels of applied Zn (Table 8). Linear contrast for treatment 2 versus treatment 5 indicated that in this experiment applied Cu did not interact with Zn uptake by corn.

In general, these corn tissue Cu and Zn data paralleled the previous findings by Mullins et al. (1982a). Except for data on Cu concentrations in corn grain, the differences between the two studies were in the absolute values obtained as the consequence of higher cumulative amounts of Cu and Zn application. Nevertheless, in all cases, the Cu and Zn concentrations in corn grain and ear leaves in this study (Tables 7 and 8) were still within the normal ranges (Jones, 1972; Jones and Eck, 1973; Kabata-Pendias and Pendias, 1984). It is possible that Cu and Zn were absorbed by corn roots, but not transported to aerial plant parts as has been shown by Dragun et al. (1976).

Table 8. Zinc concentrations in corn tissue after 18-annual applications of various levels of Cu and Zn to the Davidson soil.

Treatment number	Total micronutrient application		Zinc concentration in corn tissue	
	Cu	Zn	Grain	Ear leaf
	kg/ha		mg Zn/kg	
1	0.0	0.0	16.3	19.6
4	334.0	0.0	17.1	21.1
3	151.2	199.8	17.0	25.0
2	0.0	695.4	24.9	41.9
5	334.0	695.4	26.4	41.8
Analysis of variance:			14.47**	64.89**
Linear contrasts:				
Treat. 1, 4 vs 3			0.03ns	7.60*
Treat. 3 vs 2, 5			30.29**	99.61**
Treat. 1, 4 vs 2, 5			48.52**	243.34**
Treat. 2 vs 5			0.69ns	0.01ns

\*\*Significant at the 0.01 level of probability.

\* Significant at the 0.05 level of probability.

nsNot significant at the 0.05 level of probability.

### Downward Movement of Soil Copper and Zinc

Analysis of the Ap horizon samples showed that DTPA-extractable Cu was increased by 17 annual applications of Cu, which provided a cumulative total of 279.9 kg Cu/ha (Table 9). Similarly, the DTPA-extractable Cu in the underlying soil layer (25-33 cm) was increased slightly by the applied Cu (Table 9). These DTPA-extractable Cu data indicate that there was little downward movement of applied Cu in the Davidson soil. The linear-contrast analysis for treatment 4 versus 5 in the Ap horizon (Table 9) showed that the applied Zn increased the Cu concentration in the labile pool of the soil. This phenomenon will be discussed later in the discussion of soil Cu and Zn fractions.

Similar to that for Cu, the DTPA-extractable Zn data indicate that there was little downward movement of Zn following 17 annual applications of the element, which provided a cumulative total of 560.1 kg Zn/ha (Table 10). In comparison to Cu, however, Zn moved downward in a greater quantity (Tables 9 and 10). The linear contrast analyses for treatment 2 versus 5 for both the Ap and underlying horizons (Table 10) showed that applied Cu did not affect Zn concentration in the labile pool of the soil.

The fact that there was less downward movement of applied Cu and Zn during earlier years of this long-term study

Table 9. DTPA extractable Cu concentrations in two soil layers after 17 annual applications of Cu to a Davidson soil.

Treatment number	Total micronutrient application		DTPA extractable Cu concentration in two soil layers	
	Cu	Zn	0 - 20cm	25 - 33cm
	----- kg/ha -----		----- mg Cu/kg -----	
1	0.0	0.0	2.1	0.9
2	0.0	560.1	2.8	0.8
4	279.9	0.0	19.2	1.3
5	279.9	560.1	22.8	1.6
			----- F value -----	
Analysis of variance:			448.11**	4.74*
Linear contrasts:				
Treat. 1, 2 vs 4, 5			1318.88**	12.22**
Treat. 4 vs 5			24.39**	1.99ns

\*\*Significant at the 0.01 level of probability.

\*Significant at the 0.05 level of probability.

ns Not significant at the 0.05 level of probability.

Table 10. DTPA extractable Zn concentrations in two soil layers after 17 annual applications of Zn to a Davidson soil.

Treatment number	Total micronutrient application		DTPA extractable Zn concentration in two soil layers	
	Cu	Zn	0 - 20cm	25 - 33cm
	----- kg/ha -----		----- mg Zn/kg -----	
1	0.0	0.0	2.5	0.4
4	279.9	0.0	2.5	0.5
2	0.0	560.1	39.6	3.6
5	279.9	560.1	39.3	2.0
			----- F value -----	
Analysis of variance:			194.58**	4.47*
Linear contrasts:				
Treat. 1, 4 vs 2, 5			583.72**	10.86**
Treat. 2 vs 5			0.03ns	2.52ns

\*\*Significant at the 0.01 level of probability.

\*Significant at the 0.05 level of probability.

ns Not significant at the 0.05 level of probability.



