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Use of a municipal sewage sludge as a source of fertilizer nitrogen : nitrogen availability and cadmium-zinc interactions

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To the Graduate Council:

I am submitting herewith a thesis written by Frank J. Sikora entitled "Use of a municipal sewage sludge as a source of fertilizer nitrogen : nitrogen availability and cadmium-zinc interactions." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Plant, Soil and Environmental Sciences.

J. D. Wolt, Major Professor

We have read this thesis and recommend its acceptance:

G. Lessman, D. Weeter

Accepted for the Council:
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(Original signatures are on file with official student records.)

To the Graduate Council:

I am submitting herewith a thesis written by Frank J. Sikora entitled "Use of a Municipal Sewage Sludge as a Source of Fertilizer Nitrogen: Nitrogen Availability and Cadmium-Zinc Interactions." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Plant and Soil Science.

J D Wolt

J. D. Wolt, Major Professor

We have read this thesis
and recommend its acceptance:

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USE OF A MUNICIPAL SEWAGE SLUDGE AS A SOURCE OF FERTILIZER NITROGEN: NITROGEN AVAILABILITY AND CADMIUM-ZINC INTERACTIONS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Frank J. Sikora
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ABSTRACT

A mixture of primary and aerobic secondary municipal sewage sludge was obtained from Maryville, Tennessee to determine its suitability as a fertilizer for corn (Zea mays L.). In the field experiment, a check, an inorganic N fertilization rate (168 kg ha^{-1} as NH_4NO_3), and three application rates of sludge (17, 34, and 51 Mg ha^{-1} at 0.18 kg kg^{-1} solids were compared for crop response at two levels of soil pH ($pH < 5.5$ and $pH \geq 6.0$). Sludge additions increased silage and grain yields due to increased available N supplied by the sludge. The silage yields from the sludge application of 51 mg ha^{-1} were similar to the inorganic N application rate of 168 kg ha^{-1}. Grain yields from the highest sludge application were not as great as from the inorganic N application, probably due to a lower availability of N from the organic source. When considering potential toxicity to the crop as well as to potential consumers, there were no harmful levels of Cu, Ni, Cd, and Zn present in leaf tissues or grain even with a moderately acidic soil (pH 5.2).

A greenhouse experiment was initiated to analyze the interaction of Cd and Zn in a soil, sludge, and plant system. Sludge obtained from Maryville, Tennessee was spiked with four rates of Cd and Zn in a completely randomized factorial arrangement and applied to soil at application rates of 7, 229, 451, and 673 μmol Cd kg^{-1} and 0.9, 4.7, 8.5, and 12.3 mmol Zn kg^{-1}. The highest Cd and Zn additions resulted in yield increments of 11% and 20% respectively. The modest yield reduction due to Cd was attributed to the high percentage of fixed by the sludge and sequestered in the roots. Zinc effectively competed with Cd uptake as evidenced by a decrease in Cd content of roots with increased Zn additions. While decreasing Cd uptake, Zn had an effect of increasing Cd translocation from roots to tops. Cadmium, on the other hand, decreased Zn translocation from roots to tops. Estimations of Cd^{+2} and Zn^{+2} activities in soil solution were attempted using chelator and total soil solution methods. Calculated Cd^{+2} and Zn^{+2} activities proved to be overestimates of actual activities in soil solutions. Total soil solution Zn concentration and DTPA extractable Zn were good measurements of soil Zn availability.

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CHAPTER I

INTRODUCTION

The benefits of human excreta as a fertilizer amendment have been realized throughout history. The Chinese have used human wastes to fertilize their crops from ancient times to the present (97). The earliest sewage crop system documented in literature was the sewage farm irrigation system established in Bunglau, Germany in 1531 (56). In the early 1800's, England began extensive use of sewage farming (114). Other European cities, such as Paris and Berlin, began using land-disposal of sewage sludge in the late 1800's. The first sewage farm irrigation system in the United States was at Augusta, Maine in 1872 (56). By the late 1800's, several eastern and western U. S. cities were using sewage farm systems.

The use of sewage as fertilizer began to decline in the early 1900's for a number of reasons. With the advent of chemical fertilizer production, sewage sludge use as a fertilizer became more expensive (97,114). Also, with the population increase in the eastern U. S. cities and the land intensive nature of land disposal, transportation costs for sludge farms increased (97). Public health became a concern with the intermittent use of sewage on farmland since sewage that was not applied on land in the colder months would be discharged into streams and rivers (97,114). Principally as a consequence of public health concerns, sewage farming was largely abandoned in favor of biological methods for wastewater treatment where cleaner effluents were discharged into surface waters continuously. Another reason for the reduction of sewage farms was the need for careful and continuous management of the sewage farm systems (56,114). In the early 1900's, sewage managers were politically appointed and did not have the technical knowledge needed for use of sludge as fertilizer.

Land application of sludge in the U. S. did not become a viable idea again until the passing of the Federal Water Pollution Control Act in 1972 (97). The Act states that all technological means for waste disposal should be considered by a wastewater treatment facility. In 1977, Congress passed the Clean Water Act which states that federal grants for any construction of waste treatment plants should not be given unless there is serious consideration of all means of waste disposal (97). With the advent of the Clean Water Act, there has been increased interest in the application of municipal sewage sludge to farmland.

In the present study, a municipal sewage sludge was applied at three levels of addition as a complete fertilizer to field grown corn (*Zea mays* L.). Yield response and elemental concentration of plant tissues were compared among sludge additions as well as to an inorganic fertilizer addition to determine the fertilizing potential of the sludge. Liming was also considered to determine if soil acidity had an effect on plant availability of cadmium (Cd), zinc (Zn), nickel (Ni), and copper (Cu).

In addition, a greenhouse experiment was conducted to determine the effects of high levels of Cd and Zn in sludge on corn growth and elemental uptake. This experiment was also initiated to evaluate the effect of high levels of Zn in the soil upon the quantity of Cd uptake exhibited by plants grown on sludge-amended soil. A factorial arrangement of treatments was performed to determine where and how Cd and Zn interacted in the soil, sludge, and plant system.

CHAPTER II

LITERATURE REVIEW

Benefits and Risks from Municipal Sludge Application

Sludge application on farmland has several beneficial aspects. The primary benefits are the addition of essential nutrients to the soil and the improvement of the physical properties of the soil due to the addition of organic matter (21). Sludge application to farmland is also becoming economically attractive with fertilizer and fuel prices increasing and the close proximity of farmlands to rural wastewater treatment plants. In 1978, the nutrient value of sewage sludge was estimated to be 15 to 30 dollars per megagram on a dry weight basis (21).

Sludge use on farmland resolves the problem of disposal while providing essential plant nutrients. Sludge is predominantly applied to cropland to supply plants with nitrogen (N) and phosphorous (P). Anaerobically digested sewage sludge applied at 112 mg ha^{-1} increased stover and grain yields of corn and resulted in higher levels of N and P in ear leaves from sludge-amended plots as compared to ear leaves from plots with no sludge addition (99). Other researchers (23,51,63) have found an increase of corn silage and grain yield and an increase of N and P in corn ear leaves with additions of digested sewage sludge to soil. In a greenhouse experiment, barley (*Hordeum vulgare* L.) grain yields increased with a 101 mg ha^{-1} addition of air dried sewage sludge (82). Liquid sewage sludge increased the yields of rye (Secale cereale L.) seeded in a Coastal bermudagrass (Cynodon dactylon L. Pers.) sod (65). Fescue (Festuca arundinacea Schreb.) on sludge-amended soils contained adequate levels of P for the nutritional requirements of feed for ruminants (102).

The use of sludge on farmland is not without its risks. There are some disadvantages that may necessitate other means of waste disposal. In some instances, land application of sludge may not be cost effective. If the distances are great between sources of sludge production and a farming community, transportation costs for a high analysis fertilizer may be less than costs for a low analysis sludge. Other critical concerns are the addition of pathogens, toxic organics, and heavy metals to the soil (85). An increase in potentially toxic elements in the soil can lead to increased concentrations of these elements in the food chain.

There are some lessons to be learned from past experiences with sludge utilization on farmland. Sewage use was phased out in the early 1900's because it was becoming cost inefficient and the sewage farms were being poorly managed. Today, land application of sludge is becoming more cost efficient and can be safely done in well-managed systems. The key to safe, well-managed sludge utilization systems is knowledge of pathogen, organic, and heavy metal mobilities in sludge, soil, and plant systems.

The heavy metals of most concern in sludge-amended soils are Cd, Zn, Ni, and Cu (21). Of these heavy metals, Cd and Zn are prevalent in many municipal wastes and are often the potentially toxic metals of principal concern. Cadmium and Zn, which are chemically similar, can both reach hazardous levels in sludge-amended soils. Cadmium is more hazardous since phytotoxicity does not result when toxic levels of Cd are present in plant tissues. Also, only small concentrations of Cd in the food chain can result in adverse health effects. Because of their chemical similarity, moderately high levels of Zn in sludges may be beneficial by suppressing the uptake of Cd into plant tissues.

Cadmium and Zinc in Man and Animals

High levels of Cd and Zn in man's diet can cause deleterious health effects. Toxic levels of Cd cause proteinuria and osteomalacia and may cause other disorders such as emphysema, hypertension, and cancer (124). Toxic Zn levels are known to cause severe anemia and gastrointestinal disorders (10,15). Although both Cd and Zn can be toxic to man, there is more concern placed on Cd toxicity since low levels can cause ill effects. Severe health effects have been observed with 44 μmol kg^{-1} Cd in the diets of domestic animals, whereas maximum tolerable levels of Zn in the animal diet can be 4,600 to 15,300 μmol kg^{-1} (84).

The daily intake of Cd by man is expected to be between 0.23 to 0.44 μmol day^{-1} (89,124). About 6% of ingested Cd is absorbed in the gastrointestinal tract with the remaining Cd predominantly discarded in the feces (80). Most of the absorbed Cd is transported to the kidneys and liver where it is stored. The kidney accumulates a greater amount of Cd and is the site of Cd toxicity disorders. The first disease to occur with high Cd levels in the kidney is proteinuria which begins with a Cd concentration of 1,780 μmol kg^{-1} in the kidney cortex (124). A normal kidney cortex at the age of 50 contains 220 to 440 μmol kg^{-1} Cd (124). Proteinuria is related to renal tubular damage of the kidney which enhances the excretion of low molecular weight proteins in the urine. Extreme proteinuria can lead to a painful bone disease known as osteomalacia (124.

The daily minimum requirement of Zn for man is 230 μmole (15). Zinc is an essential element in metalloenzymes involved in catalytic processes. About 20 to 30% of ingested Zn is absorbed in the duodenum and the rest is predominantly discarded in the feces (15). Zinc accumulates primarily in the eyes, hair, bones, and male reproductive organs and secondarily in the kidneys, liver, and muscles. The most common disease associated with Zn toxicity is anemia (15). Excess Zn has been shown to decrease Cu and Fe tissue levels in rats which can lead to an anemic condition of low hemoglobin concentrations in blood (10). Gastrointestinal distress can also occur with high levels of Zn ingestion (91). Gastrointestinal bleeding was observed in a patient after high levels of Zn sulfate intake for acne treatment. Other systems of Zn toxicity noticed in man are dehydration, electrolytic imbalance, nausea, vomiting, lethargy, dizziness, and muscular incoordination (91).

As in other physical and biological systems, Zn and Cd interact in man and other animals. Cadmium replaces Zn in some metalloenzymes. Cadmium can replace Zn in carboxypeptidase, an enzyme necessary for the breakdown of proteins by hydrolysis (30). The carboxypeptidase containing Cd has no catalytic activity. Cadmium can also replace Zn present in carbonic anhydrase which catalyzes the interaction of carbon dioxide with water resulting in considerable reduction in enzyme activity (30).

Zinc can alleviate Cd toxicity by a reversed mass action. Powell et al. (90) found that addition of Zn to calves fed 5,700 and 22,800 μmol kg^{-1} Cd in their diets reduced Cd toxicity symptoms. Turkey poults were found to be relieved from Cd toxicity when Zn was added to their Cd-amended diets (113).

Cadmium and Zinc in Plants

Toxic levels of Cd and Zn in plant tissue can be consumed by man. Toxicity of Zn to man and animals is usually not a major concern because phytotoxicity results before toxic levels are reached (17). In contrast, toxic levels of Cd to man and animals can be present in a healthy plant.

Reduced crop yields can result when soil systems are overloaded with Cd and Zn through sewage sludge application. Phytotoxicity due to Zn occurs in most plants with a Zn concentration of 7,600 μmol kg^{-1} (17). There is a wide range of Cd concentrations in plants that cause phytotoxicity. Cadmium concentrations of 62 and 1,400 μmol kg^{-1} have caused decreased yields in soybeans (*Glycine max* L.) and cabbage (*Brassica oleracea* var. capitata), respectively (107).

Additions of Cd salts have been found to substantially decrease yields of corn plants grown in greenhouse environments. In a greenhouse study using varying levels of $CdSO_4$ mixed in dried municipal sewage sludge, 180 μmol kg^{-1} addition of Cd to the soil caused decreased yields of corn grain (6). After 31 days of growth in a greenhouse, Miller et al. (81) found a 28% yield decrease in the dry weight of corn plants with soil additions of 22 μmol kg^{-1} Cd as $CdCl_2$. The tissue concentration of Cd was 120 μmol kg^{-1}. In other greenhouse experiments using Cd salt addition, phytotoxicity occurred in corn with additions of 180 and 250 μmol kg^{-1} Cd to the soil (77,118). The concentrations of Cd in the tissues were 260 and 230 μmol kg^{-1}, respectively.

Cunningham et al. (25) found considerable yield loss in corn when applying sludge amended with $ZnCl_2$. There was a 67% yield decrease in field corn when 6,270 μmol kg^{-1} Zn was added to the soil. This decrease in yield was attributed in part to high levels of Cr, Ni, and Cu in the sludge. In two environmentally controlled experiments, the addition of 6,120 μmol kg^{-1} Zn to soil caused 12 and 26% yield decreases in field corn (9,115). The concentrations of Zn in the plant tissues were 6,930 and 8,810 μmol kg^{-1}, respectively. Maclean and Dekker (76) found a 12% yield depression in field corn with an addition of 7,340 μmol kg^{-1} Zn to soil. The Zn concentration in the leaf tissue was 10,800 μmol kg^{-1}.

The differential accumulation of Cd and Zn is an important consideration when assessing potential toxicity of heavy metals in the food chain. In crops grown on sludge-amended soil, Cd and Zn concentrations are higher in the leaves and roots compared to the fruiting bodies. In sludge-amended strip mine soils, Garcia et al. (40) found greater concentrations of Zn and Cd in corn leaves and stems as compared to corn grain. The concentrations of Cd and Zn in corn grain were 0.18 and 430 μmol kg^{-1} compared to 13 and 1,200 μmol kg^{-1} in corn leaves, respectively. Jones et al. (62) also found lower concentrations of Cd and Zn in corn grain. As with corn, Cd and Zn accumulates less in the seeds of soybean plants (48). The ratio of leaf Cd to grain Cd is greater in the corn plant than in the soybean plant. The greater accumulation of Cd and Zn in leaf tissue is also found in other plants (29,107). Leafy vegetables such as lettuce (Lactuca sativa L.), kale (Brassica oleracea c.v. Acephala), and spinach (Spinacia oleracea) are not recommended to be grown on sludge-amended soils because of heavy metal accumulation in the edible leaf tissue (107). The toxicity of Cd and Zn to man and animals by the consumption of grain is less risky than the consumption of leafy vegetables because of differential Cd and Zn accumulation by plant tissues. As a consequence, corn grain grown on sludge-amended soil may be a safer feed than corn silage.

There are differences in the accumulation of Cd and Zn among different crop cultivars which indicates that Cd and Zn absorption and translocation may be genetically controlled (32,86). Wheat (Triticum aestivum L.) and barley seeds of various cultivars collected in Sweden indicated that within each species significantly different levels of Cd were contained in seed (87). Giordano et al. (43) found a difference in Cd and Zn concentrations of three different lettuce cultivars grown on an acid soil. Cadmium uptake and phytotoxicity effects among 11 different soybean cultivars were considerably different (22). Hinesly et al. (50) found differences in Cd and Zn concentrations of corn ear leaf and grain among 20 corn inbred lines. Cadmium and Zn concentrations of ear leaves among inbreds ranged from 22 to 63 μmol kg^{-1} and 550 to 4,310 μmol kg^{-1}, respectively.

As with other heavy metals and micronutrients, there are interactions between Cd and Zn uptake and translocation in plants. In a nutrient solution study using bush beans (*Phaseolus vulgaris* L.), Zn uptake into roots was markedly inhibited by Cd in the solution (49). Zinc content (μmol plant^{-1}) and concentration (μmol kg^{-1}) of bush bean leaves decreased with increasing Cd additions in solution culture (121). Bingham (6) found Zn concentrations to decrease in the leaves and seeds of bush beans, soybeans, wheat, and corn with increasing Cd addition to the soil. In hydroponic solutions, Zn concentrations decreased in the leaves and roots of corn seedlings with an increase in the Cd concentration of the solutions (96).

In contrast with findings of decreased Zn in plant tissues with increased Cd, some researchers have found an increase of Zn with increased Cd in the growth medium. In a greenhouse experiment, Zn content of soybean tops increased with increased soil Cd amendments (61). The Zn concentration of beets (*Beta vulgaris* L.), lettuce, radish (Raphanus sativus L.), and tomato (*Lycopersicon esculentum* Mill.) tops increased with increased concentrations of Cd in nutrient solutions (119). In another nutrient solution study, Cd increased the concentration of Zn, Mg, and calcium (Ca) in soybean seedling stems but decreased the concentration in the leaves (26). Similar results were found with bush beans in solution culture (121).

Cunningham (26) concluded that Cd toxicity in soybeans resulted from a translocation blockage of the nutrients from the stem to the leaf. A postulated mechanism is an aggregation of high molecular weight protein sieve components by a sulfhydryl protein that transports Cd. This aggregation is believed to accumulate at sieve plates causing phloem plugging and transfer cell disruption. Cadmium also displays phytotoxic effects by disrupting plant enzyme systems (33). Phytotoxicity with higher Cd additions may change the biochemical nature of transporting ligands within the root (49). Differences in the biochemical balance in roots among plant species and cultivars may be one explanation for the different results of Zn concentrations in plant tops with higher Cd additions to the growth medium.

Most literature reports a decrease of plant Cd with increased levels of Zn in the growth medium. The inhibitory effect of Zn on Cd uptake and translocation is interesting in that Zn additions to soils may be used to antagonize the movement of Cd into man's food chain. With 2.2 μmol L^{-1} Cd in nutrient solutions, Zn suppressed the uptake of Cd into the roots of ryegrass (Lolium perenne) (55). Cutler and Rains (27) also found a decrease in Cd uptake in excised root tissue of barley with increasing concentration of Zn in the solution media. In a greenhouse experiment, Haghiri (46) found a reduction of Cd concentration in soybean tops with increasing levels of added Zn. Cadmium concentration in wheat grain has also decreased with increased levels of soil Zn (7). Using nutrient solutions, Zn additions suppressed Cd uptake and translocation in radish when the concentrations of Cd in the nutrient solution were 0.018 and 0.178

μmol L^{-1} (70). An increase of Cd uptake and translocation was found with increased Zn additions at the 0.89 μmole L^{-1} level of Cd in the nutrient solution. In a similar study using nutrient solutions, Zn additions were found to increase Cd concentration in bush bean leaves and stems with the Cd concentration in the nutrient solution below 0.027 μmol L^{-1} (37).

Inconsistent research findings concerning crop uptake and translocation of Cd and Zn indicate the complexity of Cd and Zn interactions in the plant system. Antagonism between Cd and Zn in root uptake was attributed to competition for exchange sites on roots where the metals were assimilated by diffusion (27). The interaction between Cd and Zn translocation from root to shoot may be attributed to the competition for transporting ligands in the roots (18,117). Another possible explanation for Cd and Zn interaction in translocation is a change in the biochemical nature of transporting ligands in roots with increasing additions of either metal (49). More research is needed to ascertain the specific interactions of Cd and Zn in the plant system.

The addition of Zn to soils to decrease Cd movement into the food chain appears to be a plausible approach to control Cd cycling but Haghiri (46) and Lagerwerff and Biersdorf (70) have concluded Zn levels needed to decrease Cd may also decrease yield. Although Zn application may not be feasible, high Zn to Cd ratios in the soil are beneficial since this may lead to high Zn to Cd ratios in the plant. Chaney (40) suggested that the Cd to Zn molar concentration ratio in feeding material should not exceed 0.0058 so that the toxicity of Cd in man's food chain could be reduced.

Cadmium and Zinc in Soil

Several soil factors affect Cd and Zn mobility in a soil system. Soil pH, cation exchange capacity (CEC), binding strength, solubility relationships, and complex formations all play a role in Cd and Zn availability to plant roots.

There is considerable evidence that increasing soil pH by liming decreases Cd and Zn concentrations in crops. Seatz et al. (98) found Zn deficiencies in flax (Linum usitatissimum) and sorghum (Sorghum vulgare Pers.) when soil was limed to pH 7.6. In a growth chamber study, there were lower levels of Cd and Zn in rye grown on sludge-amended soils limed to pH 6.8 compared to soils limed to pH 5.1 (71). Lower concentrations of Cd and Zn in leaves of lettuce and beets occurred with the liming of a soil from pH 5.6 to 6.4 (59). Reduced levels of Zn extracted by DTPA, $MgCl_2$, and $CaCl_2$ were observed in an acid soil limed to pH 7.0 (75). From this evidence, it is not clear whether the decrease in hydrogen ion activity or the increase of Ca from liming is responsible for the decreased availability of Cd and Zn in soils. Wear (122) observed a decrease of Zn in sorghum solely due to an increase in soil pH. There was no decrease in sorghum Zn levels with $CaSO_4$ additions, but a decrease in Zn levels resulted with $CaCO_3$ additions. In a solution culture experiment, Cd content of corn shoots and roots decreased with increased Ca levels and remained the same within a pH range from 4 to 6 (53). In another solution culture experiment, Ca and pH did not affect Cd uptake into roots but Ca inhibited Cd translocation from roots to shoots (120). There was a decrease in the Cd concentration of oats and lettuce when nutrient solution pH was raised to pH 8 (58). The high pH may have decreased the Cd activity in the solutions by the formation of Cd hydroxide and carbonate ion pairs. By changing the pH of a soil with NaOH or H_2SO_4, Cd concentrations in corn seedlings were decreased with increasing pH (111). Mahler et al. (77) concluded that the lower Cd concentrations in corn and tomato plants grown on a calcareous soil compared to an acidic soil were due to pH differences.

It appears that Zn uptake is affected by pH alone while Cd uptake is affected by both pH and Ca content of the soil. Since Ca and Cd are chemically similar, Ca exerts its effect by competing with Cd in root uptake and translocation mechanisms in the plant. Hydrogen ion activity affects both Cd and Zn availability in soil systems by changing the adsorptive capacity of colloidal solids, solubility of minerals, complexation of metals by organic matter, and the distribution of soluble complex formations.

