

FACTORS AFFECTING THE UTILIZATION OF ZINC FROM ZINC FERTILIZER
BANDS BY WHEAT

BY

ADOLF SEVERINE NYAKI

A Thesis

Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

Department of Soil Science
University of Manitoba
Winnipeg, Manitoba

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ABSTRACT

Studies were conducted to determine the influence of some soil and plant factors on the utilization of Zn from Zn fertilizer bands by plants. In a chemical study, using a calcareous and a noncalcareous soil, concentrations of water soluble Zn and pH were measured at various distances from the point of application of ZnCl_2 or Zn-EDTA fertilizer bands. The Zn fertilizers were applied either alone or in combination with $(\text{NH}_4)_2\text{SO}_4$, urea or $\text{NH}_4\text{H}_2\text{PO}_4$.

Solubility of Zn was much greater in Zn-EDTA than in ZnCl_2 bands for both soils. Solubility of Zn in fertilizer bands treated with Zn-EDTA alone was the same for both soils. Solubility of Zn in the ZnCl_2 bands was much lower in the calcareous than in the noncalcareous soil. Application of $(\text{NH}_4)_2\text{SO}_4$, urea or $\text{NH}_4\text{H}_2\text{PO}_4$ decreased the solubility of Zn in the Zn-EDTA bands in the noncalcareous soil but increased the solubility of Zn-EDTA in the calcareous soil. $(\text{NH}_4)_2\text{SO}_4$ increased the solubility of the ZnCl_2 fertilizer in both soils while $\text{NH}_4\text{H}_2\text{PO}_4$ decreased its solubility. Urea increased the solubility of Zn in the ZnCl_2 bands in the calcareous soil but decreased Zn solubility in the noncalcareous soil. Zn movement was much greater from Zn-EDTA than from ZnCl_2 bands for both soils. Zn movement from Zn-EDTA bands was greater in the calcareous than in the noncalcareous soil. $\text{NH}_4\text{H}_2\text{PO}_4$ was most effective in enhancing Zn movement from the Zn-EDTA bands, when applied to the calcareous soil. $(\text{NH}_4)_2\text{SO}_4$ was very effective in promoting Zn movement from the ZnCl_2 bands in both soils.

Root growth and utilization of Zn from ZnCl_2 and Zn-EDTA fertilizer bands by wheat were assessed on calcareous, slightly calcareous and noncalcareous soils. The concentrations and form of

water soluble Zn in the fertilizer bands were also determined in some of the studies. Virtually all the water soluble Zn in ZnCl_2 bands was in the ionic form. Both the ionic and complexed forms of Zn were present in Zn-EDTA fertilizer bands. The amount as well as quality of roots in the fertilizer bands were severely reduced by high concentrations of ionic and complexed Zn.

Utilization of Zn by plants was remarkably increased by increasing the root to Zn fertilizer contact. Concentrations of Zn in the plant shoots increased with increases in the amount of roots in the fertilizer band as well as concentrations of Zn in soil solution.

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1.0. INTRODUCTION

Banding (placement of fertilizers in a narrow band) is a widely recommended method of application of various major plant nutrients for crops grown in Manitoba and elsewhere since it has been shown that banding of major nutrients tends to limit fixation of the nutrient by soils, thus enhancing efficiency of uptake by crops. In contrast, studies conducted to date demonstrated that regardless of the crop grown, banding of inorganic Zn fertilizers such as ZnSO_4 result in very low Zn uptakes from the fertilizer bands when compared to Zn uptake when the inorganic Zn fertilizers are thoroughly mixed with the soil (Loewen-Rudgers et al. 1978). It was also shown that the solubility of inorganic Zn fertilizers was higher when banded than when thoroughly mixed with the soil and thus the poor utilization of Zn from the fertilizer band was not due to fixation reactions. It was postulated therefore, that the poor utilization of Zn from inorganic Zn fertilizer bands was partly due to limited contact between plant roots and the Zn fertilizer due to the low mobility of ionic Zn in soil. The low mobility of Zn would result in a very small volume of soil fertilized and thus limited root to Zn fertilizer contact.

Previous studies (Loewen-Rudgers et al. 1978) also showed that Zn uptake from an organically complexed Zn fertilizer band such as Zn-EDTA was usually satisfactory and much greater than from an inorganic Zn fertilizer band. The greater Zn uptakes from organically complexed Zn fertilizer bands was thought to be a consequence of greater movement of Zn from organically complexed Zn fertilizer bands, which in turn resulted in a larger volume of soil treated with the Zn fertilizer.

However, very limited information was presented to demonstrate the extent of the differences in Zn movement from organically complexed and inorganic Zn fertilizer bands, particularly when applied to various soils found in Manitoba. In addition, there was no information in the literature regarding root growth habits (amount of roots, quality of roots etc.) in Zn fertilizer bands, in relation to Zn uptake from the fertilizer bands, to support the limited root contact theory.

Therefore, chemical studies as well as plant growth studies were conducted:

- (1) to compare the solubility as well as extent of Zn movement from organically complexed and inorganic Zn fertilizer bands;
- (2) to determine the influence of various macronutrient fertilizers on solubility and Zn movement from Zn fertilizer bands;
- (3) to determine the effect of organically complexed and inorganic Zn fertilizer bands on root growth and Zn uptake by wheat.

2.0. LITERATURE REVIEW

2.1. Factors Affecting Retention of Zn Fertilizers in Soils

Adsorption of Zn by soil constituents such as clay minerals, Fe and Al hydrous oxides, carbonates and soil organic matter, as well as precipitation reactions involving the Zn ion account for a significant amount of Zn retained in soils (Butler and Bray 1956; Holden and Brown 1965; Loneragan 1975; Shuman 1976). White (1957) as well as Mortvedt et al. (1972) reported that when the concentration of Zn in soil solution was quite low adsorption reactions were very effective as mechanisms of retention of Zn in soils. But, when the concentration of Zn in soil solution was in excess of the adsorption maximum, the amount of Zn in soil solution was largely controlled by the solubility of the precipitates formed (Kalbasi et al. 1978b). When Zn fertilizers are applied in a band, the amount of Zn in soil solution will likely be controlled by both adsorption reactions as well as the solubility of the respective reaction products formed. However, it should be noted that while reaction products will likely play a larger role at the site of application, adsorption reactions will become increasingly important with distance from the band.

2.1.1. Retention of Zn by Clay Minerals.

Zinc may be adsorbed on the exchange sites of clay minerals as Zn^{++} , ZnOH^+ or ZnCl^+ , and occasionally may substitute for Al in the octahedral layer or for Mg in minerals that contain Mg in the octahedral layer (Butler and Bray 1956; Mengel and Kirkby 1982). Studies by

White (1957) showed that about 20 to 45 percent of the Zn in soils was associated with clay minerals. Ellis et al. (1970) as well as Udo et al. (1970) showed that the amount as well as type of clay minerals involved in the retention of Zn had a significant influence on the amount of Zn retained by clay soils, undoubtedly, due to large differences in the surface properties of various clay minerals.

Using the extent of diffusion of Zn in clay minerals as an indication of the extent of retention of Zn by different clay minerals, Ellis et al. (1970) found that the extent of diffusion of Zn through the various clay minerals tested followed the order, kaolinite > illite > montmorillonite > vermiculite. Shuman (1976) reported that differences among clay minerals with respect to their adsorptive capacities for Zn were directly related to the C.E.C. of the clay. However, DeMumbrum and Jackson (1956) and Bingham et al. (1964), demonstrated that in some cases, some clay minerals such as montmorillonite retained amounts of Zn in excess of their C.E.C. at near neutral or alkaline pH. They suggested that adsorption of the hydrolysed form of Zn or precipitation of Zn as Zn hydroxide was probably the most logical explanation for the observed effect. But, Elgabaly and Jenny (1943) believed that the Zn that could not be extracted by a neutral salt was probably retained in the octahedral layers of the clay minerals.

In view of the ability of certain minerals to retain significant amounts of the Zn^{++} ion, one might be inclined to believe that retention of Zn by clay minerals would be more likely to occur with the inorganic than the organically complexed form. Wallace and Lunt (1956)

as well as Hochberg and Lahau (1978) reported that there was no evidence in their work to indicate that clay soils retained appreciable amounts of Zn from Zn-EDTA. However, in some instances other researchers reported the contrary. Wallace et al. (1957), for example, cautioned that when using metal chelates as sources of micronutrients such as Zn, one has to take into consideration the reactions of chelates in soils. Butler and Bray (1956) reported that the application of Zn-EDTA to soils high in clay was not a very effective method of supplying Zn to plants. Stewart and Leonard (1957) found that fifty percent of the Zn applied in the chelated form was adsorbed by clay minerals.

Therefore, it is quite evident that soils high in clay content can have a profound influence on the solubility as well as plant availability of both organically complexed as well as inorganic Zn fertilizers. These studies also suggest that such soils can contribute substantially in alleviating metal toxicity problems which might occur due to high concentrations of certain metals in soils.

2.1.2. Adsorption of Zn by Fe and Al Hydrous Oxides

The ability of Fe and Al hydrous oxides to adsorb significant amounts of native Zn as well as Zn from applied Zn fertilizers has long been recognised (White 1957; Chu 1968; Shuman 1976; Kalbasi et al. 1978a). Most researchers showed that the adsorption of Zn by such oxides was a pH dependent reaction increasing markedly with increase in pH, most likely due to the pH dependent surface charge of the sesquioxides. The mechanism involved in the adsorption reactions has

also contributed significantly towards a better understanding of the factors controlling the chemical availability of Zn in soils which contain significant amounts of Fe and Al hydrous oxides. Kalbasi et al. (1978a) identified two mechanisms by which Zn was adsorbed to Fe and Al oxides, i.e. specific adsorption and nonspecific adsorption of Zn. Specific adsorption of Zn involved adsorption of Zn^{++} through the formation of an olation bridge and ring structure with the oxide and the release of two H^+ for each mole of Zn^{++} adsorbed. On the other hand, nonspecific adsorption of Zn was thought to involve adsorption of ZnCl^+ or Zn^{++} plus Cl^- and the release of one H^+ for each mole of Zn^{++} adsorbed. A single bond structure in which ZnCl^+ replaced one H^+ from surface $-\text{OH}_2$ groups was postulated. Kalbasi et al. (1978a) also found that about 60 to 90 percent of the Zn adsorbed by Fe_2O_3 was specifically adsorbed while nonspecific adsorption of Zn accounted for 10 to 40 percent of the total Zn adsorbed by the Fe oxides. Specifically adsorbed Zn was considered not easily available to plants while nonspecifically adsorbed Zn was considered to be relatively more plant available.

The importance of P fertilizers in increasing the extent of Zn adsorption to Fe oxides in some soils has also been associated with the effect of the P fertilizers on the surface charge of the oxides (Stanton and Burger 1967). Saeed and Fox (1979), for example, working with some tropical soils, found that application of P fertilizers to such soils increased the negative charge on the Fe and Al hydrous oxides systems. This effect was believed to account for the increased capacity of the oxides to retain Zn. In addition, Jenne (1968) also

reported that factors such as the concentration of metal ion of interest, the concentration of competing ions, as well as other ions capable of forming inorganic complexes as well as organic chelates, all had a considerable influence on the extent of adsorption of heavy metals by sesquioxides.

In view of the role played by Fe and Al hydrous oxides in the adsorption of Zn in soils, one might be led to speculate that such properties may be useful as a potential solution to occasional metal toxicity problems resulting from high concentrations of certain metals in soil solution. However, given the fact that adsorption reactions were found to be most effective when the concentration of Zn in soil solution was quite low, the effectiveness of the sesquioxides in the adsorption of Zn at concentrations which might normally be encountered in inorganic Zn fertilizer bands has yet to be evaluated.