(Mullins et al., 1982a) indicates that large applications and lower pH levels play important roles in mobility of these micronutrients (Emmerich et al., 1982; Dowdy and Volk, 1983). The total amount of applied Cu and Zn in this study was much greater (more than twice for Cu and more than three times for Zn) than that applied when Cu and Zn mobilities were investigated by Mullins et al. (1982a). In this study, the pH of the Ap horizon was 6.3, while in the earlier study it was 6.7. The fact that Zn moved downward in a greater quantity than Cu conforms to the conclusion by Dowdy and Volk (1983) that Zn is more mobile than Cu.

#### Copper and Zinc Fractions

The forms of Cu and Zn in the Ap horizon of the Davidson soil after 17 annual applications of various levels of Cu and Zn were evaluated by fractionation analyses (Tables 11 and 12).

The Ca-Cu was increased only by the highest level of the applied Cu, whereas the AAC-Cu, PYR-Cu, and OX-Cu varied directly with rate of Cu application (Table 11). The RES-Cu was not affected by Cu application. Comparison of values obtained from the highest level of Cu application with the control indicates that the Cu concentrations in the fractions were increased in the following order: PYR-Cu > OX-Cu

Table 11. Copper fractions in the Ap horizon of the Davidson soil after 17 annual applications of Cu.

Treatment number	Cumulative micro-nutrient application		Soil fraction					Total-Cu
	Cu	Zn	Ca-Cu	AAC-Cu <sup>ⓐ</sup>	PYR-Cu <sup>ⓐ</sup>	OX-Cu	RES-Cu	
----- kg/ha -----								
----- mg Cu/kg -----								
1	0.0	0.0	0.09	1.0	5.7	10.9	40.7	58.4
2	0.0	560.1	0.08	1.5	5.4	11.6	43.3	61.9
3	142.8	188.5	0.09	5.3	14.5	20.6	43.8	84.2
4	279.9	0.0	0.12	15.8	28.9	32.3	44.2	121.4
5	279.9	560.1	0.15	20.8	27.0	32.1	43.5	123.5

Analysis of variance:		F value	
-----		-----	
10.78**	247.80**	26.18**	37.28**
0.63 <sup>ns</sup>			
57.99**			
Linear contrasts:			
Treat. 1, 2 vs 3	1.02 <sup>ns</sup>	193.67**	26.07**
Treat. 3 vs 4, 5	15.43**	132.16**	10.17**
Treat. 1, 2 vs 4, 5	36.57**	968.68**	103.23**
Treat. 4 vs 5	3.06 <sup>ns</sup>	5.02*	0.11 <sup>ns</sup>
			0.01 <sup>ns</sup>
			0.14 <sup>ns</sup>

<sup>ⓐ</sup> The analysis of variance was done on logarithmically-transformed variates.

\*\*Significant at the 0.01 level of probability.

\* Significant at the 0.05 level of probability.

<sup>ns</sup>Not significant at the 0.05 level of probability.

Table 12. Zinc fractions in the Ap horizon of the Davidson soil after 17 annual applications of Zn.

Treatment number	Cumulative micro-nutrient application		Soil fraction					Total-Zn
	Cu	Zn	Ca-Zn	AAC-Zn <sup>ⓐ</sup>	PYR-Zn <sup>ⓐ</sup>	OX-Zn	RES-Zn	
kg/ha								
1	0.0	0.0	0.9	1.3	5.3	22.6	107.3	137.4
4	279.9	0.0	1.5	1.3	6.8	22.3	110.4	142.4
3	142.8	188.5	1.7	4.4	17.8	32.6	112.2	168.8
2	0.0	560.1	4.5	42.8	38.9	63.9	118.7	268.9
5	279.9	560.1	5.5	40.2	38.3	61.9	116.4	262.3

Analysis of variance:	F value				
	12.21**	238.91**	79.01**	80.82**	0.73ns
Linear contrasts:					
Treat. 1, 4 vs 3	0.50 <sup>ns</sup>	74.85**	75.27**	13.06**	-
Treat. 3 vs 2, 5	21.05**	267.34**	32.48**	114.73**	-
Treat. 1, 4 vs 2, 5	42.09**	937.66**	309.99**	307.80**	-
Treat. 2 vs 5	1.64 <sup>ns</sup>	0.16 <sup>ns</sup>	0.06 <sup>ns</sup>	0.38 <sup>ns</sup>	-
Total-Zn					
	12.21**	238.91**	79.01**	80.82**	0.73 <sup>ns</sup>
					58.53**

<sup>ⓐ</sup> The analysis of variance was done on logarithmically-transformed variates.

\*\*Significant at the 0.01 level of probability.

\* Significant at the 0.05 level of probability.

<sup>ns</sup>Not significant at the 0.05 level of probability.