It is believed that the CEC of soil is a factor in Cd and Zn availability to plants. Haghiri (46) added muck to H_2O_2-treated soil at different rates to yield cation exchange capacities from 171 to 305 mmol(+)kg^{-1}. On the $CdCl_2$ amended soils, there was a decrease in the Cd concentration of oat shoots with increasing CEC. Yield increased with increasing CEC so the decrease in Cd concentration could be a reflection of dilution instead of CEC. Sims and Boswell (104) decreased Cd and Zn content of wheat with increasing bentonite additions to a sludge-treated soil. The decrease could not be solely attributed to CEC since pH and Ca increased with increased bentonite additions. Latterall et al. (72) diluted soil with sand to produce CEC from 52 to 185 mmol(+)kg^{-1}. In the sludge-amended soil mixtures, there was a slight decrease in Cd and Zn concentrations of soybean shoots with increasing CEC but no change in total Cd and Zn content of the soybean shoots. The differences of Cd and Zn concentrations were due to differences in plant yield and not from differences in uptake. Mahler et al. (77) used multiple regression analysis in a study of eight soils with CEC ranging from 65 to 375 mmol(+)kg^{-1}. In some instances, CEC contributed slightly to the multiple regression equation with Cd concentration of certain crops grown on sludge amended soils as the dependent variable. Hydrogen ion activity and Cd concentration in soil extracts, however, were more important than CEC in predicting concentration of Cd in corn, tomato, and swiss chard plants. Hinesly et al. (52) showed soil CEC had no affect on Cd uptake of corn grown on a sludge-amended soil. They concluded that complexes in which Cd are held in sludge limit Cd availability more than the CEC of the soil. Other researchers (22) have found CEC is not an important estimator of Cd and Zn concentrations in crops. The properties that limit Cd and Zn availability in sludge-amended soils are more complex than EPA has suggested by implicating the use of CEC and pH as the only factors regulating the loading of heavy metals to soils (68). Cation exchange capacity is best viewed as a general indicator of heavy metal availability while organic matter, clays, and sesquioxides are specific factors affecting Cd and Zn adsorption in sludge-amended soil systems.

The soil separates of a soil-sludge system have different binding strengths and adsorption capacities for Cd and Zn. The adsorptive capacity of organic matter is higher than that of clay and sesquioxides (22). Both adsorptive capacities and binding strengths are strongly dependent on soil conditions and the metal adsorbed. Stuanes (112) found an affinity series of Zn>Mn>Cd>Hg for montmorillonite, kaolinite, and vermiculite. Calcium effectively competes with Cd for clay adsorption sites (8,47). Using pure clay samples, Farrah and Pickering (34) found an affinity series of Pb>Cu>Zn>Ca>Cd>Mg for illite and Pb>Ca>Cu>Mg>Zn>Cd for kaolinite. There was a greater increase of heavy metals adsorbed following an increase in pH with kaolinite and illite as compared to montmorillonite. This reflects the greater pH-dependent charges of kaolinite and illite.

Hydrous oxides are considered to play a dominant role in limiting the amount of Cd and Zn in the soil solution (88). Specific adsorption of Cd and Zn below the zero point of charge were found to be important in the colloidal chemistry of fresh Fe and Al hydrous oxide gels (39,67). Zinc has a higher affinity than Cd for adsorption on Fe and Al oxides. The adsorption of Cd and Zn has been shown to dramatically increase from pH 4 to 5.5 (3,100), probably as a consequence of the influence of H^+ ion activity on the adsorptive capacities of Fe and Al oxides (66).

The humus material of organic matter strongly binds heavy metals. Stability constants of heavy metal-humic acid complexes have been found to decrease in the order Cu>Pb>Cd>Zn (109) while the selective order of metal adsorption by peat has been found to be Pb>Cu>Cd = Zn (13). One-half of Cd adsorbed by humus was found to be exchangeable with the remainder in coordination complexes (95). In the same study, increased Cd adsorption was observed with increased pH. Greater Zn availability to corn and rye when applied to soil as an inorganic salt than when applied in sewage sludge may result from the complexation of Zn with humic acids present in the sludge (24). Observations of Cd and Zn adsorption in pure systems of soil separates provide insight into the complexities of Cd and Zn adsorption in heterogenous sludge-amended soil systems but one must realize that Cd and Zn availability can vary substantially among sludge-amended and non-amended soils.

Other parameters that affect the availability of Cd and Zn in soil systems are the solubilities of solid minerals and the formation of soluble complexes. The principal minerals limiting Cd^{+2} activity in soil solutions are $CdCO_3$ and $Cd_3(PO_4)_2$ (73). Street et al. (110, 111) found that Cd^{+2} activities decreased with increasing pH along the $CdCO_3$ solubility line in soil water extracts. Cavallaro and McBride (16) similarly observed Cd^{+2} activity in suspension extracts were limited by the solid phase of $CdCO_3$. Franklinite ($ZnFe_2O_4$) is the principal mineral controlling Zn^{+2} activity in soil solutions (73), but analysis of extracts from soil suspensions has indicated that Zn concentrations can be controlled by the solubility of $Zn(OH)_2$ at a pH > 8.5 (69). Farrah and Pickering (34) used saturated clay suspensions to analyze the adsorption of Cd and Zn and observed the precipitation of Cd and Zn hydroxides at solubility constants lower than theoretical values indicating the activities of Cd^{+2}, Zn^{+2}, and hydroxyl ions must be higher at the clay-solute interface. Similar results were observed in other ion and suspension systems (88).

Soluble inorganic and organic Cd and Zn complexes in the soil solution decrease the activity of the respective metals. Cadmium adsorption on montmorillonite is less in chloride systems than chlorate systems as a consequence of the formation of Cd-chloride ion pairs in the solution (41). Many inorganic ligands are known to form soluble complexes with Zn, the most common of which are phosphate, sulfate, chlorite, hydroxide, and carbonate (78). Cadmium and Zn also form soluble fulvate complexes in soil solutions (28,77).

There have been many attempts to quantify the bioavailable concentration of Cd and Zn in soils. Many acidic and basic extractants have been tested to determine labile Cd and Zn in soil (12,57, 75,103). The differing results observed when comparing extracted Cd and Zn with the concentration of Cd and Zn in plants are probably due to the diversity of soils used. Organic chelate extractants are considered to be more favorable for the determination of labile Zn in soils (101). Soil extractants remove the active form of Cd and Zn in soil solution along with insoluble and adsorbed phases.

Since the activity of Cd^{+2} and Zn^{+2} in soil solution is directly available for root uptake (5,120), it is important to quantify Cd^{+2} and Zn^{+2} activities in soil solutions. Activities of Cd^{+2} and Zn^{+2} in soil solutions can be determined by separation, physiochemical, calculation, or chelator techniques. Separation techniques include dialysis, ultrafiltration, centrifugation, solvent extraction, ion exchange resins, and gel filtration (31). There is some uncertainty in the recovered species when using separation techniques. Activities of Cd^{+2} and Zn^{+2} can be measured physiochemically with ion-selective electrodes (14). Complete analysis of soil solutions can be used as input data for computer programs that can calculate Cd^{+2} and Zn^{+2} concentrations from which activities of Cd^{+2} and Zn^{+2} can be determined by using the extended Debye-Huckel or Davies equations (108). A complete analysis would include the concentrations of Na, Mg, K, Ca, Mn, Fe, Ni, Cu, Zn, Cd, HCO_3, CO_3, NO_3, PO_3, SO_4, and organic C in the soil solution. Uncertainty of chemical species recovered in the separation techniques, interaction of other ions and molecules in the electrode potentials of ion-selective electrodes, and time limitations preclude the involved use of these methods for routine analysis.

Chelator techniques have been developed for routine analysis of Cd^{+2} and Zn^{+2} activities in soil solution. Corey (20) demonstrated a method to determine Cd^{+2} and Zn^{+2} activities in soil solutions by using a series of extractants and analyzing the extracts for the total concentration of Cd and Zn (Appendix A). Cadmium activities can be analyzed by this method at concentrations as low as 0.01 mol L^{-1}. Other chelator extraction methods have been developed for the determination of Cd^{+2} and Zn^{+2} activities in soil solutions (73, D. E. Baker, Agronomy Abstracts, 1981, p. 146). The method of Baker (D. E. Baker, Agronomy Abstracts, 1981, p. 146) was found to considerably differ from Cd^{+2} and Zn^{+2} activities calculated from a total soil solution analysis.

A gross estimation of trace elements in soil solution can be obtained from electrical conductivity measurements (45). This method has been employed to estimate the activity coefficient for Cd^{+2} based on ionic strength and to in turn calculate Cd^{+2} activity based on total Cd concentration (111). This method assumes complete dissociation of inorganic and organic complexes so that total Cd concentration is equivalent to ionic Cd^{+2} concentration. The method may be a reasonable approximation for determination of activities of trace metals which exist primarily in ionic form in soil solution but would result in consequential overestimations of trace metals which are susceptible to significant complex formations in soil solution (31).

CHAPTER III

MATERIALS AND METHODS

I. FIELD EXPERIMENT

An experiment was conducted from 1980 to 1982 to evaluate a mixture of primary and aerobically digested municipal sewage sludge as a source of N for corn production. Experimental plots were established on a Sequatchie sandy loam soil (Humic Hapludult) with 0 to 2% slope at The University of Tennessee Plant Science Field Laboratory in Knoxville.

Field Methods

The experimental design consisted of a randomized complete block with a split plot factorial arrangement of treatments. The main treatments were either limed ($pH \geq 6$) or unlimed soil in plot areas of 370 m^2 replicated twice. There were five split treatments consisting of three rates of sludge addition, a conventional fertilizer treatment, and a non-fertilized check in plot areas of 74 m^2.

The limed soil received sufficient lime to maintain $pH \geq 6$ (0.93, 1.08, and 0.47 Mg ha^{-1} $Ca(OH)_2$ in 1980, 1981, and 1982, respectively) as determined by buffer pH (92). Sewage sludge was obtained at 0.18 kg kg^{-1} solids from the Maryville Regional Waste Treatment Plant and applied at 17, 34, and 51 Mg ha^{-1} at the end of April in each year. Sludge received on the day of application was evenly spread on plots with rakes and shovels and was then incorporated into the soil by disking. The fertilizer treatment plots received annual applications of 168, 59, and 111 kg ha^{-1} of N, P, and potassium (K), respectively. The non-fertilized check plots received no fertilizer amendments.

Corn (Zea mays L. cv. "Pioneer Brand 3147") was planted one week following sludge application in late April or early May. The plant density was 54,321 plants ha^{-1} and the row spacing was 76.2 cm. Each subplot contained 8 rows 12.2 m long.

Ear leaves were collected for chemical analyses at mid-silking stage in July. Corn silage was harvested in August of each year at the soft dough stage. Two 3-m rows from each plot were hand-sickled and weighed, subsamples were taken for moisture determination and silage yield was calculated on a dry weight basis.

Corn grain was harvested in October of 1980 and 1981. Two 12.2-m rows from each plot were harvested mechanically. Subsamples were taken for moisture determination and compositional analyses. Corn grain yield was calculated on a 15.5% moisture basis.

Soil samples from 0 to 15 cm depths were collected shortly after grain harvest. Three subsamples from each plot were collected and bulked for chemical analyses.

Laboratory Methods

Leaf and grain tissues were dried in a forced air oven at 60°C. The dried samples were first ground in a Wiley Mill to pass a 2-mm mesh screen and then passed through a 1-mm mesh screen in a cyclone mill. The samples were stored in polyvinyl plastic bags prior to analysis.

Leaf and grain tissues were digested by H_2SO_4 and H_2O_2 for N analysis via the colorimetric indophenol method (116). Tissues were digested by a tertiary acid mixture of concentrated HNO_3, H_2O_4, and $HClO_4$ (10:1:3) for calcium (Ca), magnesium (Mg), P, K, Cd, Zn, Ni, and Cd analysis (60). Phosphorous was analyzed by molybdovanadate colorimetry (54). Calcium, Mg, Cd, Zn, Cu, and Ni were determined by atomic absorption spectroscopy and K by atomic emission spectroscopy.

Soils collected from the field were crushed between plastic sheets with a pestle to prevent trace metal contamination. The crushed soil was stored in cardboard boxes.

Cation exchange capacity and exchangeable cations were determined from soil samples taken in the spring of 1980 by the NH_4OAc procedure (105) (Appendix B, Table 17). Particle size and moisture retention were also determined by the pipette and porous plate methods, respectively (64,94) (Appendix B, Table 18). Soil samples collected from the fall of 1980 and 1981 were analyzed for Mehlich I (0.05 M (1 HCl) and 0.025 M (1/2 H_2SO_4)) extractable P, K, Ca, and Mg (92). Extractable Cd, Zn, Cu, and Ni were determined by using the DTPA extractant procedure outlined by Lindsay and Norvell (74). Extractable nutrients and heavy metals were analyzed in the same manner as the tissue digests. Soil pH was determined using a hydrogen ion selective electrode in a 1:1 soil to water mixture.

Sludges were analyzed for total solids by drying the sludge in a forced air oven at 103°C. Total Kjeldahl nitrogen (organic N and ammonium N), ammonium N, and nitrate N were determined by the Kjeldahl distillation procedures (4). Dried sludge from total solids determination was ground in a cyclone mill to pass a 1-mm mesh screen. This material was digested in a tertiary acid mixture of $HClO_4$, HNO_3, and H_2SO_4 for the determination of P, K, Ca, Mg, Na, Cu, Zn, Ni, and Cd in the same manner as outlined for tissue digests.

Statistical Analysis

Main and split treatment effects were determined for each year by analysis of variance. A mean separation was accomplished by Duncan's New Multiple Range Test. Levels of significance were at $\alpha = 0.05$.

II. GREENHOUSE EXPERIMENT

In a greenhouse experiment, corn was grown in Sequatchie sandy loam surface soil amended with municipal sewage sludge which had been spiked with varied levels of Cd and Zn. The greenhouse experiment was conducted in the summer of 1981.

Greenhouse Methods

The greenhouse experiment had a randomized complete block design with a factorial arrangement of treatments. There were 16 treatments consisting of sludge amended with four levels of Cd and Zn sulfate solutions in all possible combinations replicated four times. The spiked sludge was incubated for 11 days at $24^{\circ}C$ in darkness before addition to the soil. During incubation, the sludges were mixed by hand daily. The seeding of Cd and Zn in the sludges resulted in sludge Cd and Zn levels of 4450, 8900, and 13,350 $\mu mol\ kg^{-1}$ Cd and 76.5, 153.0, and 229.5 $mmol\ kg^{-1}$ Zn.

Before sludge application, soil was prepared by liming to pH 5.8 through addition of 12 mmole $CaCO_3$ per kg soil, wetting to field capacity (0.12 kg kg^{-1} moisture), mixing, and incubating for one week. Following incubation, soil was air dried and the cycle of wetting, mixing, and incubating was repeated. To improve the fertility of the soil, 1059, 1519, and 624 μmol kg^{-1} P, K, and S, respectively, was applied as $Ca(H_2PO_4)_2 \cdot H_2O$, K_2SO_4, and KCl to soil before planting. Individual acid washed plastic pots received a mixture of 168 g of spiked sludge and 3 kg of air dried soil. Sludge was applied to the greenhouse soil at a rate of 125 Mg ha^{-1} to supply an EPA estimated "available" N rate of 200 kg ha^{-1} (68). The sludge rate resulted in Cd and Zn additions of 7, 229, 451, and 673 μmol kg^{-1} Cd and 0.9, 4.7, 8.5, and 12.3 mmol kg^{-1} Zn to the soil. At application, sludge was sampled for Kjeldahl N analysis. Also, sludge subsamples from each treatment were frozen at the time of application for subsequent analysis.

On 9 July 1981, six seeds of "Pioneer Brand 3147" corn were planted per pot. At seven days growth, the plants were thinned to two plants per pot. Soil was maintained at 12% moisture by daily watering throughout eight weeks of growth. Phosphorus, K, and Mg were applied to soil at 323, 693, and 829 μmol kg^{-1}, respectively, as K_2HPO_4 and $MgCl_2$ solutions on 28 July 1982. Average daily minimum and maximum temperatures in the greenhouse throughout the period of growth were 21.8 ± 4.5 and 34.5 ± 4.7°C, respectively.

Plants were harvested at eight weeks growth and partitioned into tops and roots. Roots were separated from sandy soil by hand

and then rinsed consecutively with tap water, 0.05 M HCl, and several rinses of deionized water. The tops and roots were dried in a forced air oven at 60°C and weighed.

At the termination of the greenhouse experiment, soil from each pot was subsampled for analysis of extractable nutrients, Cd and Zn. The remaining soil was then bulked by treatment for subsequent soil solution analysis.

Laboratory Analysis

Oven-dried plant tissues were ground in a cyclone mill to pass 1-mm mesh screen and samples were stored in plastic bags. One gram subsamples of plant tissues were dry-ashed at 470°C for 16 hours, digested in hot 3 M HCl, and filtered through Whatman No. 42 filter paper. Phosphorus, K, Ca, Mg, Cd, and Zn were analyzed as described previously.

Soil samples from each pot were crushed with a pestle between plastic sheets to prevent trace metal contamination and stored in cardboard boxes. Bulked soil samples of each treatment were screened with a 2-mm mesh plastic screen and stored in plastic bags.

Soil samples from each pot were analyzed for P, K, Ca, Mg, Cd, and Zn in the same methods as the soils of the field experiment. Soil pH was measured in 1:1 soil to water and 1:1 soil to 1 M KCl suspensions with a hydrogen ion selective electrode.

Bulked soil samples were analyzed for soil solution activities of Cd^{+2} and Zn^{+2} by two methods. Soil solutions were obtained from soils wetted to 0.15 kg kg^{-1} moisture by the centrifuge method outlined by Adams et al. (1). The centrifuge was run at 1850 rpm with a force of 840 g for 2.5 hours. The resulting soil solution collected was analyzed for pH by using a hydrogen selective electrode, electrical conductivity was measured by a Soil Moisture salinity bridge, and Cd and Zn were analyzed by atomic absorption spectroscopy. Electrical conductivity was used to estimate ionic strength and the activity of Cd^{+2} and Zn^{+2} in the soil solution (Appendix A).

Activities of Cd^{+2} and Zn^{+2} were also determined by a method outlined by Corey (20) (Appendix A). Bulked soil samples were extracted with 0.01 M $Ca(NO_3)_2$, 0.01 M $CaCl_2$, and 0.01 M $Ca(NO_3)_2$ plus 5×10^{-5} M Na_2 EDTA. Twelve grams of soil, which was passed through a 1-mm plastic screen, was mixed with 30 ml of extractant on a rotary shaker at 25°C for 16 hours. The samples were centrifuged for 20 minutes at 12,000 rpm. The supernatant solutions were filtered through acid rinsed Millipore filters (0.45 µm). All labware involved was rinsed with 3 M HNO_3. Cadmium and Zn were analyzed by atomic absorption spectroscopy. The difference of Cd in $Ca(NO_3)_2$ and $CaCl_2$ leachates was used to calculate Cd^{+2} activities in the soil solutions. The difference of Cd and Zn in the $Ca(NO_3)_2$ and $Ca(NO_3)_2$ + Na_2EDTA leachates and Cd^{+2} activities were used to calculate Zn^{+2} activity in soil solutions. An extractant of 0.01 M $Ca(NO_3)_2$ + 1×10^{-3} M Na_2EDTA had to be used for the soils treated with the highest level of Zn addition so an increase of Cd and Zn concentrations in the leachates could be observed.

Readily available Cd and Zn present in the spiked sludges was determined through a modification of the EPA toxicity test (35). Two hundred fifty ml of water was added to 100 grams of raw spiked sludge and mixed on a rotary shaker for 24 hours. The mixture was then filtered using 0.45 μm Millipore filters in a Soil Test vacuum extractor. The leachates were analyzed for Cd and Zn by atomic absorption spectroscopy. The pH of the leachate was also determined with a hydrogen ion selective electrode.

Statistical Analysis

Treatment effects were determined by analysis of variance (ANOVA) with the level of significance at $\alpha = 0.05$. Regression equations were determined for selected dependent and independent variables where ANOVA proved significant. Surface response curves were created for interactive dependent variables.

CHAPTER IV

RESULTS AND DISCUSSION OF THE FIELD EXPERIMENT

Sludge Analysis

Sludge obtained from the Maryville Regional Waste Water Treatment Plant had varied annual N concentrations, the majority of which was in organic form (Table 1). Annual variation in N concentration of sludge was typical of compositional variations in this organic waste which was a mixture of vacuum-filtered sludge from primary clarifiers and secondary aerobic clarifiers. Also, the low inorganic N concentration is typical for vacuum-filtered sludge (106). The annual variations in sludge N resulted in varied levels of total and "available" N additions when sludge was applied at constant rates (Table 2). The estimation of total "available" N increased from year to year due to the release of residual organic N from the previous year.

The concentrations of P, K, Ca, and Mg in the sludge were at levels which may have been beneficial to the plant (Table 3). The average levels of potentially toxic elements (Zn, Cd, Cu, Ni, and Cr) were below median levels found in aerobically digested municipal sludges (106). Due to the Zn concentration of the sludge, USEPA guidelines (68) would limit tolerable waste loadings to 31 years at an application rate of 51 Mg ha^{-1} (soil CEC = 45 mmol(+)kg^{-1} and soil pH $\geq$ 6.5).

Table 1. Nitrogen concentration of sludge from the Maryville Regional Wastewater Treament Plant used in the field experiment.

Nitrogen source[†]	Year 1980	 1981	 1982
	-------------mmol kg^{-1}		-------------
Total	400	528	435
Inorganic	36	28	28
Organic	364	500	407

[†] Concentrations are on a wet weight basis.

Table 2. Total annual N additions resulting from each level of sludge application and corresponding estimates of "available" N in the field experiment.

Sludge applied	Total N addition			"Available" N addition[†]			Total "available" N in soil[‡]		
	1980	1981	1982	1980	1981	1982	1980	1981	1982
---Mg ha^{-1}----	--------------------------------			kg ha^{-1}			------------------------------------		
17	95	126	104	22	28	24	22	39	51
34	191	252	207	45	56	47	45	78	101
51	286	377	311	67	84	71	67	118	152

[†] Estimated from (68) as kg "available" N Mg^{-1} sludge = [(mmol NH_4-N kg^{-1}) (0.014) + (mmol NO_3-N kg^{-1}) (0.028) + (mmol org-N kg^{-1}) (0.0056)]/2.

[‡] Estimated from (68) considering residual N.

Table 3. Average composition of sludge from the Maryville Regional Wastewater Treatment Plant used in the field experiment.

pH†	5.4
Total solids	0.18 kg kg^{-1}
P‡	219 mmol kg^{-1}
K	87 mmol kg^{-1}
Ca	57 mmol kg^{-1}
Mg	107 mmol kg^{-1}
Na	52 mmol kg^{-1}
Zn	15.33 mmol kg^{-1}
Cd	0.12 mmol kg^{-1}
Cu	4.14 mmol kg^{-1}
Ni	0.43 mmol kg^{-1}
Cr	3.58 mmol kg^{-1}

†pH was measured in a 1:3 sludge to water extract.