2.1.3. Retention of Zn by Soil Organic Matter

Zinc interacts with soil organic matter to form both soluble as well as insoluble Zn-organic matter complexes (Hodgson et al. 1966; Loneragan 1975). Therefore, among other effects, organic matter obviously plays a significant role as an agent for mobilization and transport of metal ions in soils (Himes and Barber 1957; Schnitzer and Skinner 1966). Miller and Ohlrogge (1958) as well as Singh and Sekhon (1977) found that addition of large amounts of manure to the soil resulted in significant decreases in the amount of Zn available to plants. On the other hand, other workers found that in some instances, high levels of organic matter in the soil may have some advantages.

Follet and Lindsay (1970), for example, suggested that high levels of organic matter in surface soils were, at least in certain instances responsible for the greater availability of Zn in such soils. Stevenson and Fitch (1986) reported that in instances in which soluble complexing organic acids were present in appreciable amounts the concentration of polyvalent cations in soil solution was significantly higher. Consequently, the movement of such cations in the soil was increased. Some researchers have indicated that an increase in movement of Zn results in a greater contact between plant roots and the Zn fertilizer and therefore promotes the availability of the Zn fertilizer to plants.

Stevenson and Ardakani (1972) compiled a detailed review on reactions between micronutrients and organic matter in soils, from which they concluded that soluble Zn-organic matter complexes were mainly associated with amino, organic and fulvic acids, while insoluble organic Zn complexes were mainly derived from humic acids. Hodgson et al. (1966) estimated that about 60 percent of the soluble Zn in soil solution occurred in the form of soluble Zn-organic matter complexes. Randhawa and Broadbent (1965a, 1965b) found that strongly bound Zn represented less than one percent of the total amount of Zn retained in the soils studied.

2.1.4. Solid Phase Reaction Products of Zn Fertilizers in Soils

The knowledge of the various reaction products formed at the site of application of Zn fertilizers, as well as the various factors which affect their solubility in soils is fundamental to a better

understanding of the factors affecting plant availability of Zn from banded Zn fertilizers.

Various studies have been conducted to characterize the solid phases of banded Zn fertilizers in terms of their solubility products (Mortvedt and Giordano 1969). Such information is obviously quite important in the prediction of the amount of Zn in soil solution for banded Zn fertilizers. Kalbasi et al. (1978b) found that when inorganic Zn fertilizers were applied to a noncalcareous soil the main reaction product detected was $\text{Zn}(\text{OH})_2$. On the other hand, when such fertilizers were applied to a calcareous soil ZnCO_3 and/or $\text{ZnCO}_3(\text{OH})_6$ were the main solid phase reaction products formed. In both cases the solubility of the respective reaction products decreased markedly with increase in pH (Jackson et al. 1962; Richards 1969; Kalbasi et al. 1978b). Based on these observations, Melton et al. (1973) concluded that the commonly observed Zn deficiency problems in crops grown on calcareous soils even when treated with inorganic Zn fertilizers was a consequence of the decrease in the solubility of the various reaction products due to high pH. Earlier, Bingham et al. (1964) using the same principles suggested that the retention of Zn by clay soils in excess of their C.E.C. could also be attributed to precipitation of $\text{Zn}(\text{OH})_2$ in the clay system.

To date, no solid phase reaction products have been detected when organically complexed Zn fertilizers such as Zn-EDTA are applied in a band (Kalbasi et al. 1978b), suggesting that in such instances most of the Zn was probably retained by mechanisms other than precipitation. Nevertheless, it is quite reasonable to speculate that if the stability

of a particular Zn-chelate was quite low in a given soil, amounts of Zn in excess of the adsorption maxima may be present in soil solution, particularly in banded Zn fertilizers. Therefore, under such situations solid phase reaction products might be expected to form. Lehman (1963) reported that this was found to be the case with Fe chelates.

The influence of macronutrient fertilizers, particularly P on the types of reaction products formed, as well as their effect on the solubility as well as plant availability of Zn from inorganic Zn fertilizers has also been recognized (Jackson et al. 1962; Hossner and Blancher 1969; Giordano et al. 1971; Kalbasi et al. 1978b). Bingham (1963) as well as Mortvedt and Giordano (1969) found that in most cases chemical reactions between the Zn and P fertilizers resulted in a decrease in plant available Zn in soil solution.

Kalbasi et al. (1978b) found that the reaction products formed when ZnSO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ were applied in a band in a noncalcareous soil was $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, but when applied to a calcareous soil the reaction products detected were $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, NH_4ZnPO_4 and ZnCO_3 . Hossner and Blancher (1969) reported that the quantity as well as the species of Zn precipitating in the residues was markedly influenced by the pyrophosphate content as well as the pH of the MAP-Zn mixture. According to Slack et al. (1965) and Terman et al. (1966), the solubility of the various reaction products formed increased appreciably with decrease in pH. Slack et al. (1965) also realized that the type of P fertilizer applied with the Zn fertilizer had significant influence on solubility of Zn in soils. They showed, for example, that polyphosphates maintained a higher concentration of micronutrient in soil solution

than did corresponding orthophosphates.

2.2. Factors Affecting Plant Availability of Zn Fertilizers

The amount of Zn in soil solution that is readily available to plants is usually very low, particularly in calcareous soils of high pH (Hodgson et al. 1966; Lindsay 1972a; Racz and Haluschak 1974). Therefore, additional Zn is often supplied to various crops using commercial Zn fertilizers. Plant availability of Zn from Zn fertilizers is controlled by various soil as well as plant factors. However, the extent to which some of the factors are involved in controlling the uptake of Zn by plants from Zn fertilizers has not been fully documented. Such knowledge is fundamental to a better understanding of the causes of Zn deficiency and methods of correcting Zn deficiency problems in various agricultural crops.

2.2.1. Sources and Methods of Placement of Zn Fertilizers

Studies conducted to compare the effectiveness of various organically complexed and inorganic Zn fertilizers in supplying Zn to various crops have been widely reported. Different placement methods for Zn fertilizers have a significant effect on the bioavailability of applied Zn. Therefore, appropriate placement methods are quite essential in any attempt to enhance plant availability of organically complexed as well as inorganic Zn fertilizers.

Brown and Krantz (1966) compared the effectiveness of Zn-EDTA and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in supplying Zn to corn plants. They found that when the Zn fertilizers were mixed throughout the soil they were equally

effective in supplying Zn to corn plants, but when they were banded Zn-EDTA was superior to $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. They also showed that banded Zn-EDTA was just as effective as mixing it throughout the soil. Judy (1967) compared the bioavailability of Zn from Zn-EDTA and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ fertilizers to beans under field as well as greenhouse conditions, and found that Zn-EDTA was more effective than $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Holden and Brown (1965) conducted greenhouse experiments in which they showed that Zn-EDTA increased the concentration of Zn in alfalfa plants twice as much as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ when the plants were grown on a neutral soil and six times as much as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ when the plants were grown on a calcareous soil. The Zn fertilizers were mixed throughout with the soil. Butler and Bray (1956), found that when Zn-EDTA was applied to a sandy soil it was very effective in increasing the concentration of Zn in ryegrass. On the other hand, they found that Zn-EDTA was not very effective in supplying Zn to the plants when it was applied to a clay soil. A few reports in the literature have also revealed that in certain instances organically complexed Zn fertilizers such as Zn-EDTA were quite ineffective in supplying Zn to plants when compared to results obtained when equivalent amounts of inorganic Zn fertilizers were applied to the plants (Miller and Ohlrogge 1958; Elgala et al. 1978; Singh et al. 1986).

Studies conducted in Manitoba under growth chamber as well as field conditions regarding the effectiveness of organically complexed and inorganic Zn fertilizers, as well as placement methods were reviewed by Loewen-Rudgers et al. (1978). The studies showed that mixing $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ throughout the soil was more effective in increasing

the concentration of Zn in blackbeans and barley shoots than banding the $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ with the seed, which was more effective than sidebanding. They also found that Zn-EDTA was about 2.5 times more effective than $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in increasing Zn uptake by blackbeans when the Zn fertilizers were mixed with the surface 15 cm of soil. McGregor (1972), in greenhouse studies, found that when $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was thoroughly mixed with a Zn deficient calcareous soil, the concentration of Zn in corn leaves was significantly increased, whereas row banded $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ had little or no effect on the concentration of Zn in the corn leaves.

In addition to the large differences in bioavailability of organically complexed and inorganic Zn fertilizers, significant differences were also reported among various organically complexed Zn fertilizers with respect to their effectiveness in supplying Zn to plants. Similarly, considerable differences in the effectiveness of various inorganic Zn fertilizers in supplying Zn to plants were also not uncommon. Terman et al. (1966), found that Zn uptake from inorganic Zn fertilizers by various grasses grown in the greenhouse followed the order $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} > \text{ZnO} > \text{ZnS}$. Singh et al. (1986) compared the effectiveness of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, Zn-EDTA and a sodium based lignosulphonate as sources of Zn for bean plants grown in a growth chamber. The results obtained showed that when the Zn sources were mixed throughout the soil, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and the lignosulphonate sources of Zn were more effective than Zn-EDTA in correcting Zn deficiency in the bean plants. Biomass production was highest in treatments that received $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, but the lignosulphonate source of Zn was most effective in increasing the plant Zn content. Brown and Krantz (1966),

found that Rayplex-Zn, an organically complexed Zn source was as effective as Zn-EDTA, or reagent grade $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, for correcting Zn deficiency in corn plants grown in the greenhouse, when it was mixed with the soil. The effectiveness of Rayplex-Zn relative to Zn-EDTA was significantly decreased when it was banded below the seed, or placed in a point in the soil. Rasmusen and Brown (1969), showed that Zn polyflavinoid was superior to Zn-EDTA as well as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ when the Zn fertilizers were applied to beans as seed treatments.

Studies designed to evaluate the effectiveness of organically complexed and inorganic Zn fertilizers as sources of Zn to plants grown in nutrient solutions have also revealed some interesting findings regarding the form of Zn absorbed by plants. However, the relevance of such findings to actual soil systems probably requires further investigations. A review of studies conducted in nutrient solutions clearly showed that organically complexed Zn fertilizers such as Zn-EDTA were not an effective source of Zn for plants grown in nutrient solutions, when compared to plant availability of Zn from inorganic Zn fertilizers (Halvorson and Lindsay 1977). Miller and Ohlrogge (1958), for example, found that addition of chelating substances to a nutrient solution containing the Zn^{++} ion, resulted in a substantial decrease in the absorption of Zn by corn as well as soybean plants from the nutrient solution. On the other hand, Hill-Cottingham (1957) found that chelated forms of Fe were effectively absorbed by tomato plants. He found that photoreduction was not an essential step in the utilization of Fe-EDTA by the plants. DeKock and Mitchel (1957) concluded that divalent metals such as Zn^{++} were more readily absorbed by plant

roots in the ionic than in the chelated form, while trivalent ions such as Al^{+++} and Cr^{+++} were preferentially absorbed by plant roots when in the chelated form. Similar findings were reported by Wallace et al. (1955). Butler and Bray (1956) found that when they added Na_2EDTA to a fine sand soil Fe uptake by ryegrass plants was markedly increased, whereas Zn^{++} , Cu^{++} and Mn^{++} uptake were not significantly affected. Halvorson and Lindsay (1977), concluded that in soils, chelation probably only helped in the transport of Zn to plant roots, otherwise plants normally absorbed the ionic form of Zn from soil solution in preference to the chelated form.

On the basis of the preceding discussion, it was quite evident from most studies reviewed that regardless of the crop grown banding of inorganic Zn fertilizers such as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ resulted in very poor utilization of Zn from the fertilizer bands when compared to utilization of Zn by plants from organically complexed Zn fertilizer bands. In most instances it was also generally implied that the greater availability of Zn from banded organically complexed Zn fertilizers was a result of greater movement of Zn from organically complexed Zn fertilizer bands when compared to Zn movement from inorganic Zn fertilizer bands, which according to most researchers resulted in greater contact between the Zn fertilizer and plant roots, as a result of a larger volume of soil treated by the Zn fertilizer. However, some of the studies reviewed also showed that in certain instances organically complexed Zn fertilizers such as Zn-EDTA were not very effective as sources of Zn to plants, particularly when the Zn fertilizer was mixed throughout the soil (Mortvedt and Giordano 1969;

Singh et al. 1986). Butler and Bray (1956) and Wallace et al. (1957) suggested that when such organically complexed Zn fertilizers were mixed with the soil some of the Zn was probably retained by soil constituents. However, the argument above ignores the fact that the Zn^{++} ion derived from dissolution of inorganic Zn fertilizers was probably equally susceptible to such retention mechanisms.