> AAC-Cu > Ca-Cu. Amounts of Cu in the AAC-Cu and PYR-Cu fractions increased exponentially with rates of Cu application. Linear contrast analysis of treatment 4 versus 5 for the AAC-Cu fraction indicated that applied Zn increased the concentration of specifically adsorbed Cu (Table 11).

Similar to the data on Cu fractions, Ca-Zn was increased only by the highest level of the applied Zn (Table 12). The amounts of Zn in the AAC-Zn, PYR-Zn, and OX-Zn fractions varied directly with rate of Zn application. The amount of Zn in the RES-Zn fraction was not influenced by Zn application. Comparison of values obtained from the highest level of Zn application with the control indicate that the Zn concentrations in the fractions were increased in the following order: OX-Zn = AAC-Zn > PYR-Zn > Ca-Zn. Like those of Cu, the values of AAC-Zn and PYR-Zn increased exponentially with increasing rates of Zn application.

Perhaps due to the higher rate of Cu and Zn applications, in some cases, the above results (Tables 11 and 12) started to depart from the earlier results of this field study (Mullins et al., 1982a). But the general trends were still similar. The applications of various levels of Cu and Zn increased the amounts of Cu and Zn in the potentially available forms (Ca-, AAC- and PYR-Cu and -Zn) in the Davidson soil. Zinc concentrations in ear leaves (Table 8) were

higher where applied Zn increased the AAC- and PYR-Zn fractions (Table 12). However, unlike the results by Mullins et al. (1982a), Cu concentrations in ear leaves (Table 7) were increased by the highest levels of applied Cu that also increased the amounts of Cu in the AAC- and PYR-Cu fractions (Table 11).

The 17 annual applications of Cu and Zn increased Cu and Zn concentrations in the relatively plant-unavailable forms (OX-Cu and OX-Zn) in the Davidson soil (Tables 11 and 12). Reversion of a portion of applied Cu and Zn to plant-unavailable hydroxide and oxide forms, with time, also has been reported for other soils (Sommers and Nelson, 1978; Logan and Chaney, 1983). The non-significant effects of Cu and Zn applications on the amounts of Cu and Zn in the RES-Cu and RES-Zn fractions, respectively, were expected because the reversion of applied Cu and Zn to these fractions needs much longer time.

The order of increase in Cu fractions, PYR-Cu > OX-Cu > AAC-Cu > Ca-Cu, suggested that Cu has a high affinity for soil organic matter. This is in agreement with other research findings (McLaren and Crawford, 1973a; Mullins et al., 1982b). On the other hand, the order of increase in Zn fractions, OX-Zn = AAC-Zn > PYR-Zn > Ca-Zn, indicated that Zn has a high affinity to soil hydroxides and oxides. This

coincides with research findings reported by Iyengar et al. (1981).

The increase in specifically adsorbed Cu due to Zn application (Table 11) is not an easily explainable phenomenon. This phenomenon parallels the DTPA-extractable Cu data in the Ap horizon (Table 9). A possible explanation of this phenomenon is that a portion of Cu, which would occupy the more stable pools (OX-Cu and PYR-Cu) when Cu was applied alone, could not occupy these pools due to competition for sites with applied Zn. This can be seen from Table 11 in which the values of PYR-, OX- and RES-Cu for treatment 5, where Cu was applied together with Zn, were consistently lower than those for treatment 4, where Cu was applied alone. The portion of Cu that could not occupy the more stable pools occupied the specifically adsorbed sites (AAC-Cu), which is less stable. Applied Zn also underwent a similar mechanism. The values of PYR-, OX- and RES-Zn for treatment 5 (Table 12), where Zn was applied together with Cu, were consistently lower than those for treatment 2, where Zn was applied alone. But, unlike Cu, the portion of Zn, which could not occupy the more stable pools, could not occupy the specifically adsorbed site either. This is because, as pointed out by Kurdi and Doner (1983), Zn has less ability than Cu to compete for the sorption sites. Therefore, this

portion of Zn remained in the soluble and exchangeable forms and consequently was subject to leaching and plant uptake.

The above phenomenon combined with the fact that Cu and Zn concentrations in specifically adsorbed and organically bound sites increased exponentially may be interpreted in two ways. First, much more time may have been required for reversion of the large amount of applied Cu and Zn to plant-unavailable forms. Second, it is possible that the large amount of Cu and Zn applied together almost exceeded the capacity of the adsorption sites in the Davidson soil. Regardless of which one is true, it is probable that the non-significant responses of corn to the highest level of Cu and Zn applications were more attributable to the uptake and translocation mechanisms of Cu and Zn by corn plants than to the reversion process of applied Cu and Zn to plant-unavailable forms.