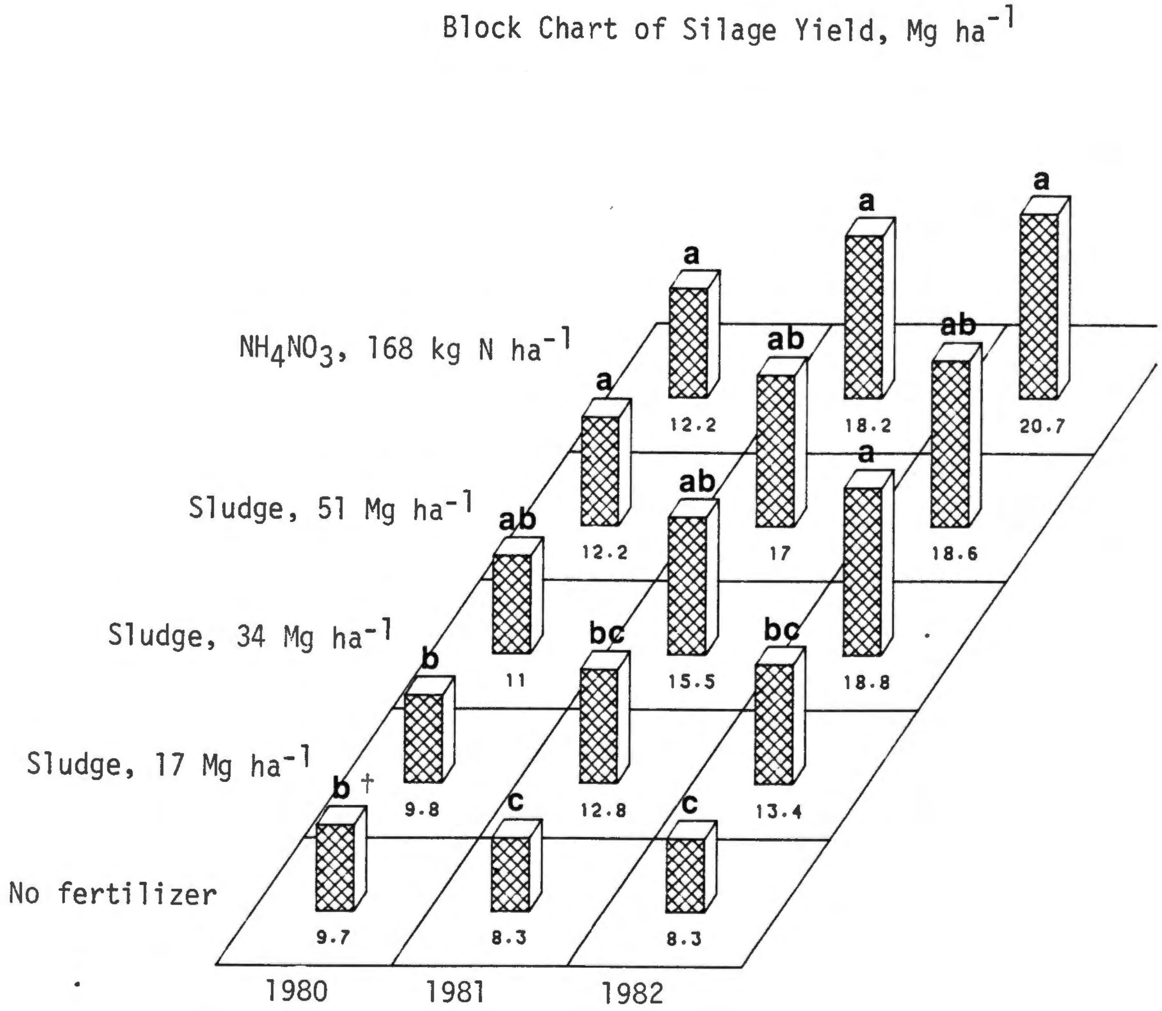
‡Elemental concentrations are on a dry weight basis.

Silage and Grain Yield

In 1980, only the highest sludge addition (51 Mg ha^{-1}) produced greater silage yield than the control plots which received no N (Figure 1). In 1981 and 1982, both the 34 and 51 Mg ha^{-1} sludge additions produced greater silage yields than the control plots. Inorganic N fertilization of 168 kg ha^{-1} and the higher additions of sludge resulted in similar silage yields in each year.

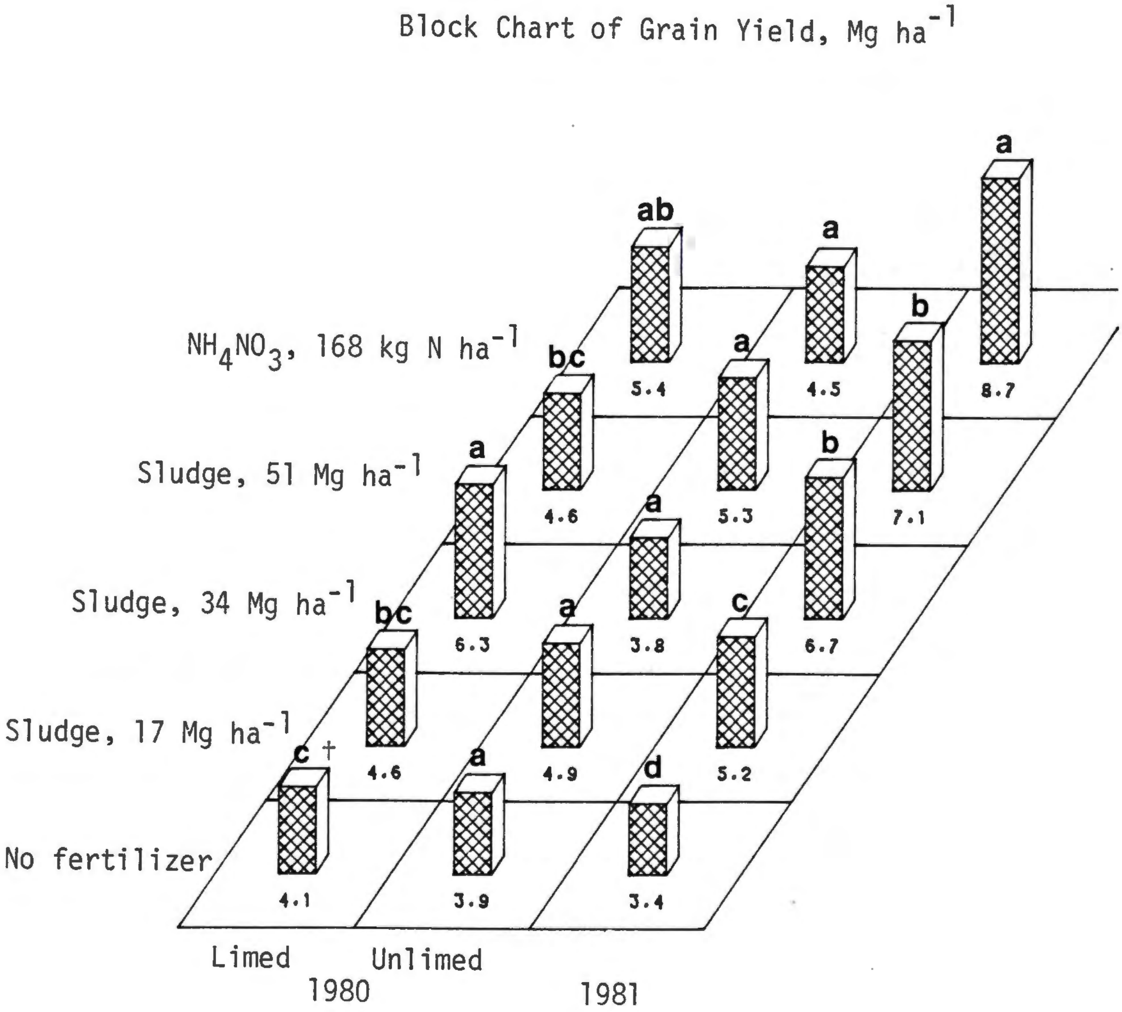
Silage yields from the same sludge amendment tended to increase from 1980 to 1982 (Figure 1). The difference in silage yield between 1981 and 1982 may be attributed to the increase of N in 1982 due to release of residual N from the previous two years of sludge addition (Table 2). The difference in yield between 1980 and 1981 was predominantly due to the hot, dry weather which limited crop yields in 1980.

In 1980, lime application and organic and inorganic N applications interacted to influence grain yield (Figure 2). There was little change in grain yield due to sludge and inorganic N applications in the limed and unlimed plots in 1980. The poor growing conditions in 1980 tended to equalize yields. In 1981, there was no interaction between lime and N applications where grain yields increased with sludge application from 0 to 34 Mg ha^{-1}. Inorganic N application produced grain yields in excess of all levels of sludge application. There was no independent lime effect on grain yield in either year.



†Within years, means followed by the same letter do not significantly differ at $\alpha = 0.05$ according to F test and Duncan's New Multiple Range Test.

Figure 1. Silage yield as affected by sludge and inorganic N additions in 1980, 1981, and 1982 from the field experiment.



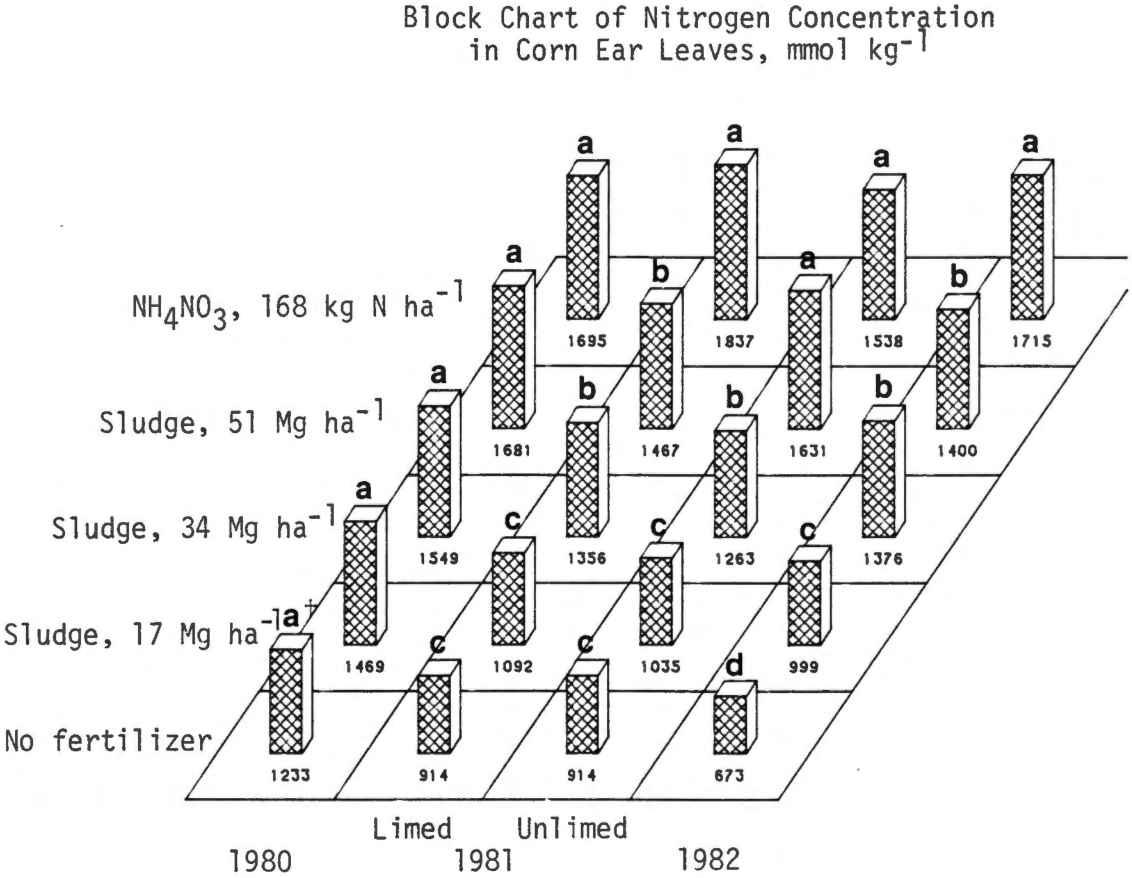
†Within years and lime treatment, means followed by the same letter do not significantly differ at $\alpha = 0.05$ according to F test and Duncan's New Multiple Range Test.

Figure 2. Grain yield as affected by sludge and inorganic N additions in 1980 and 1981 from the field experiment.

Nitrogen Concentration of Corn Ear Leaves and Grain

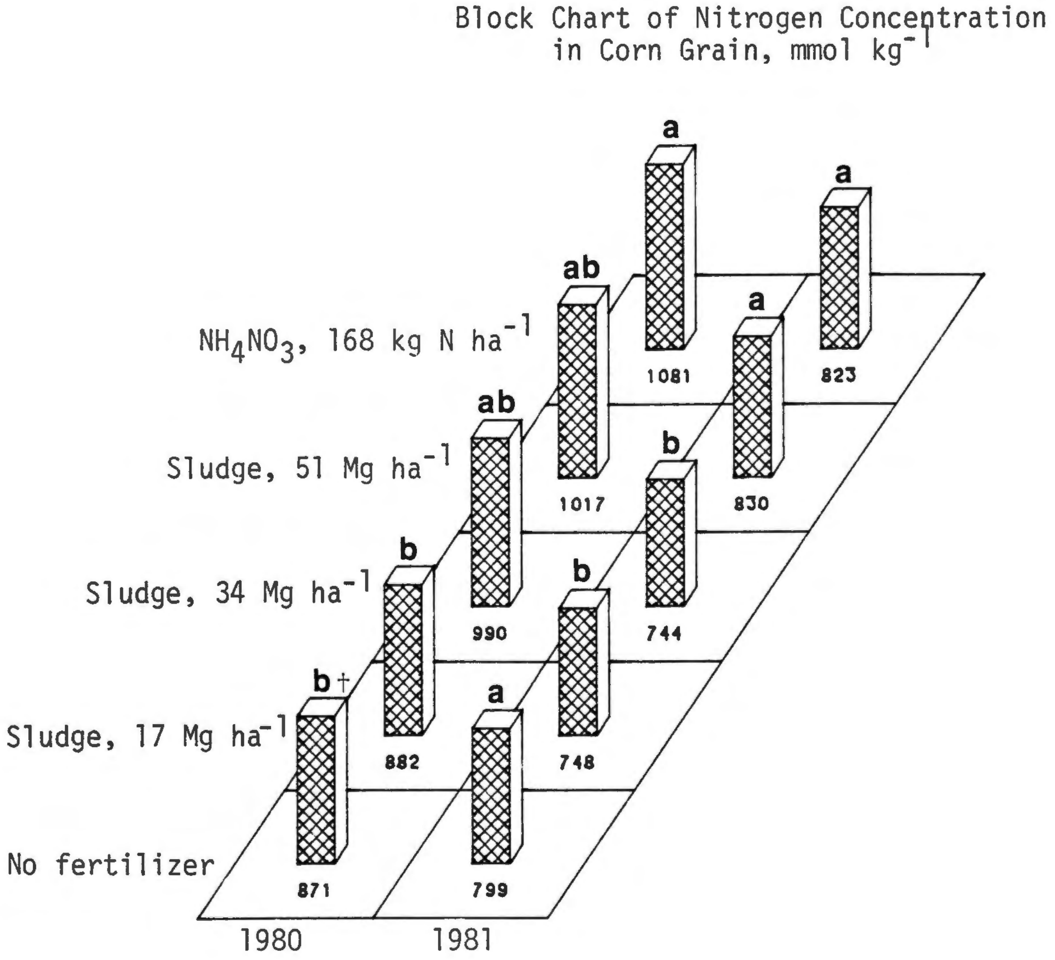
In 1980, there was no difference in N concentration of corn ear leaves due to sludge and inorganic N additions (Figure 3). In the droughty first year of the experiment, factors other than N availability most likely limited crop growth response. In 1981, lime application and organic and inorganic N applications interacted to influence N concentration in corn ear leaves. For both limed and unlimed plots, sludge additions increased nitrogen in corn ear leaves. In 1982, N in corn ear leaves increased with increased sludge additions from 0 to 34 Mg ha^{-1}. Nitrogen in the ear leaves from the inorganic N fertilizer was higher than any of the other treatments. There was no independent lime effect on corn in corn ear leaves in any year.

Grain harvested in 1980 and 1981 contained similar concentrations of N (Figure 4). Liming had no influence on N concentration of corn grain in either year. Nitrogen concentrations of corn grain did not differ with respect to levels of sludge application in 1980. Nitrogen in corn grain from the two higher sludge additions were the same as N in corn grain from the inorganic addition of 168 kg ha^{-1}. In 1981, N concentration in grain from the 17 and 34 Mg ha^{-1} sludge additions were lower than that from the other organic and inorganic N additions. Grain N was higher from no N application as compared to that of the lower sludge additions probably because of differences in growth and N utilization. Nitrogen for grain filling was possibly limited in the more vigorously growing plants from the 17 and 34 Mg ha^{-1} sludge addition. Since crude protein of grain does not change



†Within years and lime treatment, means followed by the same letter do not significantly differ at α = 0.05 according to F test and Duncan's New Multiple Range Test.

Figure 3. Nitrogen concentrations in corn ear leaves as affected by sludge and inorganic N additions in 1980, 1981, and 1982 from the field experiment.



†Within years, means followed by the same letter do not significantly differ at $\alpha = 0.05$ according to F test and Duncan's New Multiple Range Test.

Figure 4. Nitrogen concentrations in corn grain as affected by sludge and inorganic N additions in 1980 and 1981 from the field experiment.

drastically across different soil N levels (125), it is not surprising that sludge rates had little influence on grain N concentrations. Consequently, grain N level is a poor indicator of plant N status.

Nitrogen in the sludge was the predominant factor affecting corn silage and grain yield. In 1981 and 1982, nitrogen in corn ear leaves was greater with 78 to 152 kg ha^{-1} of "available" N in the soil applied with 34 to 51 Mg ha^{-1} sludge compared to the 0 and 17 Mg ha^{-1} sludge additions where there was only 0 to 51 kg ha^{-1} of "available" N in the soil (Table 2, page 32; Figure 3). Silage yields of 1981 and 1982 and grain yields of 1981 were also higher from plots amended with 34 and 51 Mg ha^{-1} of sludge due to the increase in "available" N (Figures 1 and 2, pages 35 and 36). The effect of sludge additions on silage and grain yields resembled Mitcherlisch's limited yield response (79). The "available" N levels of 78 to 152 kg ha^{-1} that produced higher silage and grain yields were similar to the application rate of 100 kg "available" sludge N ha^{-1} that has been used on crops in eight states of the northcentral U. S. (106).

In 1980 and 1981, the highest sludge additions provided enough N to produce silage yields comparable to 168 kg ha^{-1} of ammonium nitrate N (Figure 1, page 35). Compared to the inorganic N addition, the highest sludge additions failed to provide enough N for grain filling as evidenced by lower grain yields in 1981 and lower N concentrations in corn ear leaves from limed plots of 1981 and both the limed and unlimed plots of 1982.

Elemental Concentrations in Corn Ear Leaves and Grain

Nutrient availability from applied sludge was evaluated through analysis of ear leaves sampled at mid-silking for concentrations of P, K, Ca, Mg, and Zn in 1980 and 1981 (Table 4). Sludge application resulted in greater P concentration in ear leaf tissue compared to check plots in 1980. No differences in ear leaf P were noted in 1981. Sludge and N additions had no effect on K concentrations in ear leaves in either year. While sludge application had no influence on ear leaf Ca in 1980, leaves from the 34 and 51 Mg ha^{-1} sludge additions contained higher Ca than the ear leaves from the 0 and 17 Mg ha^{-1} sludge additions in 1981. In both years, the highest level of sludge addition produced corn ear leaves with higher Mg concentrations compared to the other additions of sludge and inorganic N. In 1981, increased sludge additions produced corn ear leaves with higher concentrations of Zn. A similar trend was observed in 1980. More vigorous plant growth was probably the main reason for increased ear leaf P and Ca concentration with the highest sludge addition since plants grown on soil fertilized with inorganic N produced corn leaves with similar P and Ca concentrations. In addition to N, sludge probably supplied P and Ca to the growing plants. The sludge did supply the plant with available Mg and Zn since the highest sludge treatment resulted in higher Mg and Zn concentrations in ear leaves as compared to the inorganic N treatment where Mg and Zn was not amended to the soil. Although N is the predominant nutrient in sludge which aids crop growth, other nutrients such as P, Ca, Mg,

Table 4. Phosphorus, K, Ca, Mg, and Zn concentrations in corn ear leaves as affected by sludge and inorganic N additions from the field experiment in 1980 and 1981.

Treatment	Nutrient concentration of corn ear leaves									
	1980					1981				
	P	K	Ca	Mg	Zn	P	K	Ca	Mg	Zn
	--------mmol	kg^{-1}--------			μmol kg^{-1}	--------mmol	kg^{-1}--------			μmol kg^{-1}
No fertilizer	69b[†]	243a	166a	139b	474a	77a	258a	90c	79b	317c
Sludge, 17 Mg ha^{-1}	81ab	244a	158a	150b	757a	84a	240a	102bc	89b	348c
Sludge, 34 Mg ha^{-1}	86a	238a	155a	167b	780a	86a	224a	116ab	117a	470b
Sludge, 51 Mg ha^{-1}	89a	215a	152a	200a	1706a	94a	244a	127a	122a	558a
NH_4NO_3, 168 kg N ha^{-1}	90a	265a	125a	152b	673a	97a	298a	118ab	89b	440b

[†] Mean values in the same column followed by the same letter are not significantly different at $\alpha = 0.05$ according to F test and Duncan's New Multiple Range Test.

and Zn may also benefit the growth of crops on sludge-amended soil (51,65,99).

Phosphorus, K, Ca, Mg, and Zn concentrations of corn grain were not influenced by lime or organic and inorganic N additions (Appendix C, Table 19). The concentrations of Zn in ear leaf and grain tissues were below the level of 7,600 μmol kg^{-1} which is considered to be phytotoxic and harmful in the diet of cattle (84).

With the analytical techniques employed, Cd and Ni were below the detection limits in both grain and leaf tissues (Table 5). Copper was detected in a few ear leaf and grain tissue samples from sludge-amended soils (Table 5 and Appendix C, Table 20). In all instances the concentrations of Cu, Ni, and Cd were below levels considered to be phytotoxic to the plant (17), so further analysis by more sensitive techniques were deemed inappropriate. The concentrations of Cu and Ni in the plant tissues were also below dietary levels harmful to cattle while the detectable limit of Cd in the plant tissues were greater than the tolerable level of Cd in the diet of cattle (84). There is reason to believe that the Cd concentration in the ear leaf and grain tissue are well below 6 μmol kg^{-1} based on greenhouse evaluations (see Chapter V, page 58). Although the Cd detection limit of 6 μmol kg^{-1} is above the tolerable dietary levels of 4 μmol kg^{-1}, Cd probably does not warrant a major concern since the concentration of Cd in the sludge is low (see Table 3, page 33). Tolerable dietary levels of Cd may in fact be well above 4 μmol kg^{-1} since Zn, Fe, and Ca present in the sludge help reduce Cd adsorption in the animal (17).