2.2.2. Effect of Macronutrient Fertilizers on Bioavailability of Zn Fertilizers

Various N as well as P fertilizers are quite often applied together with Zn fertilizers. According to Giordano et al. (1966), the source as well as placement methods for both the Zn as well as the macronutrient fertilizers were in some instances shown to have a considerable influence on plant availability of Zn fertilizers, particularly the inorganic forms of Zn. The effect of various P fertilizers on plant availability and/or nutrition of Zn has been widely reported in the literature, particularly with respect to the phenomenon popularly referred to as PxZn interaction (Bingham 1963; Stukenholtz et al. 1966; Sharma et al. 1968; Safaya 1976; Nyaki 1981; Loneragan et al. 1982; Singh et al. 1986; Singh et al. 1988). Although the mechanism involved in the interaction has not yet been resolved it is quite well established from some of the studies reported that in most instances application of large amounts of P fertilizers resulted in significant decreases in the effectiveness of inorganic Zn fertilizers. Similarly, various N fertilizers were also found to have a significant effect on plant availability of inorganic Zn fertilizers. But, in most instances

N fertilizers were found to enhance the availability of inorganic Zn fertilizers to plants (Pumphrey et al. 1963). Boawn et al. (1960) found that the concentration of Zn in corn shoots as well as Zn uptake were significantly increased when $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was broadcast together with $(\text{NH}_4)_2\text{SO}_4$ and rototilled to a depth of 20 cm. Mortvedt and Giordano (1969) also found that plant availability of Zn from $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was significantly increased when the Zn fertilizer was incorporated into NH_4NO_3 granules. Pumphrey et al. (1963) suggested that N fertilizers promoted greater root growth as a result of enhanced N nutrition. The higher Zn uptake obtained in treatments that also received N fertilizers were therefore attributed to greater contact between the Zn fertilizer and plant roots. On the other hand, Giordano et al. (1966) suggested that the overall effect of N fertilizers on plant availability of Zn fertilizers was to increase the solubility and therefore movement of Zn, which also results in greater contact between the Zn fertilizer and plant roots.

According to several reports in the literature, application of large amounts of P to the soil affected the effectiveness of inorganic Zn fertilizers largely through their effect on the concentration of water soluble Zn in soil solution (Bingham and Garber 1960; Bingham 1963; Ellis et al. 1964; Mortvedt and Giordano 1969; Racz and Haluschak 1974). Large amounts of P were shown to decrease the concentration of Zn in soil solution. Kalbasi et al. (1978b) found that the concentration of Zn in soil solution was significantly decreased when $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was applied together with $\text{NH}_4\text{H}_2\text{PO}_4$ fertilizer, when compared to concentrations of Zn in soils treated with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ alone.

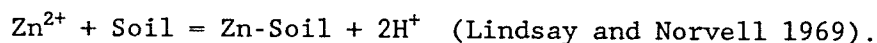
The influence of macronutrient fertilizers on plant availability of Zn from organically complexed and inorganic Zn fertilizers varied considerably. Boawn et al. (1957), for example, found that Zn uptake by Red Mexican beans was significantly decreased when $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was incorporated into N P K fertilizers on a sandy loam soil. On the other hand, when Zn-EDTA was similarly incorporated into the N P K fertilizer, its effectiveness in supplying Zn to the beans was not significantly affected. Mortvedt and Giordano (1969) found that Zn-EDTA was a very effective source of Zn when it was applied to the soil alone as well as when it was incorporated into N P K fertilizers. Mortvedt (1968) also found that forage yields in greenhouse experiments were significantly increased when Zn-EDTA was incorporated into the soil with ammoniated macronutrient fertilizers whereas $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ or ZnO applied in the same manner were not as effective as Zn-EDTA. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was more effective in increasing Zn uptake by the corn plants when it was applied alone than when it was incorporated into granular ammoniated fertilizers. Giordano and Mortvedt (1966) also showed that application of ZnSO_4 alone was more effective in correcting Zn deficiency in corn plants than when it was incorporated into NH_4NO_3 , NH_4 -polyphosphate, or concentrated superphosphate (CSP) granules and subsequently banded with the seed or mixed with the soil.

2.2.3. Concentration of Zn in Zn Fertilizer Bands

Generally, most Zn fertilizers are highly soluble in water, but when they are applied to soils, the soil fertilizer reaction products formed may have a considerable influence on the concentration of Zn in

soil solution. The Zn ion resulting from dissolution of inorganic Zn fertilizers for example, interacts quite strongly with various soil constituents through adsorption as well as precipitation reactions (Bingham et al. 1964; Holden and Brown 1965; Udo et al. 1970; Chu 1988; Shuman 1988). Kalbasi et al. (1978b) found that Zn concentrations in soils treated with Zn-EDTA were significantly higher than Zn concentrations in soils treated with ZnS. They also showed that Zn concentrations in noncalcareous soils treated with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were significantly higher than Zn concentrations in calcareous soils treated with similar amounts of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Zinc concentrations in soils treated with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in combination with P fertilizer were significantly lower than Zn concentrations in soils treated with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ alone.

The solubility of various minerals in the soil, as well as soil-fertilizer reaction products formed when Zn fertilizers are added to the soil is a pH dependent phenomenon according to the relation



Therefore, at equilibrium

$$\frac{(\text{Zn-Soil})(\text{H}^+)^2}{(\text{Zn}^{++})(\text{Soil})} = K$$

where $\log K$ for the reaction was found to be -6.0.

Therefore, $[\text{Zn}^{2+}] = 10^6 [\text{H}^+]^2$ which according to Lindsay and Norvell (1969) represents the solubility of Zn in soils. It is quite obvious from the expression above, that the solubility of Zn in soils decreases sharply as the pH is increased. Mortvedt et al. (1972) reported that the solubility of Zn in soils decreased 100 fold for each unit increase

in pH. Thus, significant changes in the pH of soil solution will likely have a significant effect on solubility as well as plant availability of inorganic Zn fertilizers since such changes will have a profound effect on the amount of Zn in soil solution. McGregor (1972), for example, working with Manitoba soils of varying pH found that Zn uptake by flax and wheat decreased with increasing pH.

Chelated as well as inorganic complexed forms of Zn also constitute an important fraction of water soluble forms of Zn in soil solution (Jurinak and Thorne 1955; Hodgson et al. 1967; Hodgson 1969). Himes and Barber (1957) suggested that in the presence of natural or synthetic chelating agents the Zn^{++} ion could be bound to the chelate molecule in such a way that to a large extent it is prevented from interacting strongly with other soil constituents, and therefore increasing the amount of water soluble Zn in soil solution. The well received success of chelating agents in enhancing Zn movement in soils is primarily attributed to their ability to increase the concentration of diffusible Zn in soil solution.

According to Soper et al. (1989) the utilization of Zn by plants from inorganic Zn fertilizers was closely related to the concentration of Zn in the fertilizer band. According to results obtained in their studies, the utilization of Zn from inorganic Zn fertilizer bands by blackbeans was described by the expression

$\% \text{ Zn fertilizer utilized} = 1.02 - 0.22 \ln [\text{Zn}]$ (ppm of Zn added to the fertilizer band) indicating that % utilization of Zn from the fertilizer band decreased with increase in the concentration of Zn in soil solution.

According to most reports available to date, it is generally believed that limited root contact with banded inorganic Zn fertilizers is probably the most logical explanation for the low utilization of Zn from inorganic Zn fertilizer bands (Brown and Krantz 1966; Loewen-Rudgers et al. 1978). On the other hand, studies regarding the uptake of other nutrients such as P from P fertilizer bands suggest that some of the arguments presented to support the limited root contact theory were not conclusive. Bullen (1981), for example, found that shoot dry matter yield, total P uptake and utilization by soybean plants increased as the size of the phosphated band was decreased. He attributed the results to greater chemical availability of P in the smaller zones of P fertilizer reaction. If the utilization of Zn by plants from banded inorganic Zn fertilizers could be enhanced, banding should be a reasonably well accepted method of application of inorganic Zn fertilizers. According to Clark and Graham (1968) as well as Akinyede (1978) it was quite evident that solubility of inorganic Zn fertilizers was significantly increased when such fertilizers were banded, most likely due to the fact that the interaction between the Zn^{++} ion and other soil constituents was appreciably decreased by banding.

2.2.4. Movement of Zn

The value of nutrients to most plants depends on their accessibility to plant roots, which in turn is related to their mobility in soils (Barrows et al. 1960; Hossner and Blancher 1969; Sinha and Prasad 1977). Bray (1954) suggested that the area of plant nutrient depletion

about a plant root depended on the mobility of the ion. According to Oliver and Barber (1966) and Elgawhary et al. (1970a and b) Zn is mainly supplied to plant roots by diffusion and only to a very limited extent by mass flow. Therefore, since diffusion is largely a concentration dependent phenomenon, factors which affect the concentration of Zn in soil solution will also affect the extent of the diffusion process. As discussed earlier the Zn^{++} ion interacts quite strongly with other soil constituents such as clay minerals (Ellis et al. 1970), Fe and Al hydrous oxides (Kalbasi and Racz 1978) as well as soil organic matter (Miller and Ohlrogge 1958). Consequently, in many instances the movement of Zn in soils can be significantly affected by such constituents. Clark and Graham (1968) demonstrated that diffusivity of Zn from $ZnCl_2$ fertilizer was highly concentration dependent increasing almost linearly with increase in concentration of Zn in soil solution for all the soils tested. Similarly, Melton et al. (1973) found that when $ZnSO_4 \cdot 7H_2O$ was applied to a calcareous soil the "modified" diffusion coefficients obtained for Zn were about 50 fold lower than the values obtained in acid soils when similar amounts of Zn were applied to both soils. The large differences in the values of "modified" diffusion coefficients obtained for the two soils were largely attributed to differences in the concentration of Zn in soil solution.

Singh (1974) studied the migration of Zn^{++} ions in two soils of varying physical and chemical characteristics using soil columns. He found that although a greater fraction of the Zn that was applied was retained in the upper 3 cm, Zn moved to a depth of 12 cm in the soil

that had a C.E.C. of $108.3 \text{ mmol kg}^{-1}$ and 18 cm in the soil with a C.E.C. of $213.6 \text{ mmol kg}^{-1}$, when the two soils were leached with water equivalent to 1200 mm of precipitation. He concluded that movement of Zn through the soils depended not only on the C.E.C. but also other factors such as water flow rate, pH as well as initial Zn content. He suggested that such factors had a significant effect on the retention of Zn in soils. Jurinak and Thorne (1955) found that when ZnCl_2 was applied to the surface of a silty clay soil, Zn moved to a distance of less than 3 cm even when the soil was heavily leached. Similarly, Brown et al. (1962) found that application of ZnO or $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ to the surface of a sandy loam or silt loam soil contained in soil columns resulted in a very limited movement of Zn from the Zn fertilizers, even when the soils were heavily leached. In contrast, Barrows et al. (1960) reported that surface applied $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was leached to a depth of 46 cm in a Lakeland fine sandy loam soil. They also found that the depth of penetration of Zn from surface applications of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ increased with amount of Zn applied and varied with soil type. More recent studies by Singh and Abrol (1986) indicated that when $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was applied to the soil a major portion of the Zn accumulated in the top 0 to 10 cm depth.

The role of chelating agents in promoting the movement of Zn in soils has been widely reported (Hodgson et al. 1967; Elgawhary et al. 1970a; Sinha and Prasad 1977). Sinha and Prasad (1977) showed that chelating agents enhanced the rate of diffusion of Zn from the soil to a simulated root to varying extents depending on their relative efficiency to increase the concentration of diffusible Zn in soil

solution. They found that Zn uptake by wheat increased linearly with increase in the concentration of soluble Zn in soil solution. Elgawhary et al. (1970b) compared EDTA, HCl, an amino acid mixture and glucose with respect to their effectiveness in enhancing the transport of Zn to a simulated root. The results obtained showed that EDTA caused the greatest increase in the transport of Zn to the simulated root.