## SUMMARY AND CONCLUSIONS

### Summary

Copper and Zn frequently are incorporated into agricultural soils as fertilizers, pesticides, and waste materials. High levels of Cu and Zn application to agricultural soils are considered to pose a potential hazard to plants and animals. Field data are needed to determine Cu and Zn levels that either injure plants or increase Cu and Zn concentrations in edible plant portions to undesirably high levels.

This study was undertaken on a Davidson silty clay (clayey, kaolinitic, thermic Rhodic Paleudult). The specific objectives of this study were to determine corn response to 18 annual applications of various levels of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$ , which provided 334.0 kg Cu and 695.4 kg Zn/ha; to evaluate downward movement of Cu and Zn following 17 annual applications of various levels of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$ , which provided 279.9 kg Cu and 560.1 kg Zn/ha; and to investigate the reversion of Cu and Zn to plant-unavailable forms following the 17 annual applications of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$ .

The 18 annual applications of various levels of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  to the Davidson soil did not affect either corn-



grain or corn-stalk yields. Copper concentration in corn grain was not affected by the various levels of applied Cu. Concentration of Cu in ear leaves was increased by the highest level of Cu application, but was not affected by the moderate cumulative level (151.2 kg/ha) of Cu application. Zinc concentration in corn grain was increased only by the highest level of Zn application, while its concentrations in ear leaves varied directly with various levels of applied Zn. In all cases, the Cu and Zn concentrations in corn grain and ear leaves were within the normal ranges.

The DTPA-extractable Cu and Zn in soils following 17 annual applications of various levels of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  indicated an accumulation of Cu and Zn in the Ap horizon, with little downward movement of the applied Cu and Zn. Zinc moved downward in a greater amount than Cu.

Copper and Zn from the 17 annual applications of various levels of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  were distributed among both potentially plant-available and -unavailable soil fractions. The highest level of applied Cu and Zn caused a larger increase in potentially plant-available specifically-adsorbed and organically-bound forms. In comparison with all fractions, Cu had tendency to revert to the organically bound soil fraction, while Zn to the free oxide-bound soil fraction. Interaction between the applied Cu and Zn in competition for sorption sites did occur in the soil.

### Conclusions

Application of up to 334.0 kg Cu and 695.4 kg Zn/ha as sulfates to a Davidson soil in 18 annual applications, which was above the suggested tolerable levels for the application of these micronutrients as sewage sludge, did not adversely affect the growth and yield of corn. However, from the observation on the reversion process of the applied Cu and Zn in the soil, there was doubt that the amount of Cu and Zn applied to the soil in 17 annual applications of up to 279.9 kg Cu and 560.1 kg Zn/ha was close to the sorption capacity of the soil. For this reason, it is concluded that the non-significant responses of corn to the 18 annual applications were more attributable to the uptake and translocation mechanisms of Cu and Zn by corn plants than to the concentrations of the metals in potentially plant-available forms. Therefore, it is suggested that the long-term field experiment discussed herein be continued and, if possible, with different crop species.

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RESPONSE OF CORN TO HIGH LEVELS OF  
CuSO<sub>4</sub> AND ZnSO<sub>4</sub> APPLICATIONS

by

Clementinus Winarko

Committee Co-Chairmen: David C. Martens  
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(ABSTRACT)

Copper and Zn deficiencies of crop plants occur in various areas throughout the world. The sulfate forms of Cu and Zn are generally used to correct these micronutrient deficiencies. In agricultural practices, Cu and Zn are applied to soils not only as a fertilizer, but also as manures, pesticides and waste materials such as sewage sludge. High levels of Cu and Zn application to agricultural soils are considered to pose a potential hazard to plants and animals. Research findings have not established Cu and Zn levels that either injure plants or increase Cu and Zn concentrations in edible plant portions to undesirably high levels. Published data on the fate of applied Cu and Zn indicate that there is little, if any, downward movement of these micronutrients in soils and that, with time, applied Cu and Zn revert to plant unavailable forms in soils.

This study was undertaken on a Davidson silty clay soil to determine corn response to high levels of CuSO<sub>4</sub> and ZnSO<sub>4</sub>

applications up to 334.0 kg Cu and 695.4 kg Zn/ha and to evaluate the fate of Cu and Zn in soil following  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  applications of up to 279.9 kg Cu and 560.1 kg Zn/ha. The results of this experiment showed that grain and stalk yields of corn were not affected by the high levels of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  applications. Concentration of Cu in corn grain was not affected, while that of Zn was increased only by the highest level of  $\text{ZnSO}_4$  application. Concentration of Cu in ear leaves sampled at early silking was increased only by the highest level of  $\text{CuSO}_4$  application, whereas that of Zn was increased by all levels of  $\text{ZnSO}_4$  application. There was accumulation of Cu and Zn in the Ap horizon, with little downward movement of the applied Cu and Zn. A portion of the applied Cu and Zn reverted to plant unavailable soil fractions, but there was tendency to build up in potentially plant-available forms.