Table 5. Copper, Ni, and Cd concentrations in corn ear leaf and grain from the field experiment in 1980 and 1981.

Element	Ear leaf	Grain	Phytotoxic levels[§] in leaves	Maximum tolerable[¶] dietary levels for cattle
	μmol kg^{-1}			
Cu[†]	≤283	≤165	394-630	1575
Ni[‡]	<256	<256	852-1704	852
Cd[‡]	<25	<25	120-260	4

[†] The concentrations of Cu reported are from 12 samples that were above the detection limit of 121 μmol kg^{-1}; all other samples were below this detection limit (Appendix C, Table 20).

[‡] The concentrations of Ni and Cd reported are detection limits. All samples had Ni and Cd concentrations below the detection limit.

[§] From Chaney (17).

[¶] From National Regulatory Commission (84).

Extractable Elements in the Soil

In 1980 and 1981, soil pH of the limed treatment was higher than that of the unlimed treatment (Table 6). Sludge application had no effect on soil pH. Also, lime application had no influence on the availability of nutrients or heavy metals in either 1980 or 1981 (Table 7). It is interesting to note that phytotoxic levels of Ca, Ni, Cd, and Zn were not absorbed by the corn crop with soil pH lower than the EPA recommended sludge-amended soil pH of 6.5 (Tables 4, 5, and 6) (68).

Only soil extractable P and Zn demonstrated variations relative to sludge and inorganic N application (Table 7). In both 1980 and 1981, 51 Mg ha^{-1} sludge resulted in levels of extractable P which were higher than either zero sludge addition or inorganic N fertilization. There was a higher amount of extractable Zn in the soil from the highest sludge addition compared to soil from the other sludge and inorganic N additions in 1981. A similar trend in extractable Zn was observed in 1980. The higher extractable Zn was in line with the higher Zn concentrations in corn ear leaves from the highest sludge addition in 1981. Extractable levels of K, Ca, and Mg were not influenced by sludge application in either year.

Extractable Ni and Cd in the soil samples from two years of the experiment were below detectable limits of 5 and 1 μmol kg^{-1}, respectively. Copper was detected in all soil samples at 16 μmol kg^{-1}.

Table 6. Soil pH of soil collected in the fall of 1980 and 1981 at 0 to 15 cm depth from the field experiment.

	Soil pH			
	1980		1981	
Treatment	Limed	Unlimed	Limed	Unlimed
No fertilizer	6.2†	5.4	6.2	5.4
Sludge, 17 Mg ha^{-1}	6.4	5.3	6.2	5.4
Sludge, 34 Mg ha^{-1}	6.0	5.4	6.0	5.4
Sludge, 51 Mg ha^{-1}	6.2	5.2	6.2	5.2
NH_4NO_3, 168 kg N ha^{-1}	6.1	5.3	6.6	5.4

†Means of log-transformed values within the same column are not significantly different at $\alpha = 0.05$ according to F test.

Table 7. Mehlich I (0.05 M HCl + 0.025 M (1/2 H_2SO_4)) extractable P, K, Ca, and Mg and DTPA extractable Zn of soil collected in the fall of 1980 and 1981 at 0 to 15 cm depth from the field experiment.

Treatment	Extractable elements in soil									
	1980					1981				
	P	K	Ca	Mg	Zn	P	K	Ca	Mg	Zn
	μmol kg^{-1}									
No fertilizer	775c[†]	812a	8832a	4515a	19a	646b	710a	11951a	4104a	15b
Sludge, 17 Mg ha^{-1}	1171ab	787a	9288a	4412a	19a	815ab	708a	15694a	3271a	19b
Sludge, 34 Mg ha^{-1}	1203ab	870a	8464a	3507a	23a	605a	703a	15145a	2767a	15b
Sludge, 51 Mg ha^{-1}	1477a	870a	10123a	3991a	27a	1203a	665a	14097a	3919a	34a
NH_4NO_3, 168 kg N ha^{-1}	1033bc	902a	9830a	4412a	19a	573b	667a	14970a	3754a	15b

[†] Mean values in the same column followed by the same letter are not significantly different at $\alpha = 0.05$ according to F test and Duncan's New Multiple Range Test.

CHAPTER V

RESULTS AND DISCUSSION OF THE GREENHOUSE EXPERIMENT

Sludge Analysis

The total N concentration of the sludge applied to soil in the greenhouse experiment was 378 mmol kg^{-1} of which 92 mmol kg^{-1} of the N was in inorganic form (wet weight basis). The sludge application rate of 125 Mg ha^{-1} resulted in an application of 200 kg ha^{-1} of estimated "available" N to the greenhouse soil. The physical and chemical properties of the Maryville municipal sludge have been previously summarized (Table 1, page 31).

The water-soluble (extractable) fraction of Cd and Zn in the seeded sludges indicated that soluble Cd increased substantially with increasing Zn additions at the same level of added Cd (Table 8). There was also an increase of soluble Zn with increasing Cd additions at the lowest and medium level of Zn addition. Cadmium and Zn must have competed for binding and exchange sites of the organic matter in the sludge (13,109). Cadmium and Zn may have also competed in precipitation of inorganic constituents in the sludge (22). The normal percentages of heavy metals in the insoluble solid phase in sludge are 99.5% and greater (106). By these standards, only the sludges spiked with Cd at the zero and lowest Zn additions were good models of actual sludge with respect to Cd concentrations. Although the other percentages of Cd and Zn fixation do not reach 99.5%, the amount of Zn fixed at the lowest Zn addition and the amount of

Table 8. Zinc and Cd extracted, added, and fixed in the Maryville sewage sludge as affected by different levels of Zn and Cd addition into the sludge of the greenhouse experiment.

Treatment[†]	Extractable Zn	Added Zn	% Zn[‡] fixed	Extractable Cd	Added Cd	% Cd[‡] fixed	pH
	mmol kg^{-1}			µmol kg^{-1}			
0 Zn 0 Cd	0.03	0[¶]	--	<1	0[¶]	--	5.2
0 Zn 1Y Cd	0.06	0[¶]	--	2	4450[¶]	>99.9	5.2
0 Zn 2Y Cd	0.09	0[¶]	--	3	8900	>99.9	5.2
0 Zn 3Y Cd	0.03	0[¶]	--	10	13350	99.9	5.3
1X Zn 0 Cd	1.87	76.50[¶]	97.6	<1	0[¶]	--	5.0
1X Zn 1Y Cd	4.10	76.50[¶]	94.6	6	4450[¶]	99.9	5.1
1X Zn 2Y Cd	7.19	76.50[¶]	90.6	57[§]	8900	99.4	5.1
1X Zn 3Y Cd	8.96	76.50[¶]	88.3	415[§]	13350	96.9	5.1
2X Zn 0 Cd	42.47[§]	153.00	72.2	<1	0[¶]	--	4.8
2X Zn 1Y Cd	31.73[§]	153.00	79.3	91[§]	4450[¶]	98.0	4.8
2X Zn 2Y Cd	83.19[§]	153.00	45.6	510[§]	8900	94.3	4.8
2X Zn 3Y Cd	55.87[§]	153.00	63.5	1378[§]	13350	89.7	4.8
3X Zn 0 Cd	89.06[§]	229.50	61.2	<1	0[¶]	--	4.7
3X Zn 1Y Cd	103.27[§]	229.50	55.0	160[§]	4450[¶]	96.4	4.8
3X Zn 2Y Cd	109.56[§]	229.50	52.3	897[§]	8900	89.9	4.8
3X Zn 3Y Cd	100.57[§]	229.50	56.2	2126[§]	13350	84.1	4.8

[†] Base levels of Zn and Cd addition to sludge were X = 76.50 mmol kg^{-1} and Y = 4.45 mmol kg^{-1}, respectively.

[‡] % M (metal) fixed = [added M - (extracted M - extracted M of control sludge)] x 100/ added M.

[§] Values of M that result in a hazardous waste (36).

[¶] Values of M that are in the reported concentration range of M in municipal sewage sludge (106).

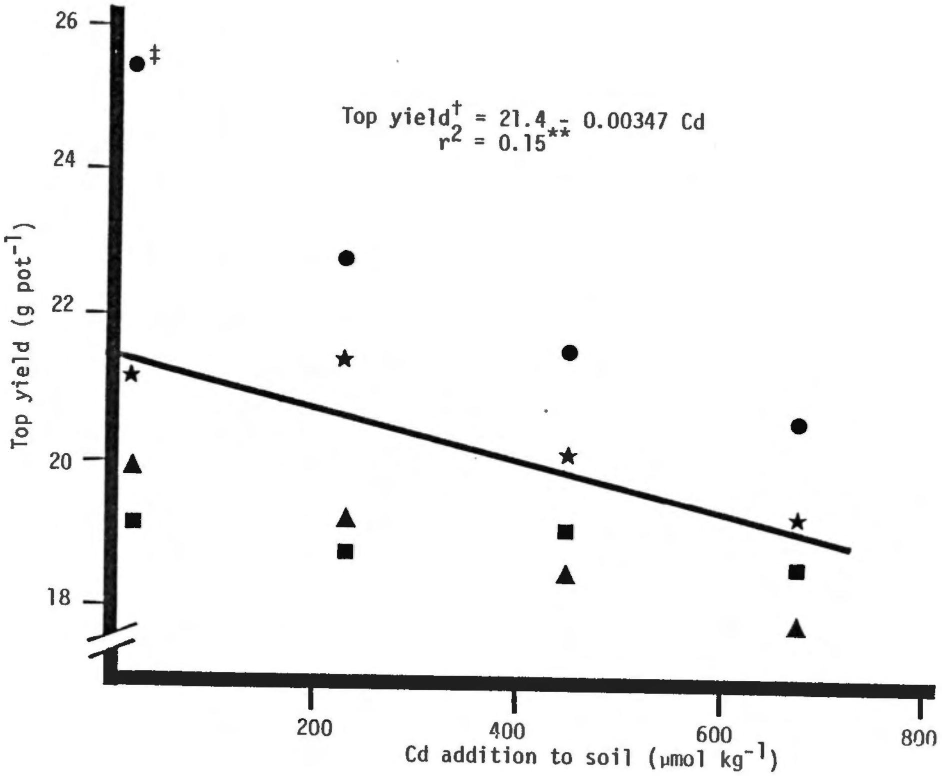
Cd fixed at the two higher Zn additions approximated the Cd and Zn fractions in actual sludges.

In the case of Zn, the two highest additions of Zn (Table 8) resulted in sludges that would have been considered hazardous wastes (36). The two highest additions of Cd at all three additions of Zn and the lowest additions of Cd at the two higher additions of Zn resulted in sludges considered hazardous wastes due to a high amount of soluble Cd (36). In most cases, the Cd and Zn concentrations in sludges considered hazardous were greater than the ranges of Cd and Zn found in municipal sewage sludges (106).

The pH of sludge leachates decreased with increased Zn additions to the sludge (Table 8). This may have been attributed to Zn competition with exchangeable aluminum and hydrogen on exchange sites. Also, hydrogen may have been released upon the specific adsorption of Zn by organic matter.

Yield of Corn Tops and Roots

Yield of corn tops decreased linearly with increased levels of Cd addition to soil (Figure 5). The considerable variation observed with the significant regression of top yield on Cd addition was associated with the noninteractive effect of Zn additions on top yield. Top yield at the highest level of Cd addition was reduced 11% when compared to no Cd addition. This was much lower than the 40 to 70% yield decrements found by other researchers at similar Cd levels in greenhouse tests (77,81,118). The higher yield decrements observed by other researchers may be attributed to the fact that Cd



**Significant at α = 0.01.

†Regression equation from 64 observations.

§Symbols are mean values from each treatment. ●, ★, ▲, and ■ represent 0.9, 4.7, 8.5 and 12.3 mmol kg^{-1} ·Zn addition, respectively.

Figure 5. Yield of corn tops as influenced by Cd additions to soil in the greenhouse experiment.

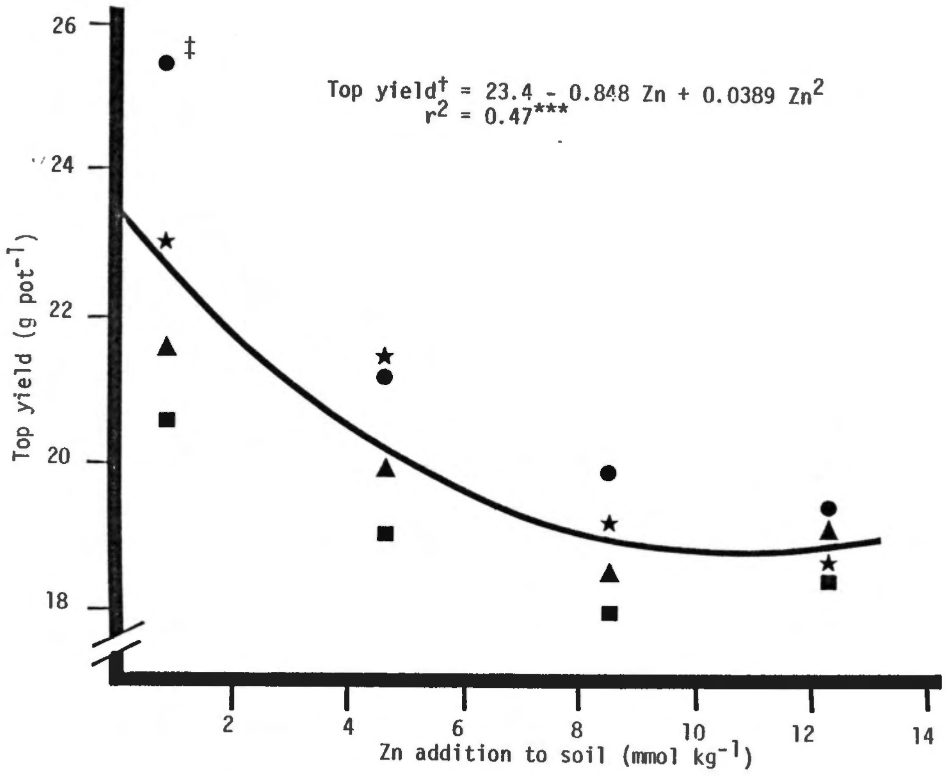
was added to the soil as a salt alone or as a salt in dried sewage sludge. As was observed with leachate analysis of the incubated sludge, the majority of added Cd was fixed and apparently not available to the plant.

Levels of Zn addition resulted in a greater phytotoxic effect than Cd additions with respect to top yield (Figure 6). There was a 20% yield decrement with the 10 mmol kg^{-1} Zn addition. Other researchers have found comparable yield decrements with similar Zn additions in greenhouse experiments (9,76,115). The yield response remains constant past the 10 mmol kg^{-1} Zn addition. The noninteractive influence of Cd additions on top yield resulted in some variability in the regression of top yield on Zn additions.

There was a significant interaction of Cd and Zn additions to soil on root yield (Figure 7). Cadmium increased root yield at higher levels of Zn addition whereas Zn decreased root yields at all levels of Cd addition. At higher Zn additions, Zn decreased root yield whereas top yield did not decrease from the addition of 10 to 12.3 mmol kg^{-1} of Zn to soil (compare Figure 7 with Figure 6).

Concentrations and Contents of Cd and Zn in Corn Tops and Roots

Cadmium and Zn concentrations in tops interacted to produce an effect on top yield as shown in Figure 8. Cadmium and Zn concentrations in tops were predominant factors that affected top yield ($r^2 = 0.59$). The effect of Zn concentrations on top yield at lower Cd concentrations was similar to the phytotoxic effect of Zn additions on top yield (compare Figure 8 with Figure 6). Increasing Zn

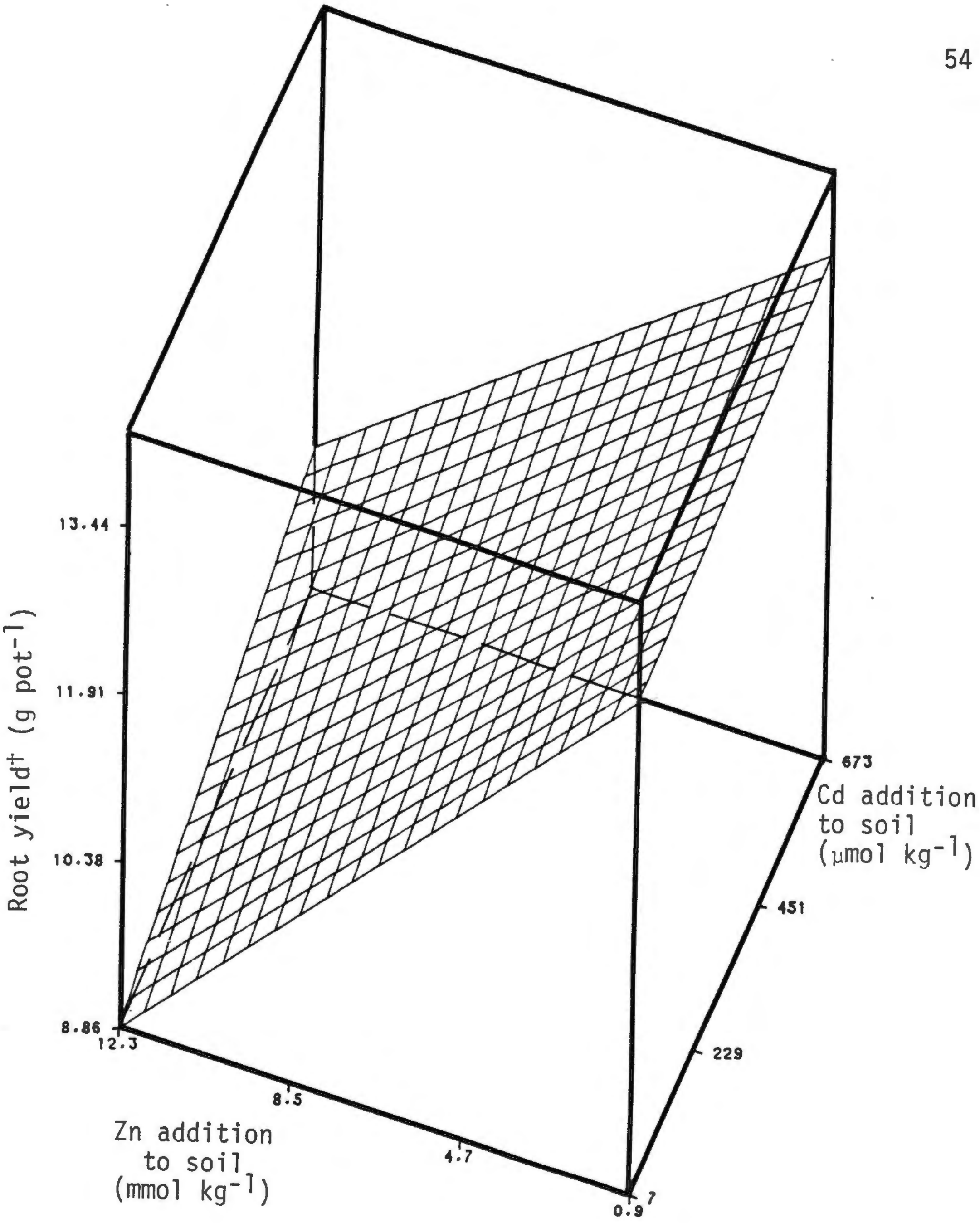


***Significant at $\alpha = 0.001$.

†Regression equation from 64 observations.

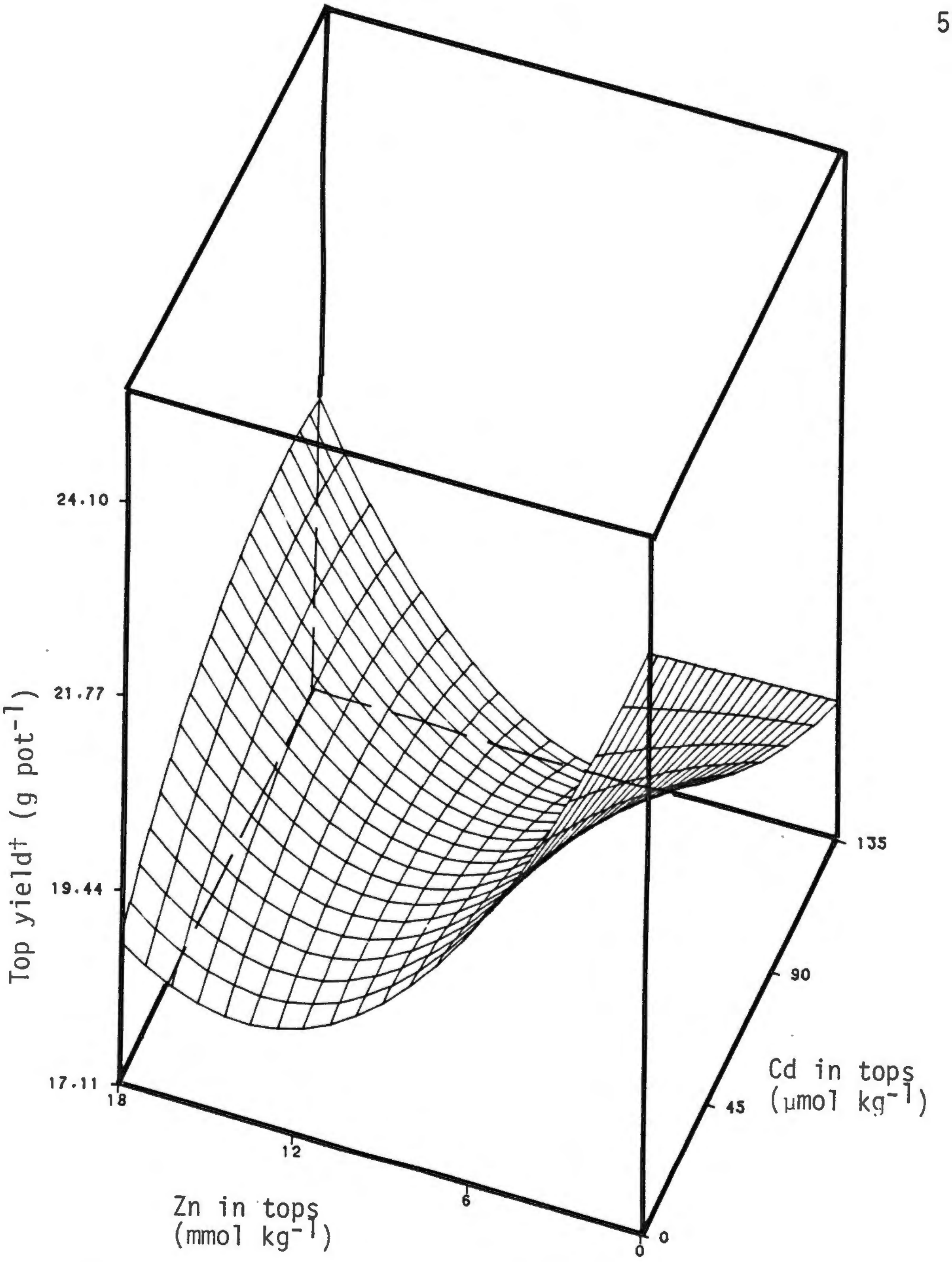
§Symbols are mean values for each treatment. ●, ★, ▲, and ■ represent 7, 229, 451, and 673 μmol kg^{-1} Cd addition, respectively.