The discussion presented above clearly suggests that the degree of stability of Zn chelates in soils will likely have a profound effect on the movement of Zn from organically complexed Zn fertilizer bands since more stable Zn chelates will result in higher concentrations of Zn in soil solution and consequently greater movement of Zn. According to Halvorson and Lindsay (1972) the pH of soil solution probably plays the most important role in influencing the stability of Zn chelates, since it has a remarkable effect on the equilibrium relationships of metal chelates in soil solution. The H^+ ion can compete with the Zn^{++} ion for the chelate molecule in cases where the equilibrium constant for the metal chelate is quite low, or can also directly affect the concentration of other competing ions in soil solution. Lehman (1963), demonstrated that the metal chelate with the highest stability constant with the chelating agent was the first to be chelated. Holden and Brown (1965) showed that below a pH of about 6.5, Fe competed quite effectively with Zn for the EDTA molecule. But, at high pHs Ca^{++} competed more favourably for the chelate. According to Norvell and Lindsay (1969) the Zn^{++} ion was most effectively complexed by EDTA at pHs between 6.5 and 7.5.

Macronutrient fertilizers were also found to have a significant influence on movement of Zn from Zn fertilizers. Mortvedt and Giordano (1967) found that the maximum distance of detectable Zn movement was 2.0 cm from NH_4NO_3 granules, 1.5 cm from concentrated superphosphate (CSP) and monoammonium phosphate (MAP) granules and 1.0 cm from triammonium pyrophosphate (TPP) granules after one wk of incubation when $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ fertilizer was applied with the respective macronutrient fertilizers. The distance of movement increased very slightly after 8 wk of incubation. They also showed that the distance moved by the Zn in limed soils after 1 wk and 8 wk of incubation was 1.0 cm and 1.5 cm, respectively, for all macronutrient fertilizer treatments. Melton et al. (1973) showed that when high rates of KH_2PO_4 were applied together with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ the resulting "modified" diffusion coefficients for Zn were relatively low since the concentration of diffusible Zn was significantly decreased, indicating that Zn movement from the $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was also decreased by high rates of the P fertilizer.

Various reports in the literature have indicated that in some instances inorganic complex ions involving the Zn^{++} ion and the other ions can also significantly enhance the movement of Zn from inorganic Zn fertilizers, as a result of increasing the concentration gradient of diffusible Zn in soil solution (Jurinak and Thorne 1955; Hodgson et al. 1967). Such situations were occasionally experienced when inorganic Zn fertilizers were applied in a band together with $(\text{NH}_4)_2\text{SO}_4$. Lindsay (1972b) suggested that the presence of large amounts of the $\text{SO}_4^{=}$ ion in the fertilizer band resulted in the formation of ZnSO_4 (aq) which was neutral and quite stable, and was therefore

thought to account for the greater movement of Zn from such treatments. On the other hand, Cotton and Wilkinson (1962) indicated that when $(\text{NH}_4)_2\text{SO}_4$ was added to inorganic Zn compounds a $\text{Zn}(\text{NH}_3)_4^{++}$ complex could also form. Jurinak and Thorne (1955) compared the distance moved by the Zn^{++} ion, zincate ion ($\text{Zn}(\text{OH})_4^{=}$) and $\text{Zn}(\text{NH}_3)_4^{++}$ by diffusion and mass flow in soil columns. They found that the zincate complex moved the greatest distance (3 cm), while the Zn^{++} ion and the $\text{Zn}(\text{NH}_3)_4^{++}$ complex both moved to a depth of 2 cm when the columns were leached with 47.2 cm of water. The differences in the distance moved by the ions was attributed to the differences in sign of charge between the Zn ions. Mortvedt et al. (1972) reported that the effect of $\text{Zn}(\text{NH}_3)_4^{++}$ complex in increasing the solubility of Zn in soils at pHs below 6.5 was negligible. Therefore, they concluded that unless the pH of the soil solution was quite high the distance moved by such a complex was also very limited.

Lastly, it should also be noted that soil moisture content as well as bulk density were also found to have a significant influence on the diffusion of Zn in soils (Warncke and Barber 1972a and 1972b). They reported that increasing the soil moisture content made the path of diffusion less tortuous and therefore increased the diffusion of Zn. They also found that soil moisture content may also have a significant effect on the concentration of the Zn^{++} ion in soil solution which, as discussed earlier, is also an important factor controlling the diffusion process. The bulk density of a soil is normally very closely related to the water holding capacity of the soil. Therefore, the effect of bulk density on apparent diffusion may also be related to

soil moisture content. Warncke and Barber (1972b) found that the apparent diffusion of Zn increased as bulk density was increased from 1.1 to 1.5 g cm⁻³. However, as the bulk density was increased further from 1.5 to 1.6 g cm⁻³ there was a sharp decrease in apparent diffusion. They attributed the decrease in the coefficient of diffusion as the bulk density was increased from 1.5 to 1.6 g cm⁻³ to an increase in the degree of interaction between the Zn⁺⁺ ion and the soil constituents as well as an increase in tortuosity.

2.2.5. Root Accessibility to Zn in Zn Fertilizer Bands

Limited accessibility of plant roots to inorganic Zn fertilizer bands has repeatedly been inferred in various research reports as one of the most important factors limiting the uptake of Zn from the fertilizer bands. (Pumphrey et al. 1963; Mortvedt and Giordano 1969; Hedayat 1978; Soper et al. 1989). However, although there is convincing evidence in the literature to show that plant roots respond in various ways to the environment in their vicinity (Rios and Pearson 1964; Foy et al. 1965; Strong and Soper 1974a 1974b; Brewster et al. 1976; Blamey et al. 1983; Cumbus 1985) very limited or no direct evidence was available regarding root growth habits (amount of roots, quality of roots, root distribution in the fertilizer reaction zone etc) in relation to Zn uptake from Zn fertilizer bands. It has been demonstrated, at least with other nutrients such as P, that such information was very useful in accounting for the large variability among crops in their utilization of P from banded P fertilizers. Strong and Soper (1974a), for example, assessed the influence of root

development within the fertilizer reaction zone on utilization of applied P for flax, wheat, rape and buckwheat. They found that root systems of crops which recovered large amounts of P from P fertilizer bands or pellet-like application (rape and buckwheat) proliferated extensively within the reaction zone of applied P. Similarly, Brewster et al. (1976) believed that the greater ability of rape to extract P from soils low in plant available P appeared to be related to its long and abundant root hairs in such soils. On the other hand, Blancher and Caldwell (1966a and 1966b) showed that when the concentration of P in soil solution was too high (>1000 ppm) the growth of corn roots into MAP fertilizer zones was significantly reduced.

Using a mathematical model, Bouldin (1961) demonstrated the importance of root fineness (root surface area) in nutrient uptake. He showed that the flux per unit area of roots increased by a factor of 10 as the radius of a simulated root was decreased from 5×10^{-2} cm to 7.5×10^{-4} cm (approximate radius of root hairs). The importance of root surface area per unit weight of root in nutrient uptake by plants was also emphasized by Sommer (1936), Bray (1954), Nye (1966), as well as Jeffrey (1967).

The ability of plants roots to modify the chemical environment around them under certain conditions has also been widely accepted. In most cases, such effects will obviously impact on the chemical and most likely plant availability of various plant nutrients from the soil, including Zn. Changes in chemical properties of the soil solution may influence the form and distribution of plant roots in the soil in ways which may affect the absorption of nutrients from the soil

solution. Brown et al. (1960) and Loneragan (1975) reported that some plant roots had the ability to increase the concentration of chelating substances around the root surface, which has a considerable influence on the concentration of plant nutrients in soil solution. They also showed that certain plant roots had the ability to influence the oxidation state of certain cations, in order to make them more available to plants. For instance, Brown et al. (1960) found that certain plant roots promoted the reduction of Fe^{+++} to Fe^{++} which was found to be more available to plants.

A few attempts have been made to account for differential Zn uptake by various crops. Unfortunately, most of the work reported was done in nutrient solutions. Clarke (1978), for example, found that different corn inbreds showed some obvious differences in Zn uptake from a nutrient solution. He noted that there were appreciable differences in the amount as well as quality of roots recovered from three inbreds, but was convinced that the variation in Zn uptake was more likely caused by differences in translocation, utilization and requirement for Zn for the three inbreds, rather than differences in the amount of roots in contact with the nutrient solution. Carroll and Loneragan (1969), reported more or less similar trends in Zn uptake by eight different plant species, but their conclusion was slightly different. They believed that the differences in the rate of Zn uptake among the species studied were at least in part responsible for the differences in Zn uptake. Bar-Yosef et al. (1980) was of the opinion that root permeability to water and ions was probably the most effective mechanism controlling Zn uptake by plants.

In view of the above discussion it is quite obvious that a knowledge of the behaviour of roots in Zn fertilizer bands may be of great agricultural significance, particularly when assessing the role played by plant roots in the uptake of Zn from banded Zn fertilizers.

2.2.6. Vesicular-arbuscular mycorrhizae (VAM)

Reports in the literature indicate that infection of plant roots by vesicular-arbuscular mycorrhizae can improve the supply of nutrients such as Zn, Cu, P and K to higher plants. Such effects were reported in barley (Jensen 1982), soybean (Pacovsky et al. 1986), wheat (Kucey and Jansen 1987) and sorghum (Raju et al. 1987). Cooper and Tinker (1978) reported that VAM hyphae can readily transport Zn as well as sulfate to the host roots. Lambert et al. (1979) reported that in annual species, roots infected with VAM increased the uptake rate of micronutrient cations such as Zn and Cu. Pairunan et al. 1980 working with subterranean clover showed that roots infected with VAM took up more Zn than non infected roots.

In some instances mycorrhizal infection of plant roots was found to influence the interaction between P and Zn. Hayman (1978) and Tinker (1980) reported that high levels of P in the soil inhibited infection of plant roots with VAM. As a result Zn uptake in such treatments was decreased. Lambert et al. (1979) found that increased P supply decreased the concentration of Zn in soybean plants infected with VAM, but hardly affected the Zn content of non infected plants. Singh et al. (1986) found that roots of wheat plants treated with high rates of P contained significantly lower levels of vesicular-arbuscular

mycorrhizal (VAM) infection than the control. They also found that high levels of Zn in the foliage, grain and straw were associated with higher percent mycorrhizal infection of wheat roots.

3.0. GENERAL ANALYTICAL METHODS FOR THE SOILS USED

3.1. Soil Solution pH

Soil pH was determined potentiometrically by the method described by Peech (1965). Fifty ml distilled water was added to 50 g air dried soil and shaken for 30 min. The pH of the suspension was then determined using a Fisher Accumet 825 MP pH meter.

3.2. Conductivity

The electrical conductivity of the suspension used for the pH determination was determined using a Radiometer conductivity meter type CDM2d.

3.3. Inorganic Carbon

A 1.0 g sample of air dried soil was heated with 40 ml 0.1 M HCl for 10 min. The CO_2 evolved was drawn by suction through a drying and adsorption frame consisting of concentrated H_2SO_4 , a tube of $\text{Mg}(\text{ClO}_4)_2$ and CaCl_2 . The amount of CO_2 evolved was collected using an ascarite absorption tube, and the inorganic carbon content was calculated from the weight change of the ascarite absorption tube.

3.4. DTPA-Extractable Zn

DTPA-extractable Zn was determined using the method described by Lindsay and Norvell (1969) as modified by the Kansas State University Soil Testing Laboratory. A 25 g sample of air dried soil was treated with 50 ml of DTPA (Diethylene-triaminepentaacetic acid) solution

adjusted to pH 7.3. The mixture was shaken for two hours and then filtered through Whatman No 42 filter paper. The concentration of Zn in the filtrate was determined using Perkin Elmer Model 560 Atomic Absorption Spectrophotometer.