Figure 6. Yield of corn tops as influenced by Zn additions to soil in the greenhouse experiment.



†Regression equation: root yield = 13.7 - 0.395 Zn + 0.000159 Zn Cd, r^2 = 0.19 and was significant at α = 0.01.

Figure 7. Yield of corn roots as influenced by Cd and Zn additions to soil in the greenhouse experiment.



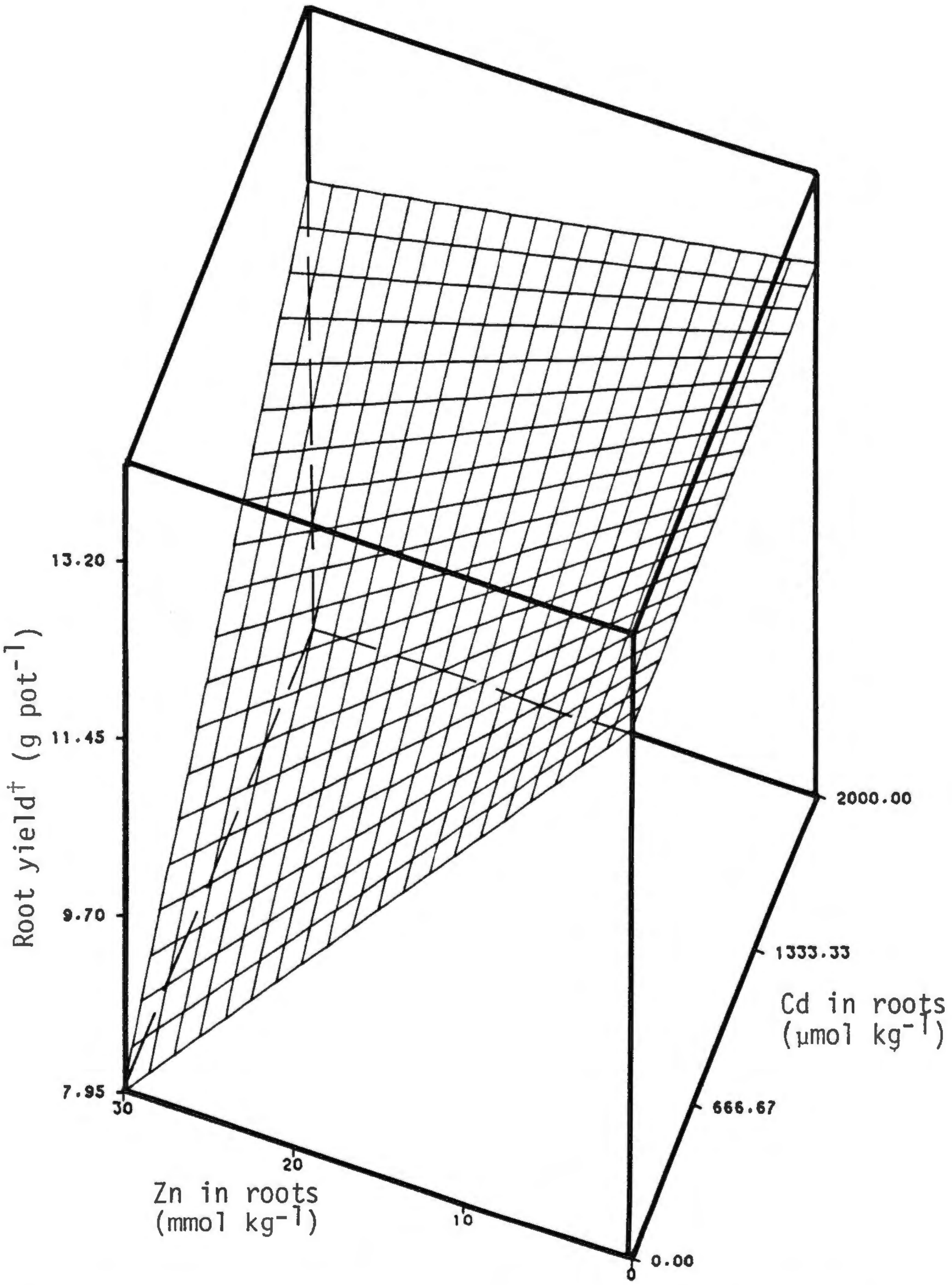
†Regression equation: top yield = 24.1 - 0.844 Zn - 0.0395 Cd + 0.0306 Zn^2 + 0.00415 Zn Cd - 0.00000916 Zn Cd^2, r^2 = 0.59 and was significant at α = 0.001.

Figure 8. Yield of corn tops as influenced by concentrations of Cd and Zn in tops from the greenhouse experiment.

concentrations increased top yield at higher Cd concentrations in tops. As was observed in animal studies (91,113), Zn may have reduced the toxic effects of Cd by replacing Cd in nonactive enzyme systems. Increasing Cd concentrations in tops tended to decrease top yield except at high Zn concentrations where yield was actually increased.

Cadmium and Zn concentrations of roots interacted to produce an effect on root yield which was similar to the response of root yield on Cd and Zn addition to the soil (compare Figure 9 with Figure 7). Increasing Zn concentrations in roots decreased root yield irrespective of Cd concentrations. The yield decrease of roots compared to no yield decrease of tops from 10 to 12.3 mmol kg^{-1} Zn addition to soil (see Figure 6 and Figure 7) may be attributed to the higher Zn concentrations in the roots (compare Figure 9 with Figure 8). Increased Cd concentrations in roots tended to increase root yield. Cadmium concentrations were much higher in corn roots compared to corn tops (compare Figure 9 with Figure 8). A sequestering of Cd in corn roots and the high fixation of Cd in spiked sludges may have both played a role in limiting Cd phytotoxicity of tops (see Figure 5, page 51).

The interactions of Cd and Zn in uptake and translocation are reflected in total plant Cd and Zn content and the fraction of total metals in plant tops (Table 9). An increase in the percentage of the metals in the tops was attributed to an increase in translocation of the metals from roots to tops (49,70). Cadmium content of the tops increased with increasing Zn additions at the highest level of Cd



†Regression equation: root yield = 13.2 - 0.175 Zn + 0.0000731 Zn Cd, r^2 = 0.19 and was significant at α = 0.01.

Figure 9. Yield of corn roots as influenced by concentrations of Cd and Zn in roots from the greenhouse experiment.

Table 9. Content of Cd and Zn in corn tops and roots and percentage of Cd and Zn in corn tops as affected by Cd and Zn additions to soil in the greenhouse experiment.‡

Treatment[†]	Cd Tops	Cd Roots	Cd % in tops	Zn Tops	Zn Roots	Zn % in tops
	μmol pot^{-1}					
1 Zn 1 Cd	<0.1[§]	<0.1[§]	--	5	26	16
1 Zn 2 Cd	1.0	11.1	8	4	19	17
1 Zn 3 Cd	1.3	17.3	7	8	8	50
1 Zn 4 Cd	1.4	17.4	7	6	5	55
2 Zn 1 Cd	<0.1[§]	<0.1[§]	--	79	105	43
2 Zn 2 Cd	0.6	5.9	9	73	104	41
2 Zn 3 Cd	0.8	16.8	5	58	122	32
2 Zn 4 Cd	1.5	22.9	6	51	124	29
3 Zn 1 Cd	<0.1[§]	<0.1[§]	--	143	185	44
3 Zn 2 Cd	0.5	4.7	10	141	193	42
3 Zn 3 Cd	1.0	15.3	6	146	228	39
3 Zn 4 Cd	2.3	18.4	11	150	238	39
4 Zn 1 Cd	<0.1[§]	<0.1[§]	--	337	208	62
4 Zn 2 Cd	0.7	1.4	33	299	244	55
4 Zn 3 Cd	1.2	3.6	25	194	222	47
4 Zn 4 Cd	2.1	7.1	23	235	267	47

[†] 1 Zn, 2 Zn, 3 Zn, and 4 Zn correspond to 0.9, 4.7, 8.5, and 12.3 mmol kg^{-1} Zn addition to soil, respectively. 1 Cd, 2 Cd, 3 Cd, 4 Cd correspond to 7, 229, 451, and 673 μmol kg^{-1} Cd addition to soil, respectively.

[‡] Surface response curves and regression equations of Cd and Zn in tops and roots and percentages of Cd and Zn in corn tops vs. Cd and Zn additions are in Appendix D.

[§] Calculated from the detection limit of Cd concentration in tops and roots being 6 μmol kg^{-1}.

addition (673 μmol kg^{-1}). Other researchers have reported limited findings of this nature (37,44,70) but have provided no interpretation of this observation. Both Cd and Zn are known to form insoluble organometallic compounds in plants (26,44). Higher Zn concentrations may have effectively competed with Cd for sites on insoluble organometallic compounds in the root. As a consequence, increased concentrations of soluble Cd would translocate to the tops as evidenced by an increase in the percentage of plant Cd in the tops at the high addition of Zn. Cadmium concentrations in the roots decreased with increasing Zn additions at constant levels of soil Cd additions. This occurrence was due to antagonism of Cd root uptake by Zn that has been observed by other researchers (27). Even with higher concentrations of soluble Cd in the sludge with increasing levels of added Zn (see Table 8, page 49), Zn effectively competed with Cd for root uptake.

Zinc content of roots decreased with increasing Cd additions at the low Zn addition to soil (Table 9). This was an indication of antagonism of Zn root uptake by Cd (49). There was decreased Zn translocation with increasing Cd addition at higher Zn additions. This phenomenon may have occurred due to Cd competing with Zn for sites on soluble organometallic compounds that are transported from root to shoot (18). A more probable explanation is that increased Cd additions changed the biochemical nature of transporting ligands in plant roots and left Zn immobile in the root system (49).

Concentrations of Nutrients in Corn Tops, Corn Roots, and Soil

There was no effect of Cd on P, K, Ca, or Mg in corn tops or roots. The effects of Zn addition on P, K, Ca, and Mg concentrations in corn tops and roots are shown in Table 10. Phosphorus concentrations in tops and roots decreased with increased Zn additions probably due to a P and Zn interaction in the soil (79,83). Zinc additions had no effect on K in corn tops but slightly increased K in roots. The Zn additions tended to increase Ca in tops and to decrease Ca in roots while they decreased Mg in tops but tended to slightly increase Mg in roots.

Added Cd had no effect on the extractable nutrients or pH of the soil (Table 11). Zinc, however, had considerable influence on these parameters. Unlike the trend in decreased P uptake in response to Zn additions, extractable P increased with increasing Zn additions. Extractable soil K tended to decrease with increasing Zn while Ca and Mg demonstrated increases relative to increasing Zn. In each instance, changes were too slight to be consequential with regard to overall soil fertility status (19).

The highest Zn addition caused the soil pH from 1:1 soil:H_2O pastes to decrease 0.5 pH unit relative to the lowest Zn addition (Table 11). This was compatible with the lower pH of sludge leachates seeded with higher Zn additions (see Table 8, page 49). Lesser pH changes were observed in the 1:1 soil-KCl pastes and displaced soil solutions.

Extractable Soil Cd and Zn

Cadmium and Zn additions interacted to influence DTPA extractable Cd (Table 12). Increased DTPA extractable Cd corresponded with an increase in Zn additions at the higher levels of Cd addition.

Table 10. Concentrations of P, K, Ca, and Mg in corn tops and roots as affected by Zn additions to soil in the greenhouse experiment.‡

$Zn^{\dagger}$ treatment	Tops				Roots			
	P	K	Ca	Mg	P	K	Ca	Mg
	------------------------------mmol kg^{-1}	------------------------------						
1 Zn	36	319	113	131	45	140	92	74
2 Zn	32	270	133	142	44	174	97	82
3 Zn	32	306	138	118	43	199	101	94
4 Zn	28	269	144	111	34	193	77	82
r^2 =	20***	N.S.	0.13**	0.12**	0.18***	0.18***	0.20**	0.21***

,*Significant at α = 0.01 and 0.001, respectively.

†1 Zn, 2 Zn, 3 Zn, and 4 Zn correspond to 0.9, 4.7, 8.5, and 12.3 mmol kg^{-1} Zn addition to soil, respectively.

‡Regression equations of P, Ca, and Mg in tops and P, K, Ca, and Mg in roots on Zn additions are in Appendix D.

Table 11. Mehlich I (0.05 M (1 HCl) and 0.025 M (1/2 H_2SO_4)) extractable nutrients in soil and pH of soil as affected by Zn additions to soil in the greenhouse experiment.‡

Zn† treatment	pH			Nutrients			
	1:1 soil:H_2O	1:1 soil:KCl	Soil solution	P	K	Ca	Mg
				--------------µmol kg^{-1}--------------			
1 Zn	5.4	4.8	5.2	1451	898	31184	3394
2 Zn	5.2	4.6	5.1	1709	841	30924	3381
3 Zn	5.0	4.6	5.1	1771	805	30748	3512
4 Zn	4.9	4.5	5.0	1877	817	32173	3857
r^2 =	0.90***	0.68***		0.38***	0.23***	0.19**	0.60***

,*Significant at α = 0.01 and 0.001, respectively.

†1 Zn, 2 Zn, 3 Zn, and 4 Zn correspond to 0.9, 4.7, 8.5, and 12.3 mmol kg^{-1} Zn addition to soil, respectively.

‡Regression equations of P, K, Ca, and Mg in soil on Zn addition are in Appendix D.

Table 12. DTPA extractable Cd and Zn from soil as affected by Cd and Zn additions to soil in the greenhouse experiment.[‡]

Treatment[†]	Cd	Zn
	-------μmol kg^{-1}----------	
1 Zn 1 Cd	<1	57
1 Zn 2 Cd	109	57
1 Zn 3 Cd	129	54
1 Zn 4 Cd	185	50
2 Zn 1 Cd	<1	1614
2 Zn 2 Cd	90	1496
2 Zn 3 Cd	159	1541
2 Zn 4 Cd	258	1610
3 Zn 1 Cd	<1	3351
3 Zn 2 Cd	93	3129
3 Zn 3 Cd	178	3125
3 Zn 4 Cd	321	3446
4 Zn 1 Cd	<1	5592
4 Zn 2 Cd	115	5301
4 Zn 3 Cd	236	5439
4 Zn 4 Cd	321	5236

[†] 1 Zn, 2 Zn, 3 Zn, and 4 Zn correspond to 0.9, 4.7, 8.5, and 12.3 mmol kg^{-1} Zn addition to soil, respectively. 1 Cd, 2 Cd, 3 Cd, and 4 Cd correspond to 7, 229, 451, and 673 μmol kg^{-1} Cd addition to soil, respectively.

[‡] Surface response curves and regression equations of DTPA extractable Cd and Zn on Cd and Zn additions to soil are presented in Appendix D.

This occurrence was due to the soluble Cd fraction in sludges increasing with increased Zn additions (see Table 8, page 49). Increasing Zn additions resulted in increased DTPA-extractable Zn in soils, while Cd addition had no influence on DTPA-extractable Zn.

The concentrations of Cd and Zn determined in $CaCl_2$, $Ca(NO_3)_2$, and $Ca(NO_3)_2$ plus EDTA for estimation of Cd^{+2} and Zn^{+2} activities by Corey's method are presented in Table 13 (20,38). In the calculation of Cd^{+2} and Zn^{+2} activities, Cd and Zn concentrations in the $Ca(NO_3)_2$ leachate were considered indicative of total Cd and Zn concentrations in the soil solution. As observed with DTPA-extractable Cd and Zn, Cd and Zn additions both increased $Ca(NO_3)_2$ extractable Cd while Zn additions alone increased $Ca(NO_3)_2$ extractable Zn.

Cadmium and Zn concentrations in the $Ca(NO_3)_2$ leachate (Table 13) were transformed to activities of ionic Cd^{+2} and Zn^{+2} through a series of calculations (Table 14 and Appendix A). Ionic activities were then transformed to ionic concentrations of Cd and Zn using the extended Debye-Huckel equation. The activities of Cd^{+2} and Zn^{+2} calculated in this manner were poor estimates of the actual activities of Cd^{+2} and Zn^{+2} in the soil solution. The activities of Cd^{+2} were overestimated in instances where the ionic distributions in soil solutions were greater than 100% (Table 14). It is quite likely the activity of Cd^{+2} may have been overestimated in other cases as well. Overestimation of Cd^{+2} activities can cause an overestimation of Zn^{+2} activity as shown by equation 10 in Appendix A. The ionic distributions of Cd^{+2} less than 100% were at similar levels found by other researchers (31,38). The ionic distributions of Zn^{+2}

Table 13. Cadmium and Zn concentrations in extracts of 0.01 M $CaCl_2$, 0.01 M $Ca(NO_3)_2$, and 0.01 M $Ca(NO_3)_2$ plus EDTA as affected by Cd and Zn additions to soil in the greenhouse experiment.

	Cd			Zn	
Treatment[†]	$CaCl_2$	$Ca(NO_3)_2$	$Ca(NO_3)_2$[‡] plus EDTA	$Ca(NO_3)_2$	$Ca(NO_3)_2$[‡] plus EDTA
	μmol L^{-1}				
1 Zn 1 Cd	<0.25	<0.25	<0.25	2.56	8.30
1 Zn 2 Cd	3.28	1.65	13.63	5.74	7.42
1 Zn 3 Cd	3.71	2.13	39.92	1.68	9.70
1 Zn 4 Cd	9.70	2.45	36.37	1.63	6.83
2 Zn 1 Cd	<0.25	<0.25	<0.25	60.72	86.95
2 Zn 2 Cd	2.85	1.81	2.48	62.13	84.10
2 Zn 3 Cd	4.98	2.86	5.74	55.51	85.53
2 Zn 4 Cd	8.13	4.58	6.84	54.59	77.97
3 Zn 1 Cd	<0.25	<0.25	<0.25	213.79	248.65
3 Zn 2 Cd	7.07	2.55	5.12	200.96	222.52
3 Zn 3 Cd	9.54	6.21	6.26	212.36	223.95
3 Zn 4 Cd	40.80	9.73	11.26	205.23	227.33
4 Zn 1 Cd	<0.25	<0.25	<0.25	481.87	1061.13
4 Zn 2 Cd	7.16	4.82	11.82	501.55	1077.74
4 Zn 3 Cd	13.58	8.86	24.52	467.17	1086.05
4 Zn 4 Cd	58.80	21.83	38.30	557.94	1090.21

[†] 1 Zn, 2 Zn, 3 Zn, and 4 Zn correspond to 0.9, 4.7, 8.5, and 12.3 mmol kg^{-1} Zn addition to soil, respectively. 1 Cd, 2 Cd, 3 Cd, and 4 Cd correspond to 7, 229, 451, and 673 μmol kg^{-1} Cd addition to soil, respectively.

[‡] EDTA concentration was 5×10^{-5} M except for the highest Zn additions where EDTA concentration was 1×10^{-3} M.

Table 14. Calculated activities and ionic distributions of Cd^{+2} and Zn^{+2} from $CaCl_2$, $Ca(NO_3)_2$, and $Ca(NO_3)_2$ plus EDTA extracts as affected by Cd and Zn additions to the soil in the greenhouse experiment.

	Cd				Zn			
Treatment[†]	(Cd^{+2})[‡]	$[Cd^{+2}]$	Cd_T[§]	%$[Cd^{+2}]$	(Zn^{+2})[‡]	$[Zn^{+2}]$	Zn_T[§]	%$[Zn^{+2}]$
	----------μmol L^{-1}--------				----------μmol L^{-1}--------			
1 Zn 1 Cd	--	--	<0.25	--	--	--	2.56	--
1 Zn 2 Cd	0.81	1.53	1.65	93	0.22	0.40	5.74	7
1 Zn 3 Cd	0.79	1.49	2.13	70	0.27	0.49	1.68	9
1 Zn 4 Cd	3.62	6.83	2.45	>100	1.05	1.91	1.63	>100
2 Zn 1 Cd	--	--	<0.25	--	--	--	60.72	--
2 Zn 2 Cd	0.52	0.98	1.81	54	2.21	4.02	62.13	6
2 Zn 3 Cd	1.06	2.00	2.86	70	2.54	4.62	55.51	8
2 Zn 4 Cd	1.77	3.34	4.85	69	4.22	7.67	54.59	14
3 Zn 1 Cd	--	--	<0.25	--	--	--	213.79	--
3 Zn 2 Cd	2.26	4.26	2.55	>100	4.85	8.82	200.96	4
3 Zn 3 Cd	1.66	3.13	6.21	50	25.27	45.95	212.36	22
3 Zn 4 Cd	15.51	29.26	9.73	>100	43.70	79.45	205.23	39
4 Zn 1 Cd	--	--	<0.25	--	--	--	481.87	--
4 Zn 2 Cd	1.17	2.21	4.82	46	7.87	14.31	501.55	3
4 Zn 3 Cd	2.36	4.45	8.86	50	11.00	20.00	467.17	4
4 Zn 4 Cd	18.46	34.83	21.83	>100	77.80	141.45	557.94	25

[†] 1 Zn, 2 Zn, 3 Zn, and 4 Zn correspond to 0.9, 4.7, 8.5, and 12.3 mmol kg^{-1} Zn addition to soil, respectively. 1 Cd 2 Cd, and 4 Cd correspond to 7, 229, 451, and 673 μmol kg^{-1} Cd addition to soil, respectively.

[‡] Activities of Cd^{+2} and Zn^{+2} calculated by equations in Appendix A.

[§] Determined from 0.01 M $Ca(NO_3)_2$ extracts.

found in this investigation were much lower than the values of 40 to 70% found by other researchers (31,38). An increase of Zn^{+2} activities and ionic distributions of Zn^{+2} with increased Cd additions could have been a partial consequence of ion pair competition, but trends in Zn^{+2} activities cannot be ascertained with overestimations of Cd^{+2} activity.

One assumption necessary for estimation of activities by the method of Corey and coworkers (38) is that substantial amounts of Cd and Zn are not extracted from the solid phase (Appendix A). Fujii (personal communication, 1982) has suggested that the amount of Cd and Zn extracted should be less than 10% of labile Cd and Zn determined by DTPA extraction. He used a modification of the DTPA extraction method of Lindsay and Norvell (74) to determine labile Cd and Zn using a soil solution ratio of 1:5 and a shaking time of 16 hours. In this investigation, Lindsay and Norvell's (74) method of 1:1 soil solution ratio and shaking time of 2 hours was utilized. Assuming that the DTPA extractable Cd and Zn in the present study is the labile form, percent labile Cd and Zn extracted by $CaCl_2$, $Ca(NO_3)_2$, and $Ca(NO_3)_2$ plus EDTA was calculated (Table 15). The percentages of labile Cd extracted by $CaCl_2$, where a greater than 100% ionic distribution of Cd was calculated (see Table 14) were 13, 19, 32, and 46%. In fact, greater than 10% labile Cd extraction occurred in all but five $CaCl_2$ extracts. The excess Cd extracted by $CaCl_2$ is most likely above the soil solution activity of Cd^{+2} supported by the solid phase, thus resulting in overestimations of soil

Table 15. Percentage of labile Cd and Zn extracted by 0.01 M $CaCl_2$, 0.01 M $Ca(NO_3)_2$, and 0.01 M $Ca(NO_3)_2$ plus EDTA as affected by Cd and Zn additions to soil in the greenhouse experiment.

	% Labile Cd[§]			% Labile Zn[§]	
Treatment[†]	$CaCl_2$	$Ca(NO_3)_2$	$Ca(NO_3)_2$[‡] plus EDTA	$Ca(NO_3)_2$	$Ca(NO_3)_2$[‡] plus EDTA
1 Zn 1 Cd				11	36
1 Zn 2 Cd	8	4	31	25	32
1 Zn 3 Cd	7	4	77	8	45
1 Zn 4 Cd	13	3	49	8	34
2 Zn 1 Cd				9	14
2 Zn 2 Cd	8	5	7	10	14
2 Zn 3 Cd	6	4	9	9	14
2 Zn 4 Cd	8	4	7	8	12
3 Zn 1 Cd				16	19
3 Zn 2 Cd	19	7	14	16	18
3 Zn 3 Cd	13	9	9	17	18
3 Zn 4 Cd	32	7	9	15	16
4 Zn 1 Cd				22	47
4 Zn 2 Cd	16	10	26	24	51
4 Zn 3 Cd	14	9	26	22	50
4 Zn 4 Cd	46	17	30	27	52

[†] 1 Zn, 2 Zn, 3 Zn, and 4 Zn correspond to 0.9, 4.7, 8.5, and 12.3 mmol kg^{-1} Zn addition to soil, respectively. 1 Cd, 2 Cd, 3 Cd, and 4 Cd correspond to 7, 229, 451, and 673 μmol kg^{-1} Cd addition to soil, respectively.

[‡] EDTA concentrations were 5×10^{-5} M except for the highest Zn additions where EDTA concentration was 1×10^{-3} M.

[§] Labile Cd and Zn were determined by DTPA extraction (74).

solution Cd^{+2} and Zn^{+2} activities (as shown by equations 8 and 10, Appendix A). Also, high percentages of labile Cd and Zn extracted by EDTA at the low and high Zn additions may have caused erroneous Zn^{+2} activity estimations as well. Fujii et al. (33) found Corey's method of estimating Cd^{+2} and Zn^{+2} activities of soil solutions adequate for sludge-amended soils with a Cd and Zn application rate of 264 and 2645 μmol kg^{-1}, respectively. Other probable causes for the erroneous results in the present study may have been the high application rates of Cd and Zn to the soil (673 and 12,300 μmol kg^{-1}, respectively) and the failure to completely model actual sludges when sludges were spiked with higher levels of Cd and Zn sulfate (Table 8, page 49).

Activities of Cd^{+2} and Zn^{+2} in soil solutions estimated from total Cd and Zn of soil solutions by the extended Debye-Huckel equation (Appendix A) are presented in Table 16. Since this method assumed that total Cd and Zn measured in soil solutions was equivalent to ionic concentrations of Cd^{+2} and Zn^{+2}, these estimates represent upper limits to Cd^{+2} and Zn^{+2} activities in the soil solution. The assumption may be plausible with Cd since ionic distributions of Cd^{+2} determined by Corey's method (see Table 14) and other researchers (38) are generally high (60 to 80%). The calculated activities of Cd^{+2} were generally higher than the activities of Cd^{+2} determined by Corey's method due to the lack of ion-pair corrections (compare Table 16 with Table 14). Although there was a difference in the calculated Cd^{+2} activities, the magnitude of the differences were not great. Street et al. (110,111) found Cd^{+2}

Table 16. Calculated activities of Cd^{+2} and Zn^{+2} from total soil solution concentrations of Cd and Zn as affected by Cd and Zn additions to soil in the greenhouse experiment.

Treatment[†]	Cd		Zn	
	Cd_T	(Cd^{+2})[‡]	Zn_T	(Zn^{+2})[‡]
	μmol L^{-1}			
1 Zn 1 Cd	<0.25	<0.16	0.98	0.64
1 Zn 2 Cd	1.48	0.90	4.96	3.08
1 Zn 3 Cd	1.76	1.06	1.02	0.64
1 Zn 4 Cd	2.52	1.54	0.86	0.53
2 Zn 1 Cd	<0.25	<0.13	112.12	61.66
2 Zn 2 Cd	4.06	2.13	113.44	62.39
2 Zn 3 Cd	7.12	3.66	114.14	61.60
2 Zn 4 Cd	10.59	5.46	110.40	58.51
3 Zn 1 Cd	<0.25	<0.12	477.99	243.78
3 Zn 2 Cd	6.48	3.24	432.26	224.78
3 Zn 3 Cd	13.25	6.63	431.02	224.14
3 Zn 4 Cd	22.48	11.24	422.66	219.79
4 Zn 1 Cd	<0.25	<0.12	1090.14	555.97
4 Zn 2 Cd	10.96	5.37	1109.34	565.76
4 Zn 3 Cd	21.76	10.77	1097.15	548.58
4 Zn 4 Cd	34.22	17.11	1057.52	539.34

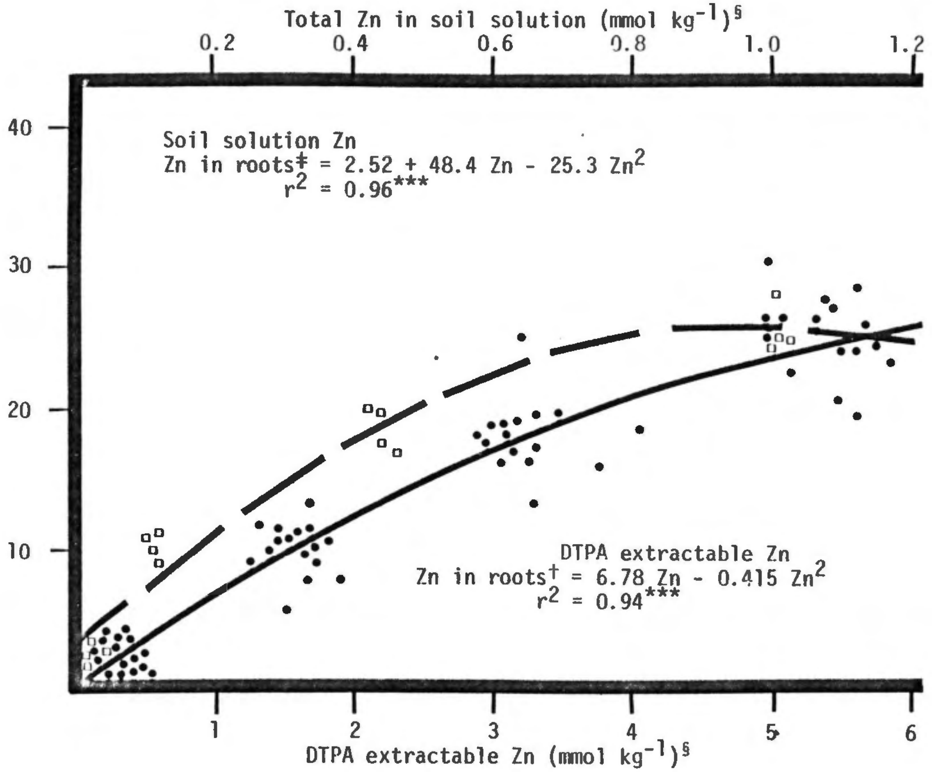
[†] 1 Zn, 2 Zn, 3 Zn, and 4 Zn correspond to 0.9, 4.7, 8.5, and 12.3 mmol kg^{-1} Zn addition to soil, respectively. 1 Cd, 2 Cd, 3 Cd, and 4 Cd correspond to 7, 229, 451, and 673 μmol kg^{-1} Cd addition to soil, respectively.

[‡] Activities of Cd^{+2} and Zn^{+2} calculated by equations in Appendix A.

activities calculated from total Cd concentrations to be similar to Cd^{+2} activities measured by an ion selective electrode.

The Zn^{+2} activities calculated from the total Zn concentrations (Table 16) were much higher than the Zn^{+2} activities calculated by Corey's method (Table 14). This was expected since low ionic Zn^{+2} distributions were calculated from Corey's method. An equivalence of total Zn concentration and ionic Zn^{+2} concentration in soil solutions could not have been assumed due to considerable ion pair formation. Although the activities of Cd^{+2} and Zn^{+2} in soil solutions calculated from total Cd and Zn concentrations are overestimations of actual Cd^{+2} and Zn^{+2} activities in soil solutions, the Cd^{+2} activity estimates are reasonable approximations whereas the Zn^{+2} activities are not.

Total Zn concentrations in displaced soil solution and DTPA extractable Zn were both good predictors of Zn availability in soil (Figure 10). Soil solution Zn and DTPA extractable Zn were also highly correlated ($r = 0.97$). The regressions of Zn in roots on soil solution Zn and DTPA extractable Zn were curvilinear probably as a consequence of these determinations failing to account for ion pair formation which would result in reduced effective concentrations of Zn at higher levels of Zn addition. Soil solution Cd and DTPA extractable Cd were not good indicators of available Cd due to Zn and Cd interactions in root uptake and fixation in metal-amended sludges. Estimations of Cd^{+2} and Zn^{+2} activities were not related to plant uptake since they failed to be accurate estimations of actual activities in soil solution.



***Significant at $\alpha = 0.001$.

†Regression equation from 64 observations.

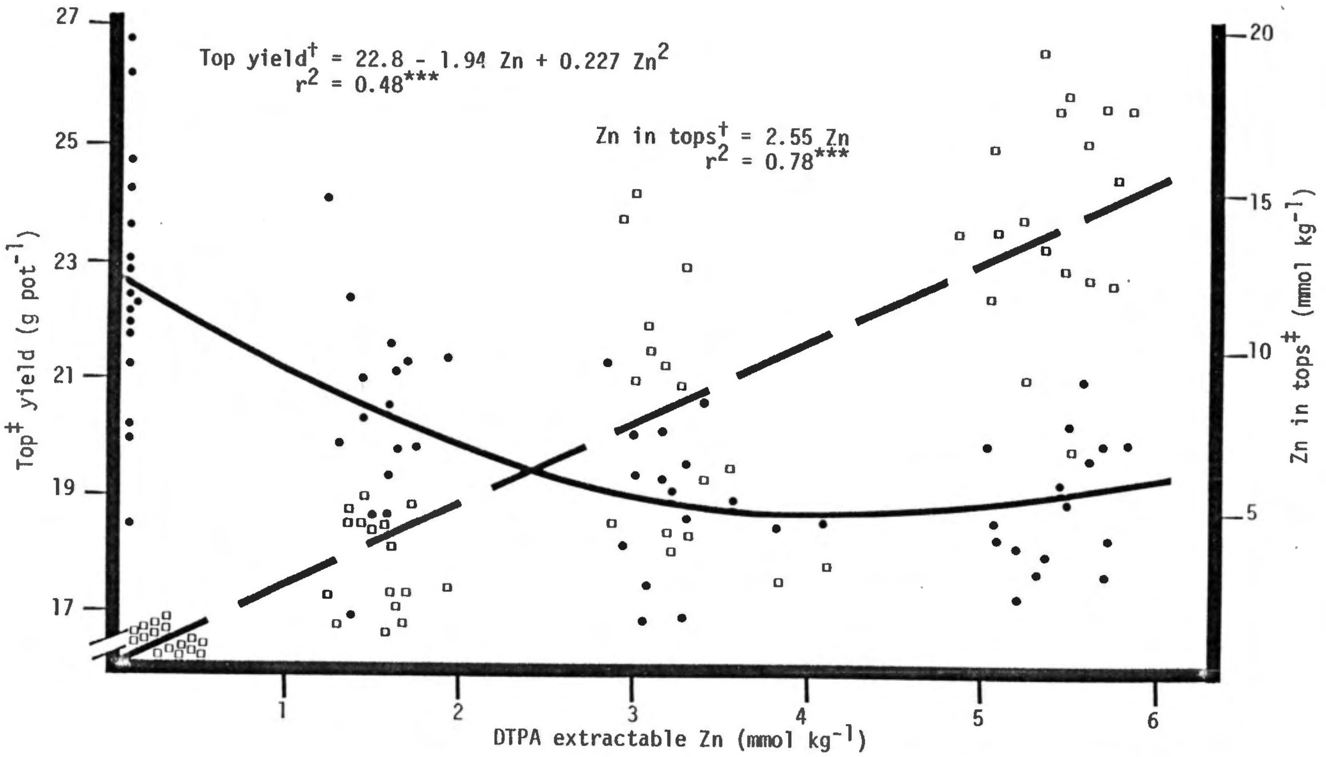
‡Regression equation from 16 observations.

§DTPA extractable Zn = ●———●, total Zn in soil solution = □------□.

Figure 10. Zinc uptake by corn roots as affected by soil solution Zn and DTPA extractable Zn in the greenhouse experiment.

The top yield response of corn to DTPA extractable Zn was similar to yield responses found with Zn additions to the soil and Zn concentrations in the tops (compare Figure 11 with Figure 6, page 53, and Figure 8, page 55). Development of similar response curves of top yield on DTPA extractable Cd was deemed inappropriate due to Zn and Cd interactions in the plant. Zinc phytotoxicity was expressed most strongly when extractable Zn concentration in the soil was 3.5 mmol kg^{-1}. The response of Zn concentrations in tops on DTPA extractable Zn was linear (Figure 11). As Zn concentrations in corn tops increased past 3.5 mmol kg^{-1} of soil extractable Zn, top yields remained relatively unchanged. Apparently, Zn must have been sequestered in the plant tops at high concentrations so it did not result in any further reduction in top growth. One possible binding site of Zn is the pectic materials in the plant cell wall (79). Yield of corn tops decreased with the potentially harmful level of 7.6 mmole Zn kg^{-1} in the diets of cattle (84).

The top yield response curve on DTPA extractable Zn:Cd (expressed as a molar concentration ratio) was similar to the top yield response on DTPA extractable Zn in the soil (compare Figure 12 with Figure 11). Apparently, Zn must have had a greater toxic effect on corn tops compared to Cd. The greatest phytotoxic effect occurred with a soil extractable Zn:Cd ratio of 30. There was a high correlation between the DTPA extractable Zn:Cd ratio and the Zn:Cd molar concentration ratio in tops ($r = 0.89$). An increase of Zn:Cd molar concentration ratio in tops and a relatively constant yield response past the DTPA extractable Zn:Cd ratio of 30 indicated

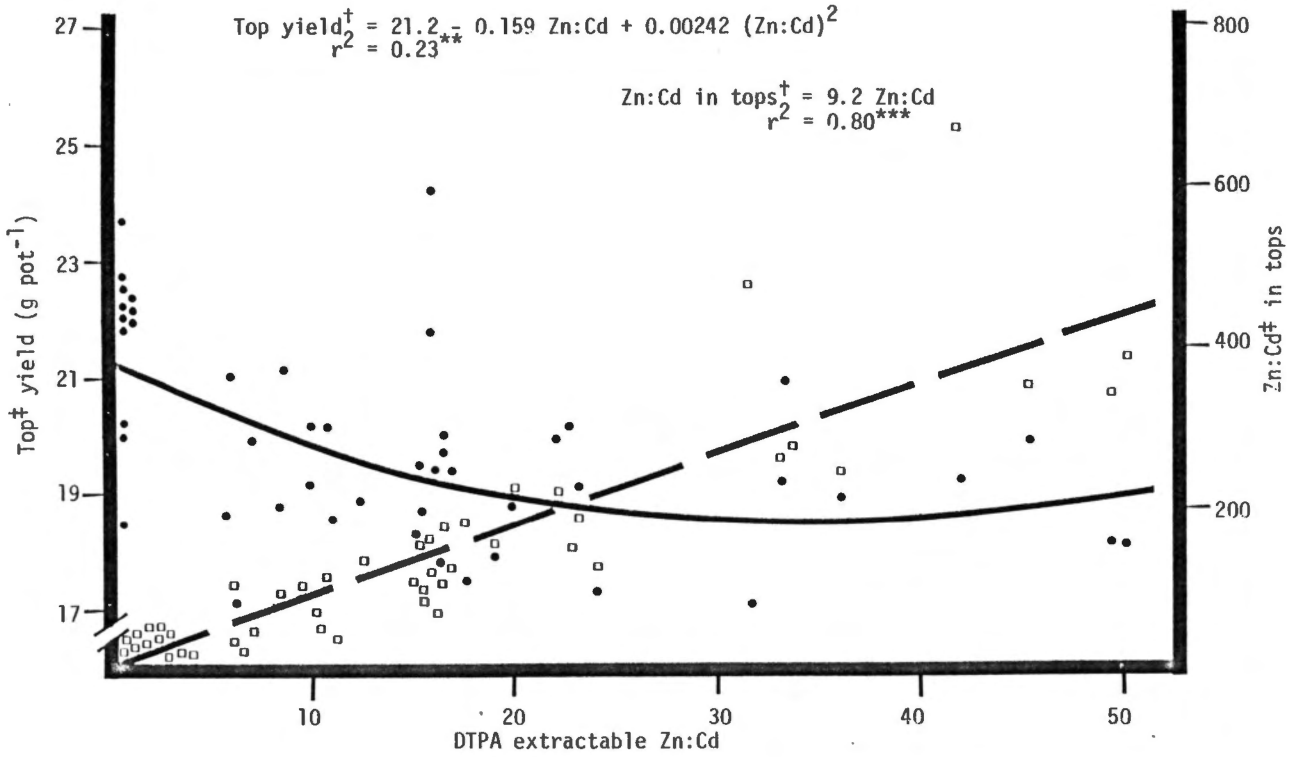


***Significant at $\alpha = 0.001$.

†Regression equations from 64 observations.

‡Top yield = ●———●, Zn in tops = □- - - - - -□.

Figure 11. Top yield and Zn concentration of corn tops as affected by DTPA extractable Zn in the greenhouse experiment.



**, ***Significant at $\alpha = 0.01$ and 0.001, respectively.

†Regression equations from 48 observations. Undetected values of Cd omitted.

‡Top yield = ●———●, Zn:Cd in tops = □- - - - - - -□.

Figure 12. Top yield and the molar concentration ratio of Zn:Cd in tops of corn as affected by DTPA extractable Zn:Cd molar concentration ratio of soil in the greenhouse experiment.

a cessation of Zn phytotoxicity. As with the response of yield and Zn in tops on DTPA soil extractable Zn, it appeared that Zn must be immobilized in a form that is not toxic to the plant (79).

Chaney (40) has suggested that the Zn:Cd molar concentration in feeding material should be greater than 172 to prevent the accumulation and toxicity of Cd in the food chain. A DTPA soil extractable Zn:Cd ratio of 18.7 would have resulted in a Zn:Cd ratio of 172 in corn tops (Figure 12). A decrease of the Zn:Cd ratio in the soil caused a decrease in the Zn:Cd ratio in corn tops and an increase in top yield. Unlike Zn, potentially toxic levels of Cd in plant tissues cannot be detected by decreased yield responses (17).

CHAPTER VI

SUMMARY AND CONCLUSIONS

Field and greenhouse studies were conducted to analyze the potential use of a municipal sewage sludge from Maryville, Tennessee as a source of fertilizer nutrients. Three application rates of the sludge (17, 34, and 51 Mg ha^{-1}) and an inorganic fertilizer application (168, 59, and 111 kg ha^{-1} N, P, and K, respectively) were compared for their ability to fertilize corn for the production of silage and grain in the field. The greenhouse experiment was initiated to determine phytotoxic levels and interactions of Cd and Zn in the soil and corn plant that may be supplied to soil by sludge application. The Maryville municipal sludge was spiked with different levels of Cd and Zn to result in application rates of 7, 229, 451, and 673 μmole kg^{-1} Cd to soil and 0.9, 4.7, 8.5, and 12.3 mmole kg^{-1} Zn to soil.

In the field experiment, sludge additions increased silage and grain yield due to increased available N in the soil. Sludge additions of 34 and 51 Mg ha^{-1} supplied enough N to produce silage yields comparable to the application of 168 kg ha^{-1} N as NH_4NO_3. Although sludge additions did increase grain yield in 1981, the yields were not as high as with the application of 168 kg ha^{-1} N due to the failure of sludge to provide enough N for grain filling. The Maryville sludge benefited corn growth by supplying nutrients other than N. Sludge applications slightly increased the concentrations of P, Ca, Mg, and Zn in corn ear leaf tissues. There were no phytotoxic levels of Cu, Ni, Cd, and Zn in the plant tissues even with the slightly acid soil of pH 5.2. It may be necessary to maintain a higher soil pH in later years, since the heavy metals may become soluble with time and increased levels of the heavy metals would result with extensive use of sludge application through the years. The levels of Cu, Ni, and Cd in the plant tissues were considered to be below levels that are harmful in the food chain of man. In this short-term experiment, sludge application benefited the growth of corn plants without elevating the concentrations of Cu, Ni, Cd, and Zn to toxic levels.

Except for Zn in the two higher Zn additions, the spiked sludges used in the greenhouse experiment were good approximations of actual sludges since the fractions of soluble Zn and Cd were low. Cadmium additions to soil and concentrations in tops did not result in large top yield reductions (11% yield decrement) due to Cd fixation in the sludge and a sequestering of Cd in the roots of the corn plant. Zinc additions had a greater phytotoxic effect than Cd with a 20% top yield decrement at a Zn addition of 10 mmole kg^{-1} to soil. Phytotoxicity reached a limit past 3.5 mmole kg^{-1} of Zn concentration in tops. Zinc must have been bound in the plant at higher concentrations so as not to exert toxic effects. Zinc additions had an effect of decreasing root yield, whereas Cd additions increased root yield at the higher levels of Zn addition. Zinc additions decreased Cd content of corn roots while increasing Cd content of corn tops. Zinc effectively competed with Cd for root uptake while increasing the translocation of Cd from roots to tops. The increased translocation of Cd from roots to tops may have been due to Cd and Zn competition for sites on insoluble organometallic compounds. Cadmium tended to decrease Zn translocation probably by upsetting biochemical balances in the root.

Activities of Cd^{+2} and Zn^{+2} determined by (1) analyzing total concentrations extracted by $CaCl_2$, $Ca(NO_3)_2$, and $Ca(NO_3)_2$ plus EDTA and (2) total Cd and Zn concentrations and electrical conductivities of displaced soil solutions resulted in overestimations of actual Cd^{+2} and Zn^{+2} activities in soil solution. The activity of Cd^{+2} was better estimated by total concentration in soil solutions than was Zn^{+2} activity due to the higher ionic distribution of Cd in soil solutions. Total soil solution Zn and DTPA extractable Zn were both good indicators of plant available Zn in soil. By analyzing top yield and Zn:Cd molar concentration ratio in tops as a function of the molar concentration ratio of DTPA extractable Zn:Cd in soil, Zn was found to exert a greater phytotoxic effect. Phytotoxicity occurred when harmful levels of Zn in the food chain were reached. Yield actually increased when harmful levels of Cd occurred with decreased DTPA extractable Zn:Cd ratios in soil.