3.5. Organic Matter

Percent organic matter was determined using the oxidation method described by Walkley and Black (1934). One-half gram of soil was oxidized using excess $K_2Cr_2O_7$ in the presence of excess H_2SO_4 . The excess $Cr_2O_7^{=}$ was then back-titrated with $FeSO_4$ using a Fisher automatic titrimeter.

3.6. Field Capacity

Air dried soil was placed in acrylic cylinders measuring 4.5 cm in diameter and 20.5 cm in height. Water was slowly added to the surface of the soil until one third of the soil was wetted. The soil was allowed to stand for 48 h, the wetted portion of the soil sampled and dried at 105C for 24 h. Moisture content was calculated and expressed as a percent of oven dry soil.

3.7. Particle Size

Particle size analysis was conducted using the standard pipette method described by Kilmer and Alexander (1949).

3.8. Particle Density and Air Filled Porosity

The particle densities of the soils used in the chemical studies were determined using the method described by Blake (1965) with some slight modifications. Air filled porosity of the soils after packing of the soil columns were calculated as follows:

$$\text{Air Filled Porosity} = [(1 - \text{BD}/\text{PD}) \times 100] - \theta$$

where BD = Wet Bulk Density

PD = Particle Density

θ = Volumetric Water Content

and $\theta = \text{BD} \times \text{W}$

where W = Gravimetric Water Content.

4.0. SOLUBILITY AND MOVEMENT OF ZINC IN ZnCl_2 AND Zn-EDTA FERTILIZER BANDS

4.1. Introduction

Placement of fertilizers in a narrow band in the soil (generally referred to as banding) is a widely recommended method of application of various plant nutrients. However, several workers have shown that Zn uptake by plants was very limited when inorganic Zn fertilizers such as ZnCl_2 were banded. In contrast, Zn uptake was usually satisfactory when organically complexed Zn fertilizers such as Zn-EDTA were banded (Boawn 1973; Loewen-Rudgers et al. 1978). Reports in the literature suggest that Zn from Zn-EDTA fertilizer bands is more effective in supplying Zn to plants than Zn from inorganic Zn fertilizer bands such as ZnCl_2 or ZnSO_4 due to greater mobility of Zn-EDTA in soils, which results in a larger volume of soil fertilized with Zn (Boawn 1973). A greater volume of soil fertilized with Zn would result in greater root to fertilizer contact enhancing Zn utilization (Soper et al. 1989). However, very limited information was available in the literature to show the extent of the differences in the movement of Zn from organically complexed and inorganic Zn fertilizer bands when applied to various soils.

N and P fertilizers applied with Zn fertilizers can influence the uptake of Zn by plants from Zn fertilizer bands (Giordano and Mortvedt 1966). Thus, in order to appreciate the role played by such fertilizers in controlling the uptake of Zn from Zn fertilizer bands, knowledge of the influence of some of the commonly used N and P

fertilizers on solubility as well as movement of Zn from organically complexed and inorganic Zn fertilizer bands is very important.

A study was conducted using two different soils to:

- (a) compare the solubility and movement of Zn applied as ZnCl_2 and Zn-EDTA fertilizer bands;
- (b) determine the influence of $(\text{NH}_4)_2\text{SO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$ and Urea on solubility and movement of Zn applied as ZnCl_2 and Zn-EDTA fertilizer bands.

4.2. Materials and Methods

4.2.1. Soils Used and Soil Column Preparation

The two soils used were obtained from the surface 10 cm of a noncalcareous Stockton fine sandy loam of pH 7.2 and a calcareous Almasippi loamy fine sand of pH 8.4 (Table 4.1). The soil columns consisted of 20 acrylic rings 0.5 cm in height and an internal diameter of 5.08 cm. The rings were fitted together using standard electrician tape. A perforated platform was attached to the bottom of the columns to support the columns as well as to provide for adequate air exchange at the bottom of the columns. Adequate aeration was also ensured at the top of the columns by covering the top end of the column with perforated parafilm.

Each soil was moistened to field capacity moisture content using deionized water, and then carefully packed into the columns to achieve an air filled porosity of approximately 28 percent for both soils. To achieve the above air filled porosity the wet bulk density for the

noncalcareous soil was maintained at 1.22 g cm^{-3} while that of the calcareous soil was maintained at 1.17 g cm^{-3} .

4.2.2. Treatments

The treatments used in the study were:

- | | |
|---|---|
| 1. ZnCl_2 Alone | 5. Zn-EDTA Alone |
| 2. $\text{ZnCl}_2 + (\text{NH}_4)_2\text{SO}_4$ | 6. Zn-EDTA + $(\text{NH}_4)_2\text{SO}_4$ |
| 3. $\text{ZnCl}_2 + \text{Urea}$ | 7. Zn-EDTA + Urea |
| 4. $\text{ZnCl}_2 + \text{NH}_4\text{H}_2\text{PO}_4$ (MAP) | 8. Zn-EDTA + $\text{NH}_4\text{H}_2\text{PO}_4$ (MAP) |

Both Zn sources as well as the N and P fertilizers were applied to the top of the soil columns as finely ground crystals or in powder form. Zn was applied at a rate of $40 \text{ mg Zn column}^{-1}$ while N and P were added at rates of 229 mg N and $58 \text{ mg P column}^{-1}$. Application rates were calculated to reflect band concentrations which may occur under field conditions, and were equivalent to a fertilizer band width of 2.5 cm , a band spacing of 36 cm and a field application rate of 16 kg Zn ha^{-1} , 80 kg N ha^{-1} and 20 kg P ha^{-1} .

The soil columns, duplicated for each treatment, were incubated for a period of 2 wk in a controlled environment room at a temperature of $20 \pm 1^\circ\text{C}$ and a relative humidity of, or close, to 100 percent. The high relative humidity was essential to minimize evaporative losses from the column surface.

After incubation the soil columns were sliced into 0.5 cm sections using a sharp knife. An 8.0 g portion of the wet sample from each section was placed in a 50 ml centrifuge bottle and the remaining portion was placed in moisture tins for determination of gravimetric

moisture content. Sixteen ml of deionized water was added to the 8.0 g sample. The samples were shaken for 1 h and then centrifuged at 10,000 rpm (13,000 G) for 20 min. The pH of the supernatant was measured, the suspensions filtered, and the concentration of Zn in solution measured using an Atomic Absorption Spectrophotometer.

Since all treatments were duplicated, results for pH and water-soluble Zn concentrations were averaged. Differences between duplicates for pH measurements were usually less than 0.1 pH units. Deviations from the mean for water-soluble Zn concentrations were approximately 10 to 15 percent.

Table 4.1. Some Physical and Chemical Characteristics of the Soils Used.

Soil Characteristics	Stockton Soil (Orthic Black)	Almasippi Soil (Gleyed Rego Black)
pH (1:1 soil : H ₂ O)	7.2	8.4
Inorganic Carbon (% CaCO ₃ Equivalent)	0.2	4.1
Organic Matter (%)	3.3	2.7
DPTA-Extr. Zn (ug g ⁻¹)	2.1	0.5
Field Capacity Moisture Content (%)	19.0	22.0
Particle Density (g cm ⁻³)	2.48	2.45
Wet Bulk Density (g cm ⁻³)	1.22	1.17
Air Filled Porosity (%)	27.8	28.3
Texture	FSL	LFS

4.3. Results and Discussion

4.3.1. Solubility of Zn in the ZnCl_2 Fertilizer Band

The solubility of Zn as affected by various fertilizer treatments for each soil was expressed as the total mg of Zn extracted by water from the entire soil column (Tables 4.2 and 4.3). Amounts of water-extractable Zn in the ZnCl_2 fertilizer band was much greater in the noncalcareous than in the calcareous soil. The amounts of water soluble Zn were very much higher in the noncalcareous soil than in the calcareous soil except for the treatments containing urea in which amounts of soluble Zn were only two fold greater in the noncalcareous than in the calcareous soil.

The difference in the solubility of Zn between the soils is likely a function of the reaction products formed. According to Kalbasi et al. (1978b) the concentration of Zn in soil solution for a noncalcareous soil is controlled largely by the solubility of $\text{Zn}(\text{OH})_2$, which decreases as the pH is increased. On the other hand Zn concentrations in soil solution for a calcareous soil was controlled by the solubility of ZnCO_3 and/or $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, which were found to be the main reaction products formed when an inorganic Zn fertilizer was applied to a calcareous soil. Therefore, the low concentrations of Zn obtained when ZnCl_2 was applied to the calcareous soil may largely be attributed to precipitation of Zn as ZnCO_3 and/or $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$.

Addition of N or P fertilizers had very large effects on solubility of Zn in the ZnCl_2 fertilizer bands (Tables 4.2 and 4.3). The solubility of Zn in the ZnCl_2 fertilizer band was greatly enhanced in both soils by the addition of $(\text{NH}_4)_2\text{SO}_4$. The slightly lower pH resulting from addition of $(\text{NH}_4)_2\text{SO}_4$ to the ZnCl_2 fertilizer band may partially explain the higher Zn concentrations obtained in the

Table 4.2. Effect of Zn, N and P fertilizers on total water soluble Zn (mg column⁻¹) - Stockton FSL.

N or P Fertilizer	Zn Source	
	ZnCl ₂	Zn-EDTA
None	0.85	39
(NH ₄) ₂ SO ₄	4.31	28
Urea	0.27	24
NH ₄ H ₂ PO ₄	0.40	22

Table 4.3. Effect of Zn, N and P fertilizers on total water soluble Zn (mg column⁻¹) - Almasippi LFS.

N or P Fertilizer	Zn Source	
	ZnCl ₂	Zn-EDTA
None	0.04	37
(NH ₄) ₂ SO ₄	0.28	41
Urea	0.14	42
NH ₄ H ₂ PO ₄	0.01	45

noncalcareous soil with $(\text{NH}_4)_2\text{SO}_4$ (Figs 4.1 and 4.2). However, pH in the Stockton soil changed only slightly when $(\text{NH}_4)_2\text{SO}_4$ was added. It is also interesting to note that addition of $(\text{NH}_4)_2\text{SO}_4$ to the ZnCl_2 fertilizer band in the calcareous soil resulted in a slightly higher pH compared to the pH obtained when ZnCl_2 was applied alone, yet Zn concentration in soil solution was higher with $(\text{NH}_4)_2\text{SO}_4$ than without. This suggests that factors other than just the pH may have been involved. The increases in solubility of Zn in such treatments are likely a result of increased ionic strength on the solubility of the precipitates formed and possibly complexation of Zn with NH_3 . At high pH values Zn forms quite stable tetrahedral as well as octahedral complexes with NH_3 (Mortvedt et al. 1972).

Although there was a large decrease in pH due to addition of $\text{NH}_4\text{H}_2\text{PO}_4$ to the ZnCl_2 fertilizer band, low concentrations of Zn in soil solution were obtained when $\text{NH}_4\text{H}_2\text{PO}_4$ was included. The low Zn concentrations are probably due to the formation of ZnNH_4PO_4 which was reported to be the reaction product formed when $\text{NH}_4\text{H}_2\text{PO}_4$ was applied with an inorganic Zn fertilizer (Kalbasi et al. 1978b). The ZnNH_4PO_4 was found to be less soluble than $\text{Zn}(\text{OH})_2$ or ZnCO_3 at pH values normally encountered in neutral and calcareous soils.