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APPENDICES

APPENDIX A

CALCULATIONS OF Cd^{+2} AND Zn^{+2} ACTIVITIES IN SOIL SOLUTION

CALCULATIONS OF Cd^{+2} AND Zn^{+2} ACTIVITY IN SOIL SOLUTION

Calculation of Cd^{+2} and Zn^{+2} Activities from Total Soil Solution Concentrations

1. Assumptions:

   a. Soluble inorganic and organic complexes are insignificant, so $M_T = [M^{+2}]$

   b. There is a direct relationship between electrical conductivity (EC) and ionic strength (μ) expressed as $\mu = 0.013$ EC (45).

2. Calculation of activity coefficient (γ) from ionic strength determined by electrical conductivity (73):

$$\log \quad = -AZ_M^2 \left(\frac{\mu^{1/2}}{1+Bd_M\mu^{1/2}}\right) . \qquad (1)$$

At 25°C, $A = 0.509$
$B = 0.328 \times 10^8$
d_M = effective size of hydrated ion (M^{+2})
Z_M = valency of ion
μ = ionic strength

3. Calculation of Cd^{+2} and Zn^{+2} activity (a_M) (73):

$$(a_M) = \gamma\ [M^{+2}] . \qquad (2)$$

Calculation of Cd^{+2} Activity by Corey's Method (20,38)

1. Assumptions:

   a. ΔCd is the difference of Cd in 0.01 M $CaCl_2$ and 0.01 M $Ca(NO_3)_2$ soil extractant leachates and is equivalent to $[CdCl^+] + [CdCl_2^o] + [CdCl_3^-] + [CdCl_4^{-2}]$.

   b. Cadmium complexed in chloride species is from the solid phase.

   c. At equilibrium,
   μ_{Cd} (solid phase) = μ_{Cd} (soil solution), so
   a_{Cd} (solid phase) = a_{Cd} (soil solution).

   c. Extractants do not remove a significant fraction of labile Cd from the solid phase.

2. Cadmium chloride equilibrium reactions:

   a. $Cd^{+2} + Cl^- \rightleftarrows CdCl^+$

   b. $Cd^{+2} + 2Cl^- \rightleftarrows CdCl^o$

   c. $Cd^{+2} + 3Cl^- \rightleftarrows CdCl_3^-$

   d. $Cd^{+2} + 4Cl^- \rightleftarrows CdCl_4^{-2}$

3. Formation constants (73):

   a. $$K_{CdCl^+} = \frac{(CdCl^+)}{(Cd^{+2})(Cl^-)} = \frac{\gamma_{CdCl^+}\,[CdCl^+]}{(Cd^{+2})\gamma_{Cl^-}[Cl^-]} = 9.55 \times 10^{-1} \qquad (3)$$

   b. $$K_{CdCl_2^o} = \frac{(CdCl_2^o)}{(Cd^{+2})(Cl^-)^2} = \frac{\gamma_{CdCl_2^o}[CdCl_2^o]}{(Cd^{+2})\gamma_{Cl^-}^2[Cl^-]^2} = 3.98 \times 10^{2} \qquad (4)$$

   c. $$K_{CdCl_3^-} = \frac{(CdCl_3^-)}{(Cd^{+2})(Cl^-)^3} = \frac{\gamma_{CdCl_3^-}[CdCl_3^-]}{(Cd^{+2})\gamma_{Cl^-}^3[Cl^-]^3} = 2.51 \times 10^{2} \qquad (5)$$

   d. $$K_{CdCl_4^{-2}} = \frac{(CdCl_4^{-2})}{(Cd^{+2})(Cl^-)^4} = \frac{\gamma_{CdCl_4^{-2}}[CdCl_4^{-2}]}{(Cd^{+2})\gamma_{Cl^-}^4[Cl^-]^4} = 3.16 \times 10^{2} \qquad (6)$$

4. Calculation of ΔCd from assumption 1a:

$$\Delta C_d = \frac{K_{CdCl^+}\,\gamma_{Cl^-}[Cl^-]}{\gamma_{CdCl^+}}(Cd^{+2}) + \frac{K_{CdCl_2^o}\gamma_{Cl^-}^2[Cl^-]^2}{\gamma_{CdCl_2^o}}(Cd^{+2})$$

$$+ \frac{K_{CdCl_3^{-1}}\gamma_{Cl^-}^3[Cl^-]^3}{\gamma_{CdCl_3^-}}(Cd^{+2}) + \frac{K_{CdCl_4^{-2}}\gamma_{Cl^-}^4[Cl^-]^4}{\gamma_{CdCl_4^{-2}}}(Cd^{+2}) \qquad (7)$$

5. Calculation of Cd^{+2} activity:

$$(Cd^{+2}) = \frac{\Delta Cd}{\sum_{n=1}^{4} \frac{K_n[Cl^-]^n(\gamma_{Cl^-})^n}{\gamma_{CdCl_n^{2-n}}}} \qquad (8)$$

$\mu = 0.03$ $\gamma_{CdCl_3^-} = 1.0^*$

$[Cl^-] = 0.02$ M $\gamma_{CdCl_4^{-2}} = 1.0^*$

$\gamma_{Cl^-} = 0.841$

$\gamma_{CdCl^+} = 0.850$

$\gamma_{CdCl_2^o} = 1.0$

$^*CdCl_3^-$ and $CdCl_4^{-2}$ formations were insignificant parameters in the calculation of Cd^{+2} activity.

Calculation of Zn^{+2} Activity by Corey's Method (20,38)

1. Assumptions:
    a. Cadmium and Zn complexed by EDTA are from the solid phase.
    b. μ_{Zn} (solid phase) = μ_{Zn} (soil solution) so
       a_{Zn} (solid phase) = a_{Zn} (soil solution).
    c. Extractants do not remove a significant fraction of labile Zn from the solid phase.
2. Cadmium and Zn EDTA (L) equilibrium reactions and formation constants (73):
    a. $Cd + H + L \rightleftarrows CdHl$ $K_{CdHL} = 3.63 \times 10^{20}$
    b. $Cd + L \rightleftarrows CdL$ $K_{CdL} = 2.29 \times 10^{17}$
    c. $Zn + H + L \rightleftarrows ZnHL$ $K_{ZnHL} = 5.50 \times 10^{20}$
    d. $Zn + L \rightleftarrows ZnL$ $K_{ZnL} = 2.75 \times 10^{17}$
3. Competitive stability constant:

$$K_{Zn}^{Cd} = \frac{[CdHL][CdL](Zn^{+2})^2}{[ZnHL][ZnL](Cd^{+2})^2} = 5.50 \times 10^{-1} \tag{9}$$

4. Calculation of Zn^{+2} activity:

$$(Zn^{+2}) = \left(\frac{0.550(Cd^{+2})^2[ZnHL][ZnL]}{[CdHL][CdL)}\right)^{1/2} \tag{10}$$

(Cd^{+2}) from previous calculation (page 95)

[ZnHL][ZnL] = difference of Zn in $Ca(NO_3)_2$ and $Ca(NO_3)_2$ + EDTA leachates

[CdHL][CdL] = difference of Cd in $Ca(NO_3)_2$ and $Ca(NO_3)_2$ + EDTA leachates.

APPENDIX B

CHEMICAL AND PHYSICAL PROPERTIES OF SEQUATCHIE SANDY LOAM

Table 17. Cation exchange capacity and exchangeable cations of Sequatchie sandy loam collected at three depths over the entire field experiment in spring 1980.

Soil Depth	CEC	Ca	Mg	K	Na
----cm----	-----------------mmol (+) kg^{-1}-----------------				
0-15	45	31	6	<1	3
15-30	44	25	4	<1	1
30-45	41	28	6	<1	1

Table 18. Mechanical analyses and field capacity of Sequatchie sandy loam collected at three depths over the entire field experiment in spring 1980.

Soil Depth	Coarse silt	Sand	Silt	Clay	Moisture at 33K Pa tension
----cm----	------------------kg kg^{-1}-------------------------				
0-15	0.06	0.72	0.10	0.12	0.11
15-30	0.06	0.72	0.10	0.12	0.14
30-45	0.03	0.69	0.10	0.18	0.17

APPENDIX C

ELEMENTAL CONCENTRATIONS OF CORN TISSUE FROM THE FIELD EXPERIMENT

Table 19. Phosphorus, K, Ca, Mg, and Zn concentrations in corn grain as affected by sludge and inorganic N additions from the field experiment in 1980 and 1981.

Treatment	Nutrient concentration of corn grain									
	1980					1981				
	P	K	Ca	Mg	Zn	P	K	Ca	Mg	Zn
	------mmol kg^{-1}------				μmol kg^{-1}	------mmol kg^{-1}-------				μmol kg^{-1}
No fertilizer N	90[†]	97	6	38	340	67	91	<1	35	536
Sludge, 17 Mg ha^{-1}	93	95	6	39	272	86	118	<1	46	585
Sludge, 34 Mg ha^{-1}	94	97	10	39	282	78	110	<1	44	704
Sludge, 51 Mg ha^{-1}	89	93	6	37	398	77	101	<1	40	555
NH_4NO_3, 168 kg N ha^{-1}	89	91	7	35	421	82	111	<1	44	740

[†] Mean values in the same column are not significantly different at $\alpha = 0.05$ according to F test.

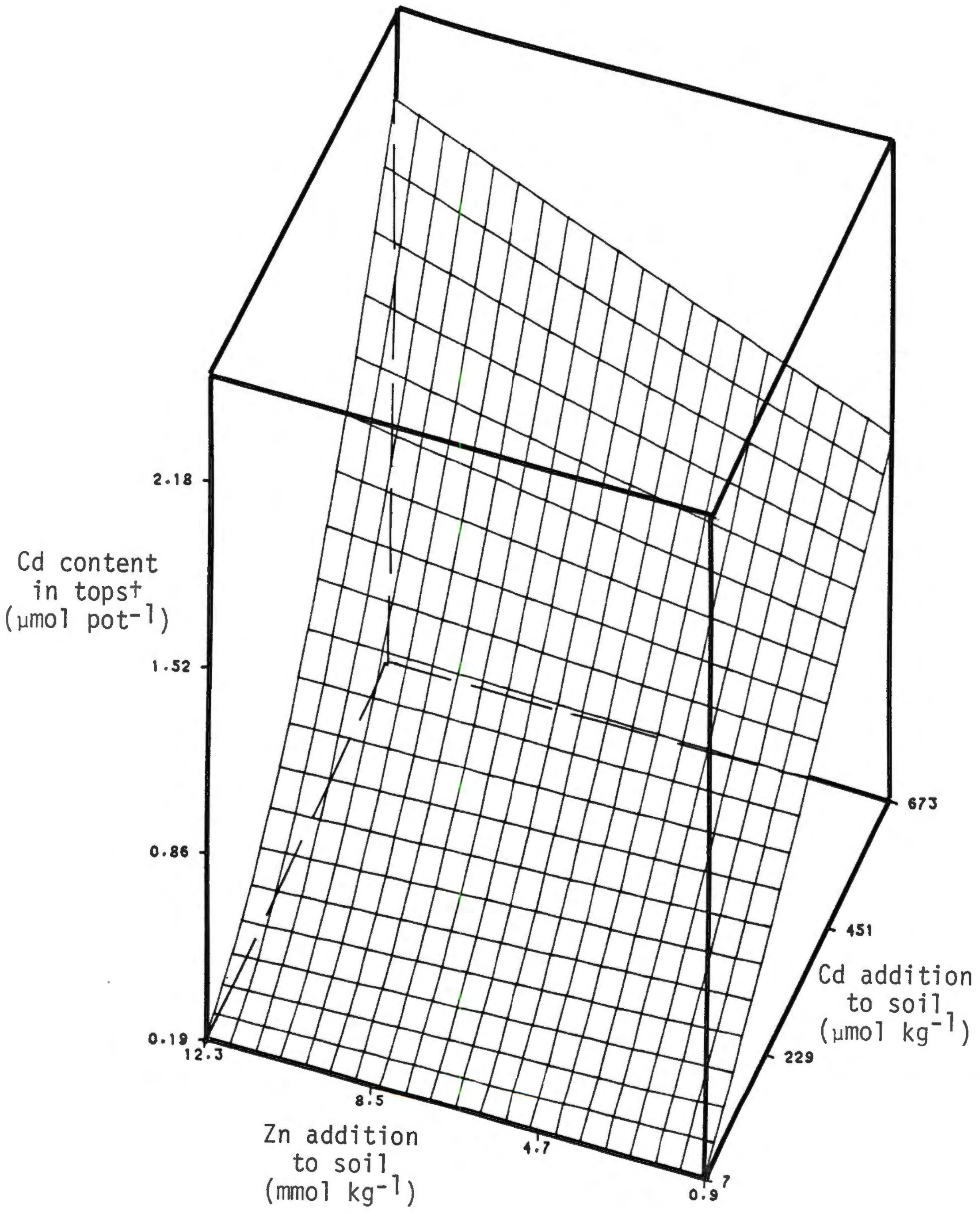
Table 20. Copper concentration in corn ear leaves and grain of field experiment in 1980 and 1981.†

Treatment	Plant tissue	Year	Cu concentration
			---μmol kg^{-1}----
Sludge, 51 Mg ha^{-1}	Corn ear leaf	1980	283
NH_4NO_3, 168 kg N ha^{-1}	Corn ear leaf	1981	189
Sludge, 34 Mg ha^{-1}	Corn ear leaf	1981	220
Sludge, 51 Mg ha^{-1}	Corn ear leaf	1981	165
NH_4NO_3, 168 kg N ha^{-1}	Corn grain	1981	165
Sludge, 34 Mg ha^{-1}	Corn grain	1981	165
Sludge, 54 Mg ha^{-1}	Corn grain	1981	165

†Copper concentrations above the detection limit of 121 μmole kg^{-1}.

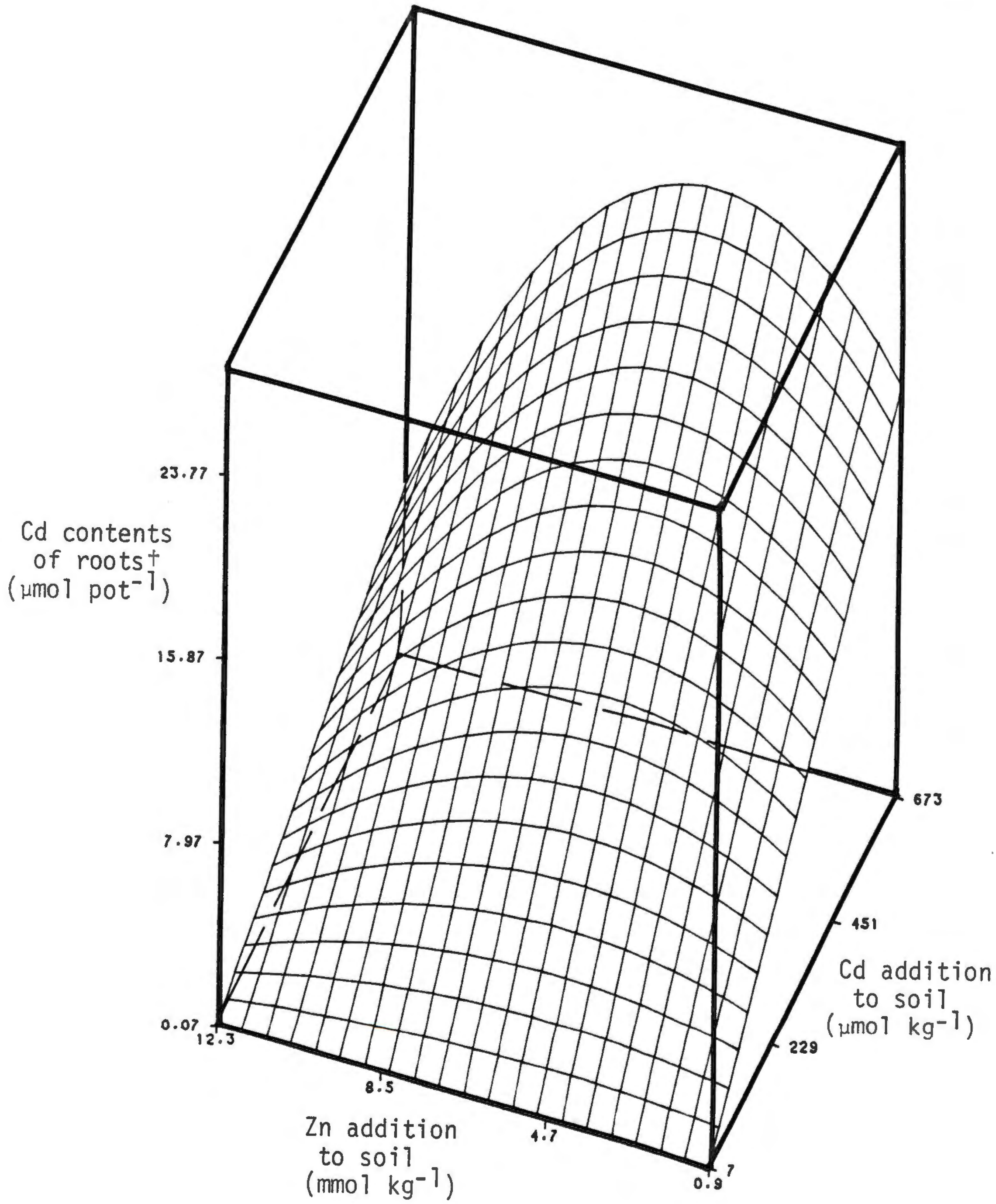
APPENDIX D

SURFACE RESPONSE CURVES AND REGRESSION EQUATIONS OF SELECTED DEPENDENT VARIABLES OF THE GREENHOUSE EXPERIMENT



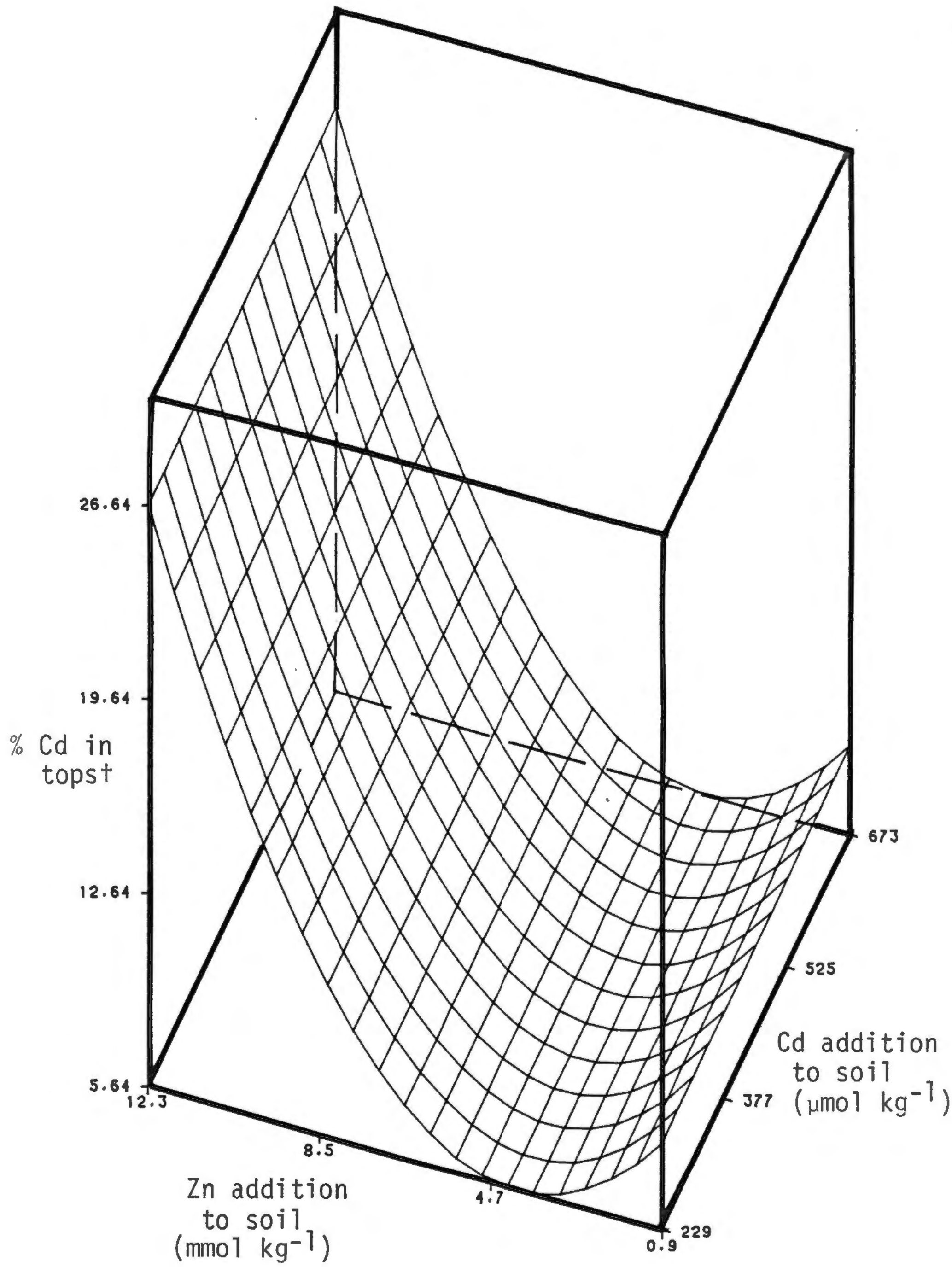
†Regression equation: Cd content in tops = 0.0000988 Zn Cd + 0.00000028 Zn Cd^2, $r^2 = 0.80$ and was significant at $\alpha = 0.001$.

Figure 13. Cadmium content of corn tops as influenced by Cd and Zn additions to soil in the greenhouse experiment.



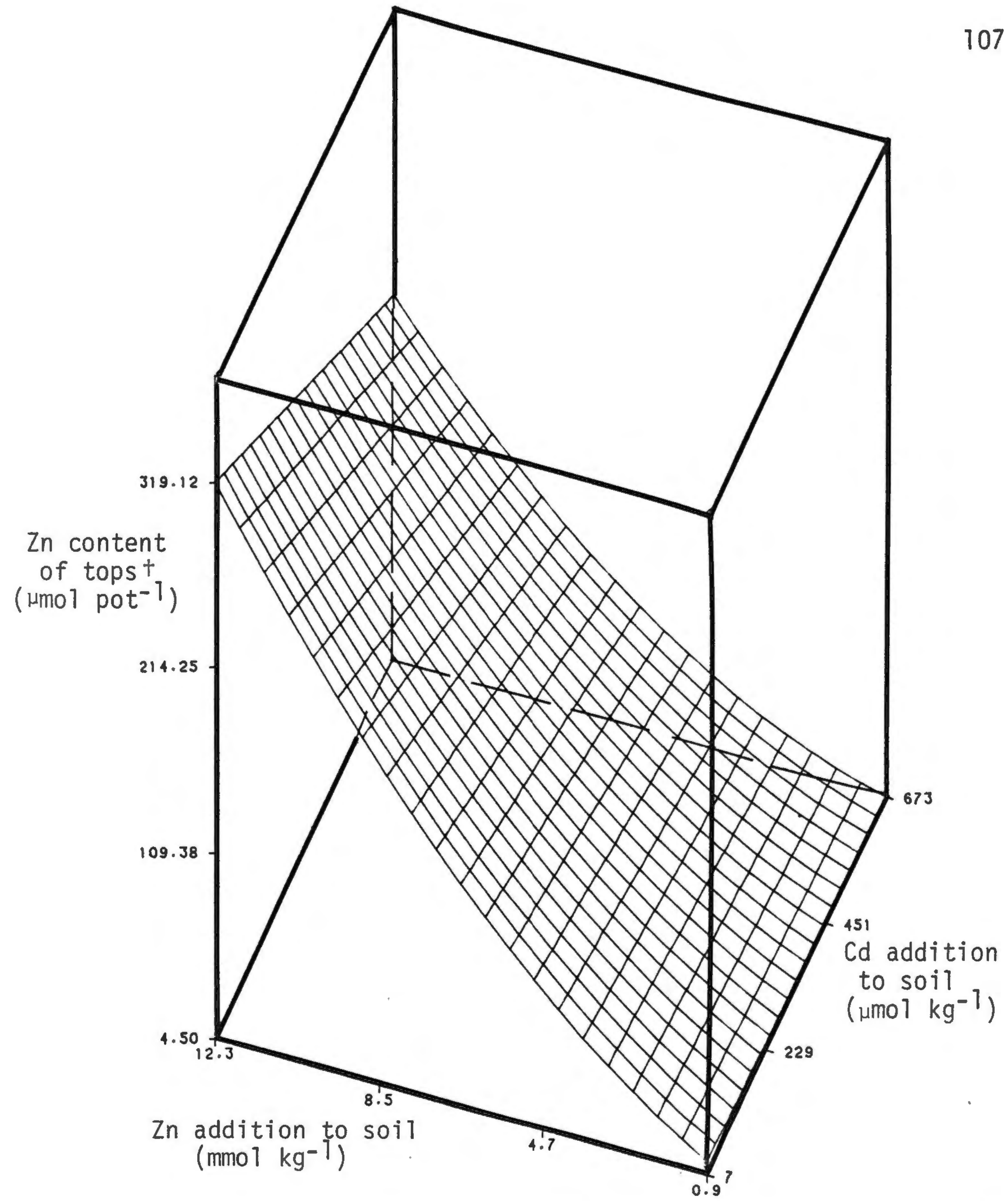
†Regression equation: Cd content of roots = 0.0221 Cd + 0.00504 Zn Cd + 0.0000000683 Zn Cd^2 - 0.000488 Zn^2 Cd, $r^2 = 0.73$ and was significant at $\alpha = 0.001$.

Figure 14. Cadmium content of corn roots as influenced by Cd and Zn additions to soil in the greenhouse experiment.



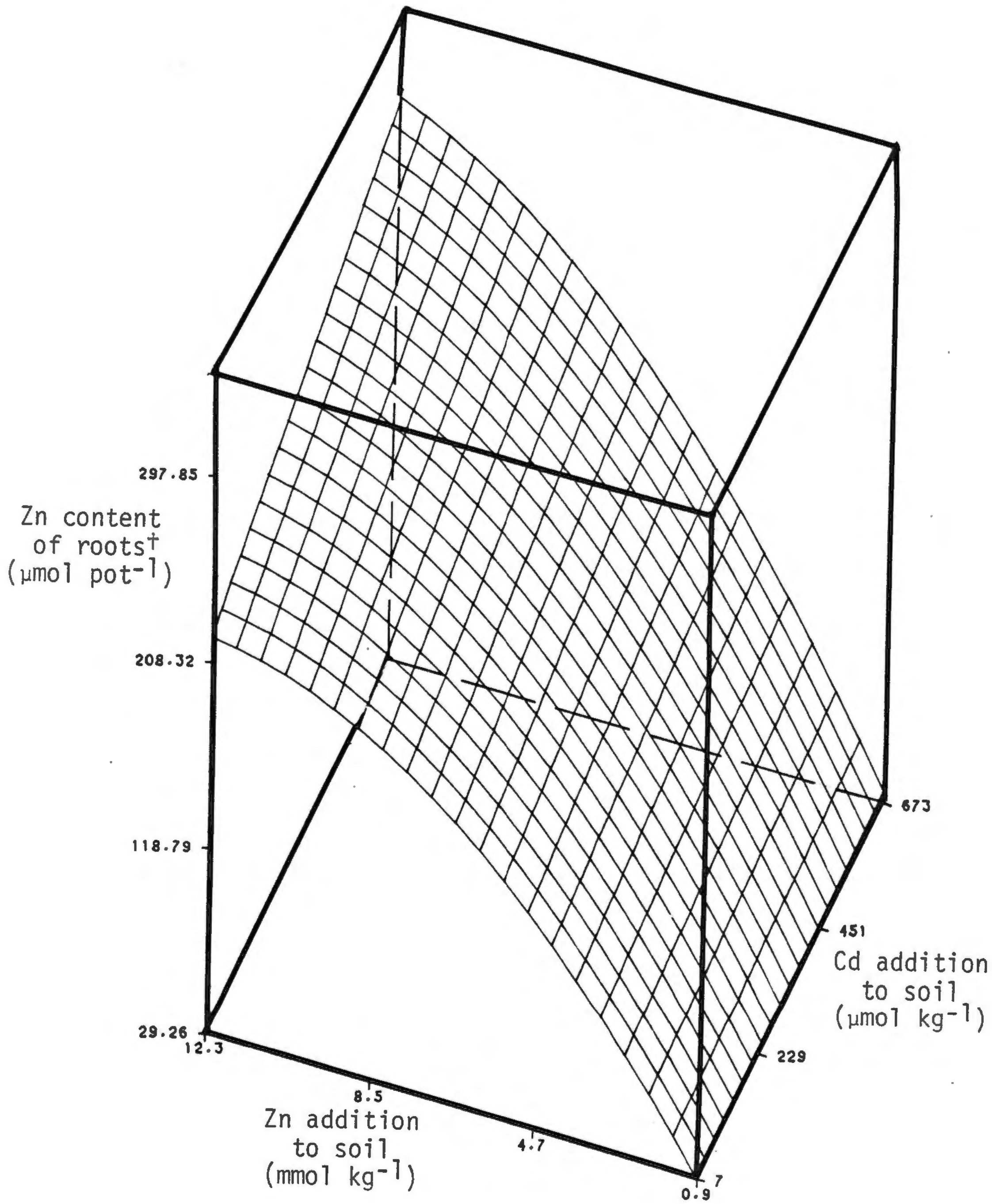
†Regression equation: % Cd in tops = 10.9 - 2.51 Zn + 0.013 Zn^2, $r^2 = 0.70$ and was significant at $\alpha = 0.001$. Undetected Cd values were omitted.

Figure 15. Percent Cd in corn tops as influenced by Cd and Zn additions to soil in the greenhouse experiment.



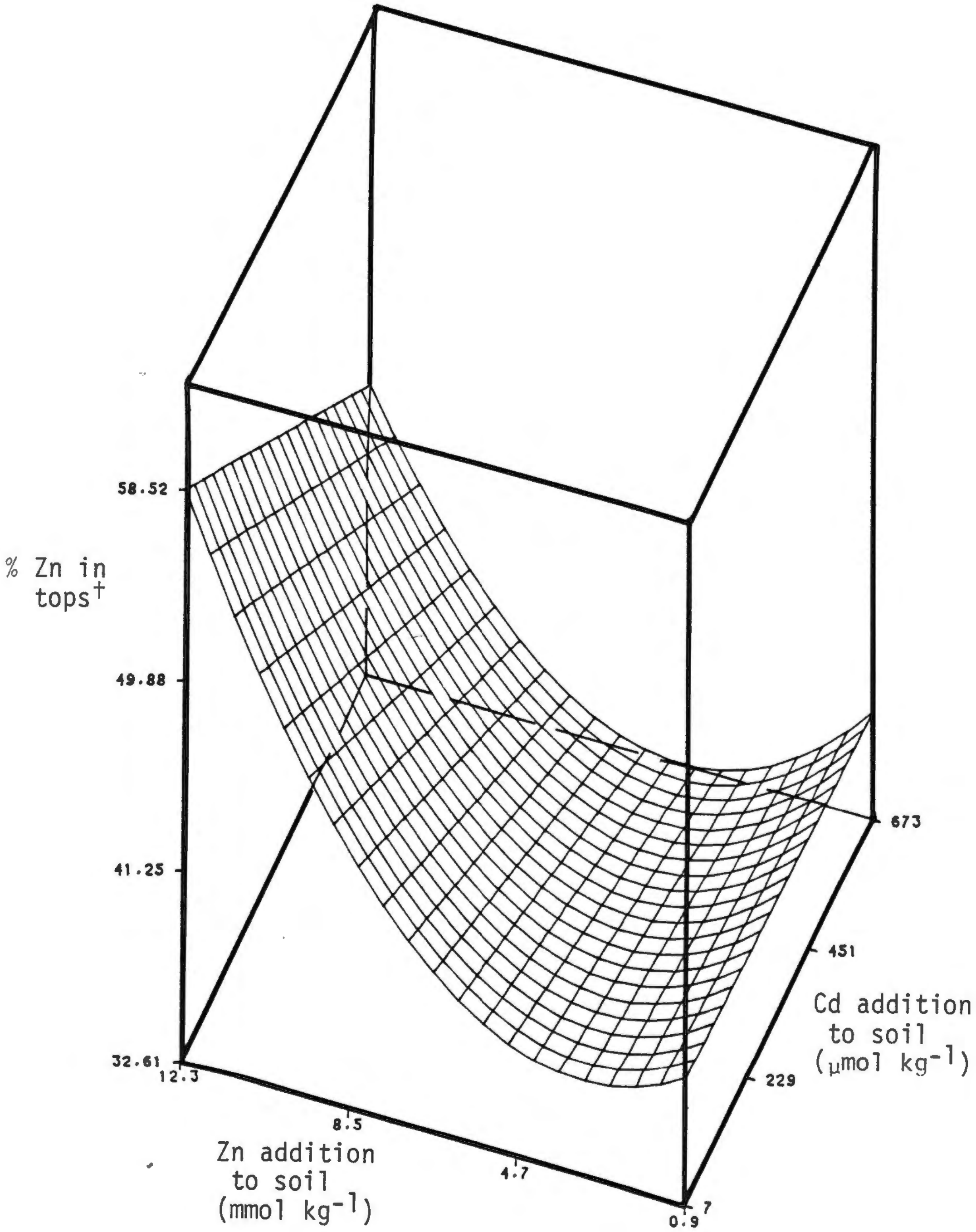
†Regression equation: Zn content of tops = 13 Zn + 1.06 Zn^2 - 0.0133 Zn Cd, $r^2 = 0.84$ and was significant at $\alpha = 0.001$.

Figure 16. Zinc content of corn tops as influenced by Cd and Zn additions to soil in the greenhouse experiment.



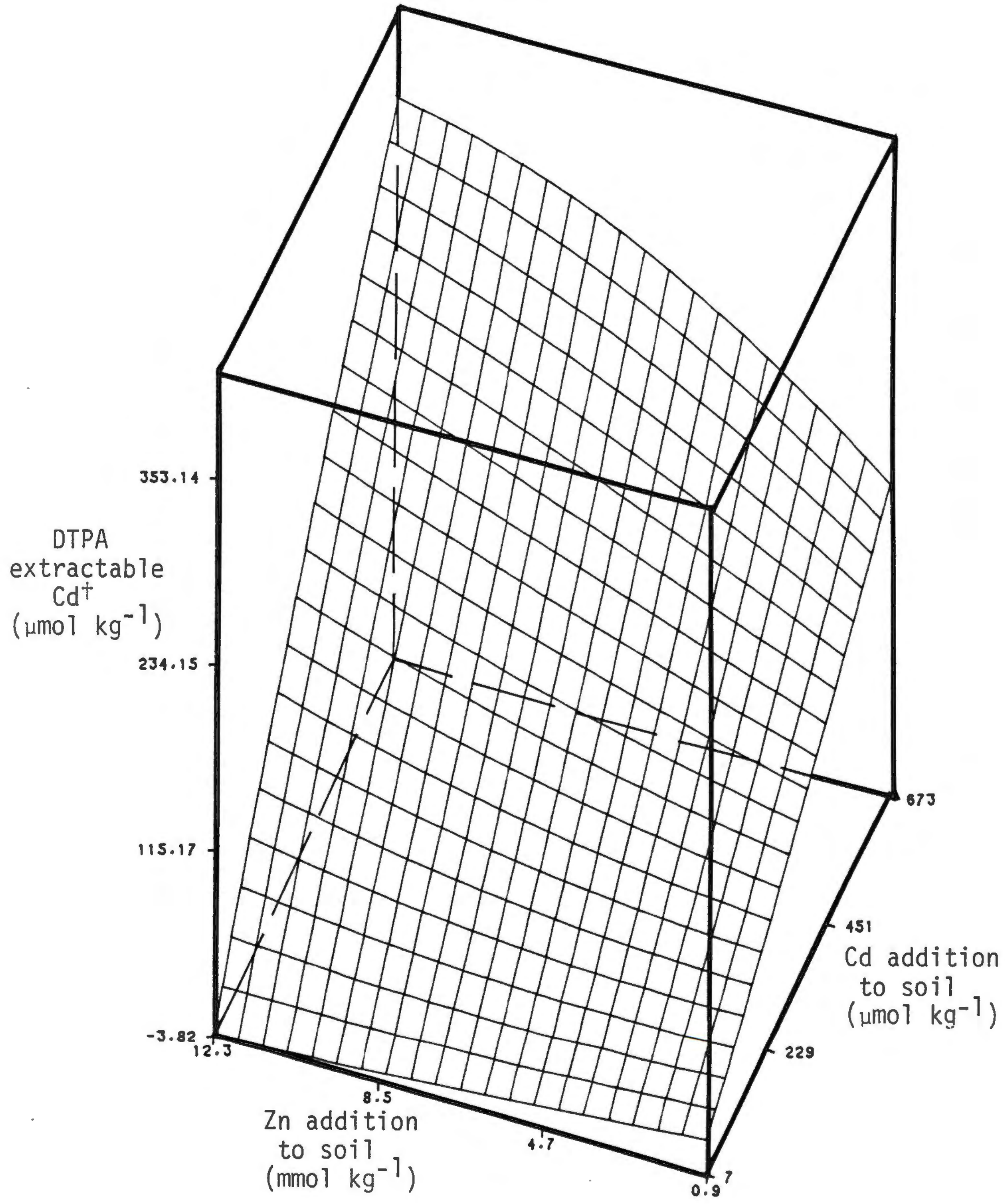
†Regression equation: Zn content of roots = 33.6 Zn - 1.28 Zn^2 + 0.00945 Zn Cd, $r^2 = 0.88$ and was significant at $\alpha = 0.001$.

Figure 17. Zinc content of corn roots as influenced by Cd and Zn additions to soil in the greenhouse experiment.



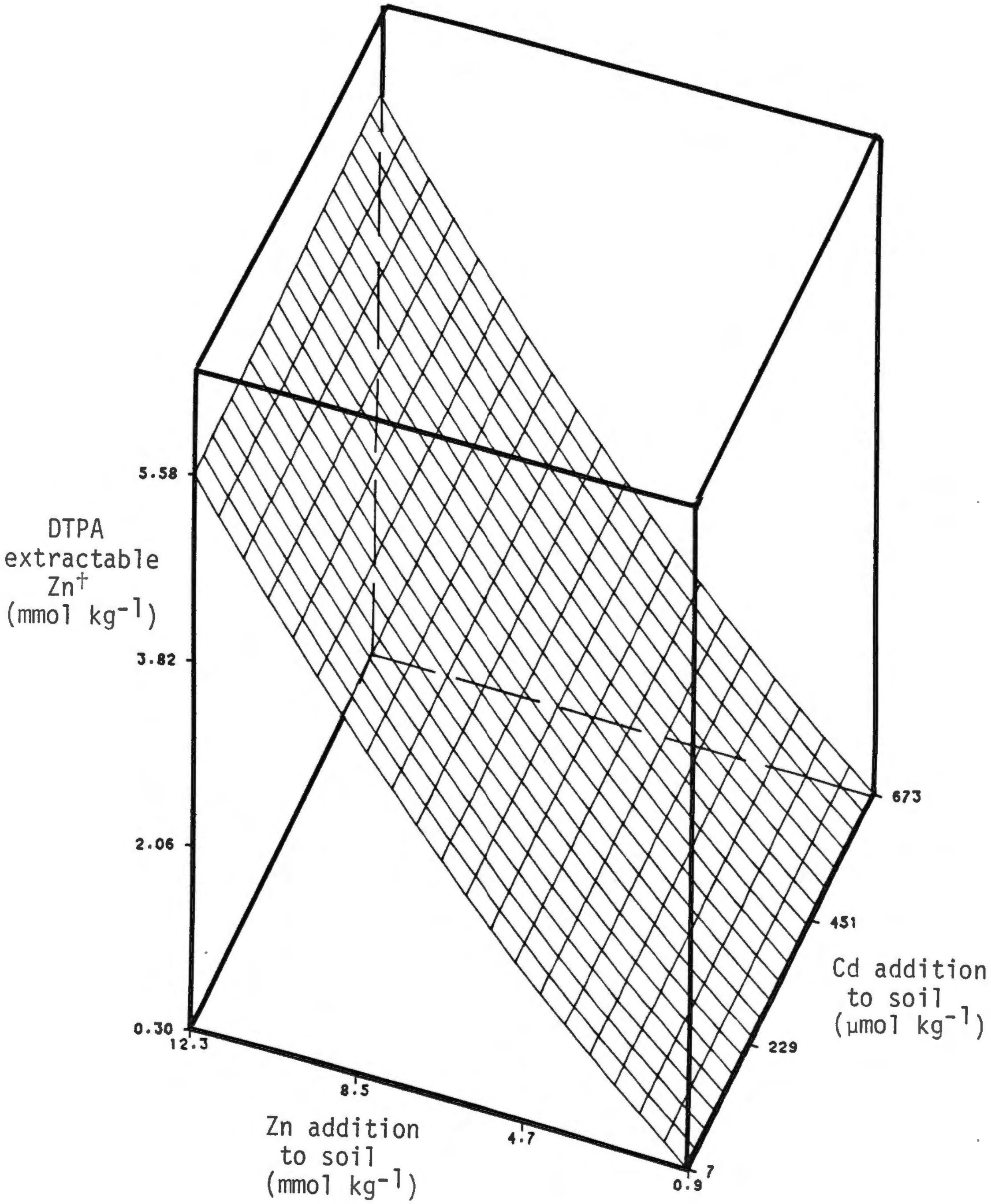
†Regression equation: % Zn in tops = 39.8 - 1.69 Zn + 0.262 Zn^2 - 0.00157 Zn Cd, r^2 = 0.24 and was significant at α = 0.001.

Figure 18. Percent Zn in corn tops as influenced by Cd and Zn additions to soil in the greenhouse experiment.



†Regression equation: DTPA extractable soil Cd = 19.4 - 2.23 Zn + 0.232 Cd + 0.0000582 Zn Cd^2 + 0.00245 Zn^2 Cd - 0.00000538 Zn^2 Cd^2, $r^2 = 0.97$ and was significant at $\alpha = 0.001$.

Figure 19. DTPA extractable Cd in soil as influenced by Cd and Zn additions to soil in the greenhouse experiment.



†Regression equation: DTPA extractable soil Zn = 0.323 Zn + 0.0106 Zn^2, $r^2 = 0.99$ and was significant at $\alpha = 0.001$.

Figure 20. DTPA extractable Zn in soil as influenced by Cd and Zn additions to soil in the greenhouse experiment.

Table 21. Regression equations and coefficients of determination for Zn additions to soil vs. selected dependent variables of the greenhouse experiment.

Dependent variable	Regression equation	r^2
P in tops	$36.6 - 0.696\ Zn$	0.20***
Ca in tops	$115 + 2.56\ Zn$	0.13**
Mg in tops	$140 - 2.14\ Zn$	0.12**
P in roots	$47.4 - 0.897\ Zn$	0.18***
K in roots	$145 + 4.79\ Zn$	0.18***
Ca in roots	$87 + 5.33\ Zn - 0.482\ Zn^2$	0.20**
Mg in roots	$67.7 + 5.63\ Zn - 0.356\ Zn^2$	0.21***
P in soil	$1470 + 35.0\ Zn$	0.38***
K in soil	$919 - 22.9\ Zn + 1.17\ Zn^2$	0.23***
Ca in soil	$31{,}500 - 309\ Zn + 28.8\ Zn^2$	0.19**
Mg in soil	$3430 - 41.3\ Zn + 6.11\ Zn^2$	0.60***
Soil:H_2O pH	$5.47 - 0.0623\ Zn + 0.00160\ Zn^2$	0.90***
Soil:KCl pH	$4.81 - 0.0482\ Zn + 0.00224\ Zn^2$	0.68***

,*Significant at $\alpha = 0.01$ and 0.001, respectively.

APPENDIX E

SI UNITS CONVERSION TABLE

Table 22. Conversion table of SI units used in the thesis.

SI unit	Equivalence
Molar concentration	
mol N kg^{-1}	1.4% N
mol P kg^{-1}	3.1% P
mol K kg^{-1}	3.9% K
mol Ca kg^{-1}	4.0% Ca
mol Mg kg^{-1}	2.4% Mg
mol Cd kg^{-1}	11.2% Cd
mol Zn kg^{-1}	6.5% Zn
mol Cu kg^{-1}	6.4% Cu
mol Ni kg^{-1}	5.9% Ni
Mass concentration	
kg kg^{-1}	100%
Amount of substance concentration	
1 M (1/2 H_2SO_4)	1 N H_2SO_4
1 M (1/3 Al^{+3})	1 N Al^{+3}
Soil application rates	
Mg ha^{-1}	0.446 tons/acre
kg ha^{-1}	0.893 lbs/acre
Cation exchange capacity	
mmol (+) kg^{-1}	0.1 meq/100 g

VITA

Frank J. Sikora was born in McKeesport, Pennsylvania on April 15, 1958. He is the son of Mr. and Mrs. Joseph Sikora of West Mifflin, Pennsylvania. In 1976 he graduated from West Mifflin North High School in West Mifflin, Pennsylvania.

In 1976 he entered West Virginia University, Morgantown, and received his Bachelor of Science degree in Plant and Soil Science with emphasis in crop science in May 1980.

In 1980 he entered the Graduate School of The University of Tennessee, Knoxville. He received his Master of Science degree in Plant and Soil Science with emphasis in soil fertility and chemistry in December 1982.

The author is a member of the Agronomy Society of America, the Soil Science Society of America, and Gamma Sigma Delta Agricultural Honorary Fraternity. Mr. Sikora will be continuing his education in Agronomy by pursuing a Ph. D. degree at the University of Illinois after graduation.