Addition of urea in the ZnCl_2 fertilizer bands resulted in a large increase in pH for both soils. The pH increased from about 6.0 to 9.0 in the noncalcareous soil and from about 8.0 to 9.0 in the calcareous

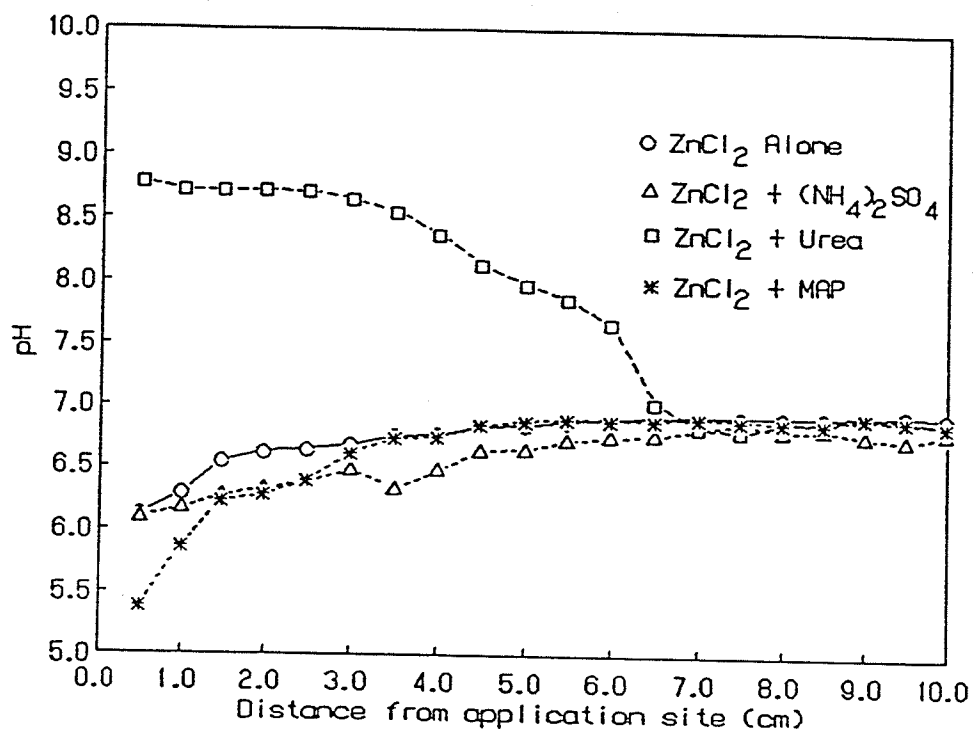


Figure 4.1. Effect of Zn, N and P fertilizers on pH of soil solution - Stockton FSL

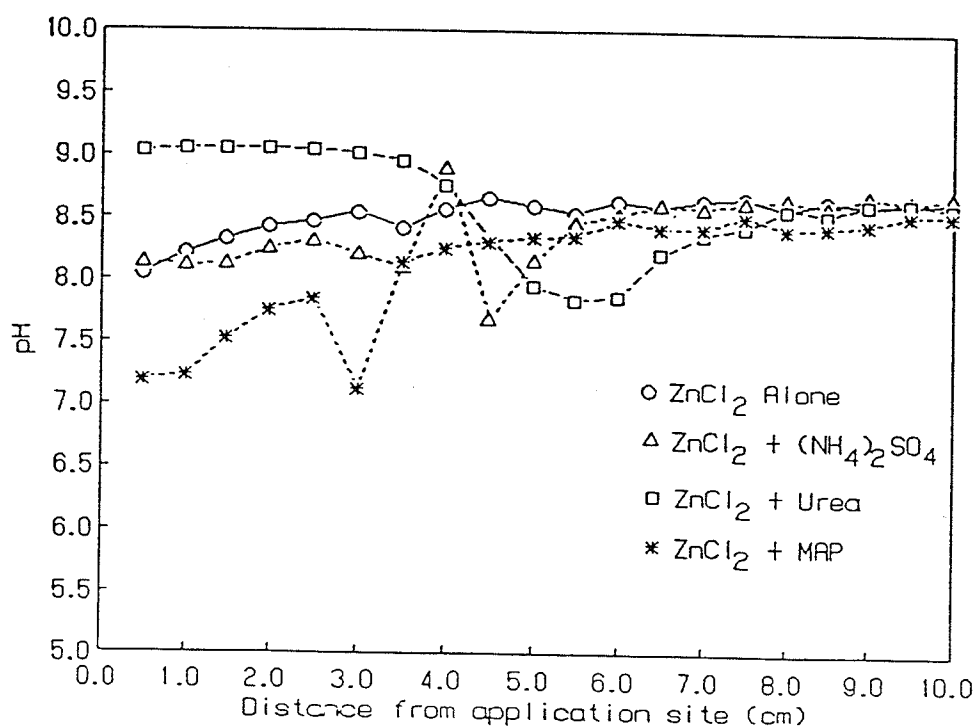


Figure 4.2. Effect of Zn, N and P fertilizers on pH of soil solution - Almasippi LFS

soil (Figs. 4.1 and 4.2). The solubility of Zn in the noncalcareous soil decreased when urea was added to the ZnCl_2 fertilizer band. If the concentration of Zn in soil solution was controlled by the solubility of Zn(OH)_2 one would expect the high pH to decrease the solubility of Zn in the fertilizer band. In this instance the very large change in pH from pH of 6.0 to 9.0 may have countered the effects of ionic strength and complex formation between Zn and NH_3 on solubility. The solubility of Zn in the calcareous soil was greater with urea and ZnCl_2 than with ZnCl_2 alone despite increases in pH. Addition of urea and the high pH would also favour increases in $\text{CO}_3^{=}$ concentrations which would have a common ion effect on the solubility of compounds such as ZnCO_3 . In this instance complex formation between NH_3 and Zn and increase in ionic strength probably more than offset the decrease in solubility as a result of the increase in pH from about 8.0 to 9.0 and increased $\text{CO}_3^{=}$ concentration.

4.3.2. Solubility of Zn in the Zn-EDTA Fertilizer Bands

Application of the various N and P fertilizers to the Zn-EDTA fertilizer band resulted in a similar trend in pH as that obtained with ZnCl_2 (Figs. 4.1, 4.2, 4.3 and 4.4). Addition of $\text{NH}_4\text{H}_2\text{PO}_4$ to the fertilizer band resulted in the lowest pH near the site of application, whereas addition of urea resulted in the highest pH. As expected, application of Zn-EDTA alone did not have as much influence on the pH near the fertilizer band as did ZnCl_2 , particularly when it was applied to the calcareous soil.

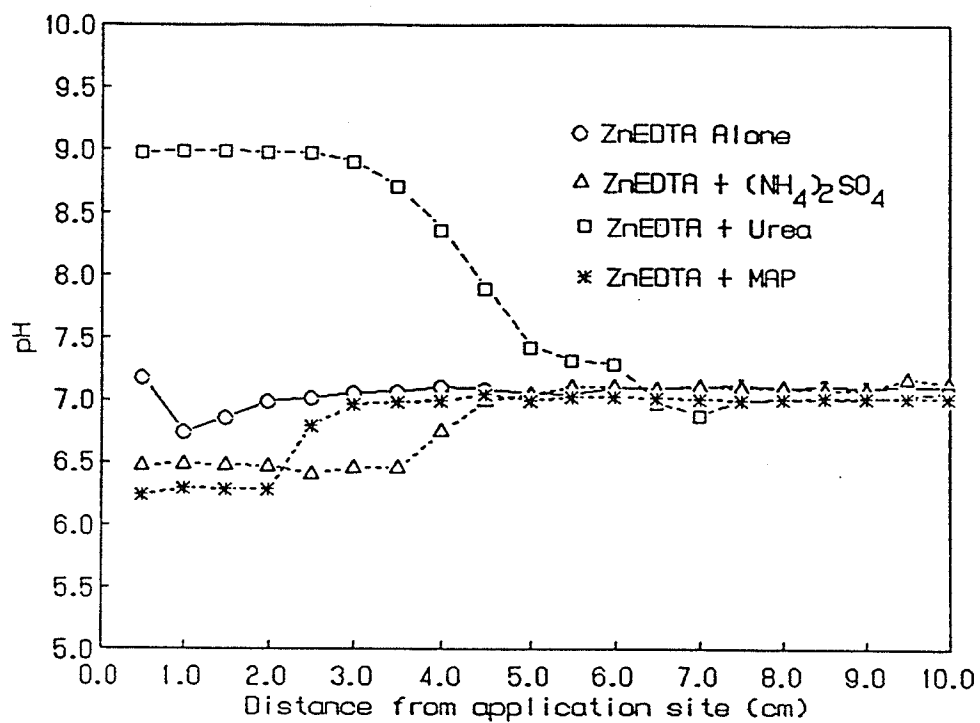


Figure 4.3. Effect of Zn, N and P fertilizers on pH of soil solution - Stockton FSL

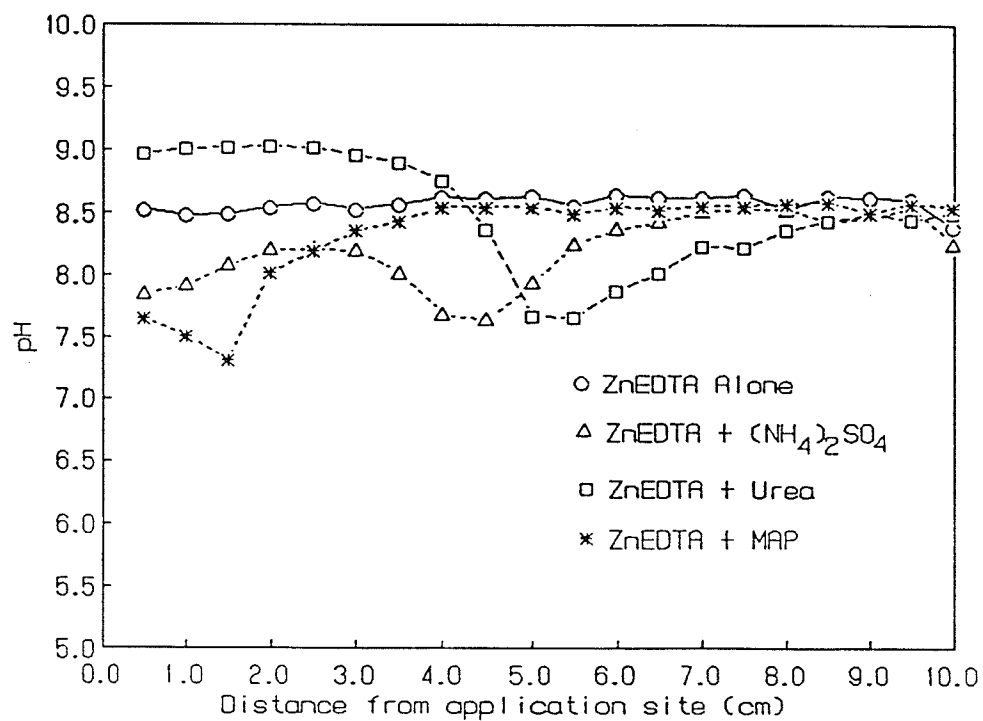


Figure 4.4. Effect of Zn, N and P fertilizers on pH of soil solution - Almasippi LFS

Solubility of Zn in the Zn-EDTA fertilizer band was remarkably high in both soils when compared to the solubility of Zn in the ZnCl_2 fertilizer band (Tables 4.2 and 4.3). It is also evident from the results that addition of the various N and P fertilizers had a significant effect on the solubility of Zn in the Zn-EDTA fertilizer band. The effects varied considerably between the two soils used. Solubility of Zn in the Zn-EDTA fertilizer band was similar for the two soils with Zn-EDTA alone. However, when N and P fertilizers were included in the fertilizer band the solubility of Zn in the non-calcareous soil was approximately 32 to 51 percent lower than the solubilities obtained in the calcareous soil.

Zinc solubility increased for the calcareous soil whereas Zn solubility decreased in the noncalcareous soil when N or P fertilizers were added. Addition of $\text{NH}_4\text{H}_2\text{PO}_4$ to Zn-EDTA for the noncalcareous soil resulted in the lowest level of water soluble Zn in the fertilizer band, while the same P fertilizer was most effective in enhancing Zn solubility when applied to the Zn-EDTA fertilizer band for the calcareous soil. The decrease in solubility in the noncalcareous soil may be attributed to the effect of the $\text{NH}_4\text{H}_2\text{PO}_4$ on pH. The low pH (6.2) resulting from addition of $\text{NH}_4\text{H}_2\text{PO}_4$ may have decreased the stability of Zn-EDTA complex. Norvell and Lindsay (1969) reported that when Fe^{+++} , Ca^{++} , Mg^{++} and H^+ were competing metal ions in soil solution, Zn-EDTA was most stable at pH values of about 6.5 to 7.5. Some of the ionic Zn from the breakdown of the Zn-EDTA may have formed the relatively insoluble reaction product, ZnNH_4PO_4 .

Addition of $(\text{NH}_4)_2\text{SO}_4$ to the Zn-EDTA fertilizer band lowered the pH to about 6.5 in the noncalcareous soil, and therefore may have also decreased the stability of the Zn-EDTA complex. The resulting ionic Zn would therefore react with the soil, decreasing its solubility.

Urea in contrast to the other fertilizer salts increased pH in the Zn-EDTA fertilizer band to about 9.0. The very high pH may have resulted in Ca^{++} and Mg^{++} displacing Zn from the Zn-EDTA complex. Lindsay and Norvell (1969) showed that Zn-EDTA decreased in stability at high pHs in the presence of competing metal ions such as Ca^{++} and Mg^{++} .

Application of N and P fertilizer salts to Zn-EDTA fertilizer band slightly increased the solubility of Zn in the calcareous soil. The increase in solubility due to addition of $(\text{NH}_4)_2\text{SO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$ are at least in part due to a more favourable pH for stability of Zn-EDTA (i.e. pH of 7.5 - 8.0) than with Zn-EDTA alone (pH 8.5). The reason for the increase in solubility with addition of urea cannot be explained on the basis of pH alone. The pH of the fertilizer band was about 9.0 compared to a pH of about 8.5 with Zn-EDTA alone and therefore Zn-EDTA should have been less stable with urea than without urea. It should be noted, however, that $(\text{NH}_4)_2\text{SO}_4$, urea and $\text{NH}_4\text{H}_2\text{PO}_4$ are soluble salts which after dissolution or in the case of urea, dissolution and hydrolysis form precipitates with calcium. Precipitation of the calcium would decrease calcium concentration in soil solution and thus reduce the competition of calcium for the EDTA molecule. Thus, the integrity of the Zn-EDTA molecule would be enhanced and the solubility of Zn increased.

4.3.3. Movement of Zn in the ZnCl_2 Fertilizer Band

Zinc movement from the ZnCl_2 fertilizer band was extremely small whether the ZnCl_2 was applied alone or in combination with any of the N or P fertilizers (Figs. 4.5 and 4.6). The results suggest that there is a very strong interaction between the soil and the applied Zn. Although the extent of movement in both soils was generally limited (1 to 1.5 cm) it appears that the extent of movement was greater in instances when Zn concentrations in the fertilizer band were relatively high than in instances in which Zn concentrations were low. This suggests that if the solubility of Zn in the ZnCl_2 fertilizer band can be enhanced then a greater movement of Zn from the fertilizer band can be achieved. In this study, $(\text{NH}_4)_2\text{SO}_4$ was most effective in enhancing Zn solubility and hence the movement of Zn from the ZnCl_2 fertilizer band, particularly in the noncalcareous soil.

4.3.4. Movement of Zn in the Zn-EDTA Fertilizer Band

Zinc movement from the Zn-EDTA fertilizer band was considerably greater than Zn movement from the ZnCl_2 fertilizer band (Figs. 4.5, 4.6, 4.7 and 4.8). Generally, the extent of Zn movement increased with increase in solubility of Zn in the fertilizer band. It is evident, for example, from Fig. 4.8 that the greatest Zn movement in the calcareous soil was obtained when $\text{NH}_4\text{H}_2\text{PO}_4$ was included in the fertilizer band. Addition of $\text{NH}_4\text{H}_2\text{PO}_4$ resulted in the highest solubility of Zn in the Zn-EDTA fertilizer band. Similarly, in the case of the noncalcareous soil, the greatest movement occurred when either Zn-EDTA was applied alone or in combination with $(\text{NH}_4)_2\text{SO}_4$. As shown before,

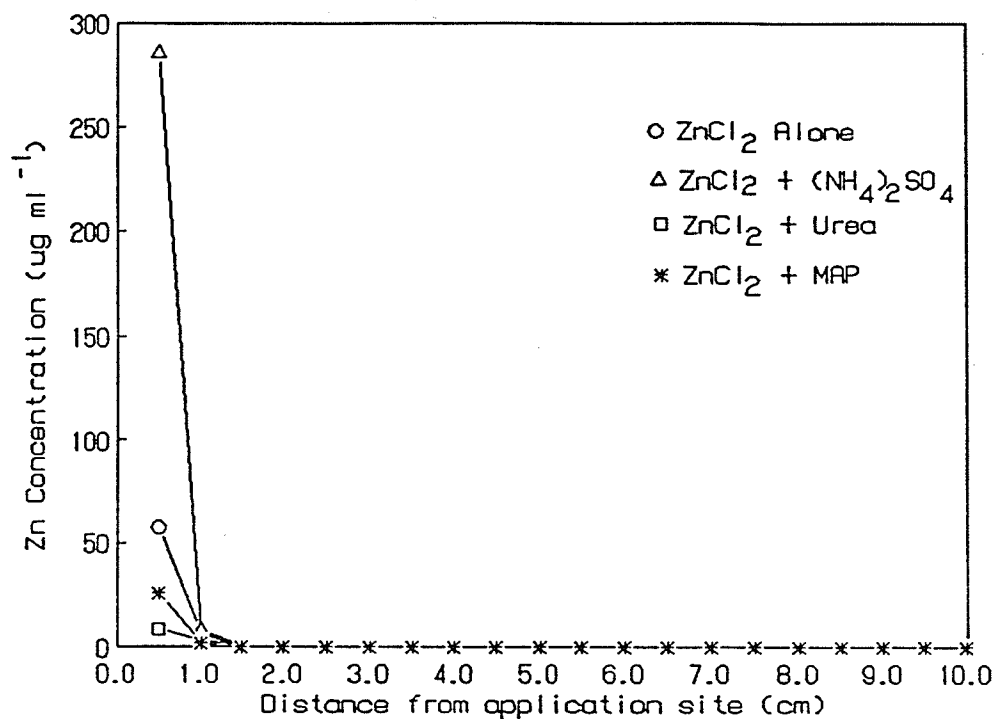


Figure 4.5. Effect of Zn, N and P fertilizers on Zn concentration - Stockton FSL

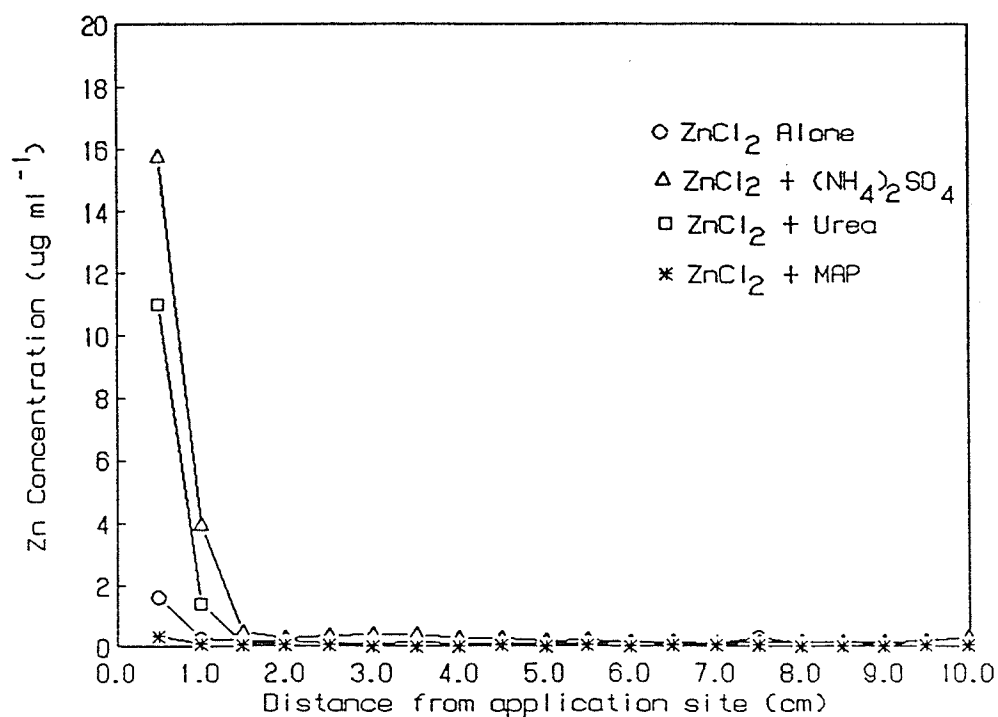


Figure 4.6. Effect of Zn, N and P fertilizers on Zn concentration - Almasippi LFS

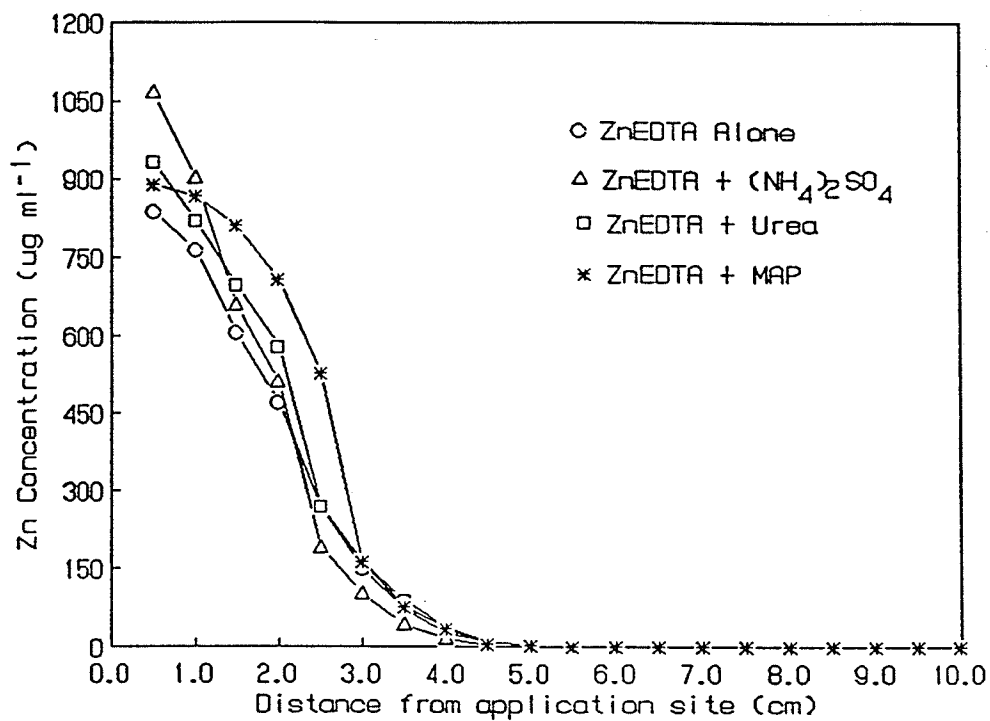


Figure 4.7. Effect of Zn, N and P fertilizers on Zn concentration - Stockton FSL

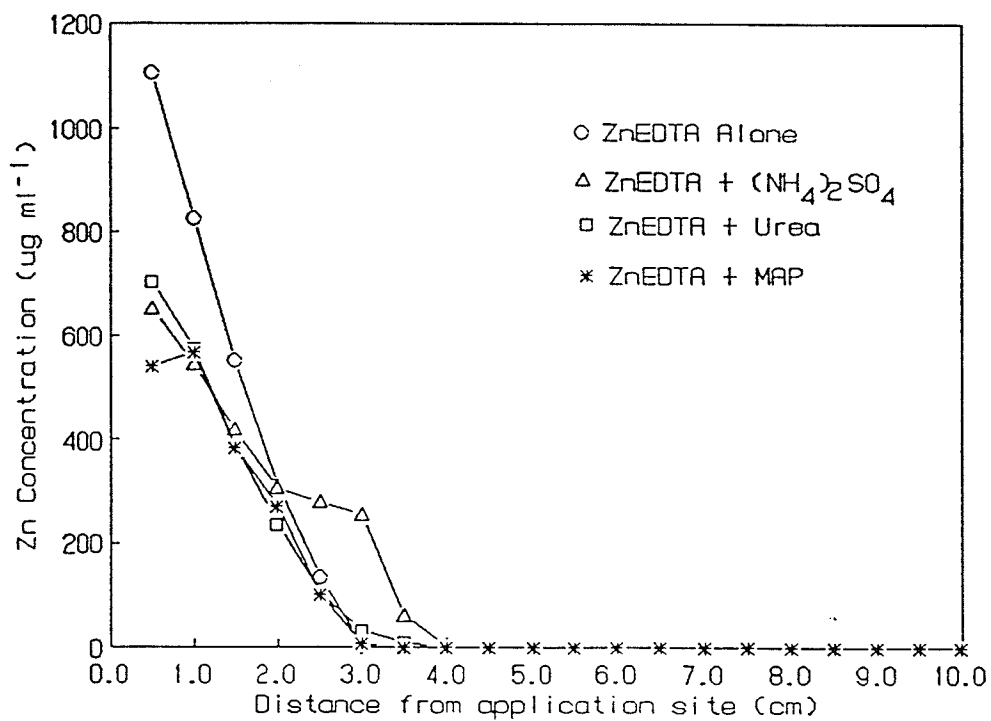


Figure 4.8. Effect of Zn, N and P fertilizers on Zn concentration - Almasippi LFS

the solubility of Zn in the Zn-EDTA fertilizer band was greatest in these two treatments.

4.4. Summary and Conclusions

The results obtained in this study showed that solubility of Zn in the two soils used was greater in the Zn-EDTA fertilizer band than in the ZnCl_2 fertilizer band.

Addition of $(\text{NH}_4)_2\text{SO}_4$ to the ZnCl_2 fertilizer band resulted in a five fold increase in the solubility of Zn in the fertilizer band for the Stockton soil and seven fold increase in Zn solubility for the Almasippi soil when compared to ZnCl_2 applied alone. Application of urea to the ZnCl_2 fertilizer band decreased Zn solubility in the noncalcareous soil but increased solubility in the calcareous soil. Addition of $\text{NH}_4\text{H}_2\text{PO}_4$ to the ZnCl_2 band decreased solubility of Zn in the fertilizer band for both soils.

When Zn-EDTA was applied alone the solubility of Zn in the fertilizer band was similar for both soils. However, when the various N and P fertilizers were included the solubility of Zn in the Zn-EDTA fertilizer band for the Stockton soil was about 32 to 51% lower than the solubilities obtained in the Almasippi soil. Addition of $\text{NH}_4\text{H}_2\text{PO}_4$ in the Zn-EDTA fertilizer band resulted in the lowest solubility of Zn in the fertilizer band in the Stockton soil, but was most effective in enhancing the solubility of Zn in the Almasippi soil.

Zinc movement from the ZnCl_2 fertilizer band was extremely small (1.0 - 1.5 cm) for both soils. $(\text{NH}_4)_2\text{SO}_4$ was most effective in enhancing Zn movement from the ZnCl_2 fertilizer band in both soils.

Zinc moved to distances of about 3.5 to 5 cm from the Zn-EDTA fertilizer band, and movement was greater for the calcareous than the noncalcareous soil. The greatest movement of Zn from the Zn-EDTA fertilizer band was obtained in the calcareous soil treated with Zn-EDTA and $\text{NH}_4\text{H}_2\text{PO}_4$.

This study showed that greater uptake of Zn by plants from Zn-EDTA fertilizer bands as compared to ZnCl_2 fertilizer bands is due, at least in part, to the greater solubility and movement of Zn from the Zn-EDTA fertilizer band. These studies also showed that addition of other fertilizer salts such as $(\text{NH}_4)_2\text{SO}_4$, urea, and $\text{NH}_4\text{H}_2\text{PO}_4$ can alter the plant availability of Zn from both Zn-EDTA and ZnCl_2 fertilizer bands due to their effect on solubility and movement of Zn from the fertilizer bands.

5.0. THE EFFECT OF ROOT TO ZINC FERTILIZER CONTACT ON ZINC
UTILIZATION BY WHEAT

5.1. Introduction

Various reports in the literature suggest that Zn uptake from inorganic Zn fertilizer bands is usually very low due largely to limited contact between plant roots and the Zn in the fertilizer bands (Brown and Krantz 1966; Boawn 1973; Loewen-Rudgers et al. 1978). The limited contact between plant roots and Zn in the fertilizer band is believed to be due to the limited mobility of Zn from the fertilizer band, which results in a very small volume of soil fertilized with Zn when an inorganic Zn fertilizer is applied. Unfortunately, no information was found in the literature which related the amount of roots in contact with Zn in the Zn fertilizer bands to Zn uptake from the bands. The amount of roots recovered from fertilizer bands has been shown to be quite useful in accounting for the uptake of nutrients such as P from P fertilizer bands by various crops (Strong and Soper 1974a). Therefore, it is quite possible that such information may also be quite useful in assessing the importance of root to Zn fertilizer contact as a factor which affects Zn utilization by plants from Zn fertilizer bands.

Some researchers have suggested that if the movement of Zn from inorganic Zn fertilizer bands could be enhanced, the uptake of Zn from such bands could also be considerably increased, supposedly as a result of a larger volume of soil treated with the Zn fertilizer. According to the results obtained in the chemical studies reported in section

4.0, addition of $(\text{NH}_4)_2\text{SO}_4$ to ZnCl_2 fertilizer bands resulted in a considerable increase in the concentration of Zn in soil solution as well as a slightly greater movement of Zn from the fertilizer band. Therefore, one would expect that Zn uptake from inorganic Zn fertilizer bands should be enhanced by addition of $(\text{NH}_4)_2\text{SO}_4$ fertilizers to inorganic Zn fertilizer bands.

Pumphrey et al. (1963), reported that addition of $(\text{NH}_4)_2\text{SO}_4$ to inorganic Zn fertilizer bands usually stimulates root growth into the fertilizer band. Thus, $(\text{NH}_4)_2\text{SO}_4$ may also enhance Zn uptake from the fertilizer bands due to increased root growth. However, there was no quantitative information in the literature on the effects of $(\text{NH}_4)_2\text{SO}_4$ on root growth in Zn fertilizer bands.

Based on the above observations, a plant growth study was conducted to :

- (a) determine the effect of the amount of roots in contact with a ZnCl_2 fertilizer band on Zn uptake by wheat;
- (b) determine the effect of adding $(\text{NH}_4)_2\text{SO}_4$ to the ZnCl_2 fertilizer band on root growth and Zn uptake by wheat;
- (c) determine the effect of funnelling the plant roots through the ZnCl_2 fertilizer band on root growth and Zn uptake from the ZnCl_2 fertilizer band.

5.2. Materials and Methods

A Willowcrest fine sand soil, low in DTPA-extractable Zn, was used for the study (Table 5.1). The soil was collected from a surface horizon (0-15 cm depth), air dried, crushed and sieved through a 2 mm

sieve.

Table 5.1. Some physical and chemical characteristics of the soil used.

Soil Characteristic	Willowcrest (Gleyed Black)
pH (1:1 Soil:H ₂ O)	7.9
Inorganic Carbon (% CaCO ₃ Equivalent)	1.0
Organic Matter (%)	2.4
DTPA-Extr. Zn (ug g ⁻¹)	0.6
Field Capacity Moisture Content (%)	21.9
Texture	FS

Prior to application of the various treatments, 5000 g of air dry soil used in each pot was thoroughly mixed with N, P, K and Cu fertilizers as basal treatments. These fertilizers were applied separately after dissolution in distilled deionized water at rates of 50 ug g⁻¹ of P as KH₂PO₄, 200 ug g⁻¹ of K as KH₂PO₄ and KCl and 5 ug g⁻¹ of Cu as CuSO₄.5H₂O. For treatments in which (NH₄)₂SO₄ was also added to the ZnCl₂ fertilizer band, 9.53 mg N cm⁻² was applied to the band, and the remaining amount was mixed throughout the soil, to give a total of 100 ug g⁻¹ of N based on 5000 g of soil.

The main experiment was conducted in a completely randomized design with 9 treatments arranged as a 3 x 3 factorial, replicated 3 times. The treatments consisted of a control, ZnCl₂ applied alone, and ZnCl₂ applied with (NH₄)₂SO₄. Each of the above treatments was

applied to three different sizes of fertilizer bands. The size of the fertilizer band was varied to obtain treatments in which the amount of roots in contact with the fertilizer band would be varied. The different sizes of the fertilizer bands were formed using three different sizes of acrylic cylinders, each 5.0 cm in height, and open at both ends. The areas at the open ends were 2.86, 15.9 and 32.2 cm² and the internal volumes of the cylinders were 15.8, 80.7 and 163 cm³, respectively.

One end of the cylinders was first covered using parafilm and then filled with soil that had been treated with N, P, K and Cu. The amounts of soil added to the small, medium and large cylinders were 20, 100 and 200 g, respectively. ZnCl₂ dissolved in distilled deionized water was then uniformly applied to the surface of the soil in each cylinder at the rate of 17.5 mg Zn cm⁻². Volumes of ZnCl₂ solution applied were proportional to the areas of the open ends of the cylinders. The respective volumes of the ZnCl₂ solution applied to the small, medium and large fertilizer band sizes were 4.0, 20.4 and 41.2 ml, respectively. In case of treatments that also received (NH₄)₂SO₄ in the fertilizer band the rate of N applied to the fertilizer band was also maintained constant at 9.53 mg N cm⁻².

The parafilm covering one end of the acrylic cylinders was carefully removed after application of the various Zn treatments and the cylinders placed in the centre of the pots, approximately 3 cm below the surface of the soil. This was achieved by removing 2500 g of soil from each pot, placing the cylinder containing the treatments on the surface of the soil remaining in the pot, and then replacing the

soil that was removed from the pot.

5.2.1. Funnel Treatments

Along with the treatments described for the main experiment, additional treatments were designed to determine if Zn uptake from the ZnCl_2 fertilizer bands could be enhanced by increasing the amount of roots in the fertilizer band, which was achieved by funnelling the roots through the fertilizer band. Funnel shaped containers were constructed using sheets of thin transparent plastic, and a hole (about 2.5 cm in diameter) was cut at the bottom of the funnels (Fig. 5.1). The funnels were connected to acrylic cylinders containing soil with or without the Zn fertilizer. The Zn treatments consisted of a control and either ZnCl_2 applied alone or in combination with $(\text{NH}_4)_2\text{SO}_4$, and were applied using the same procedure as described for the main experiment. Roots in the cylinders were determined and results obtained for the funnel treatments were compared to results obtained in treatments in which the Zn was applied to a similar size of fertilizer band (2.86 cm^2), but the roots were not funnelled through the cylinders.

5.2.2. Seeding and Maintenance

Ten wheat seeds (variety Columbus) uniformly spaced in the pots were placed approximately 2.5 cm below the soil surface, and the soil wetted to field capacity moisture content. Ten d after emergence the plants were thinned to 5 plants per pot. The plants were grown in the growth chamber for a period of 65 d. During the growing period the

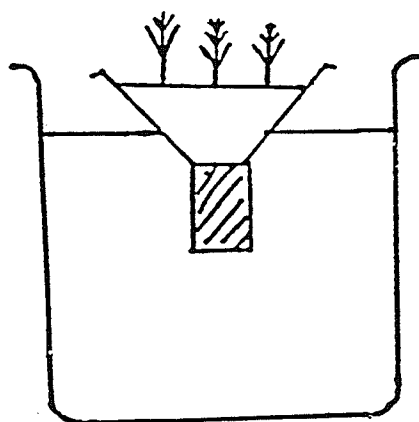
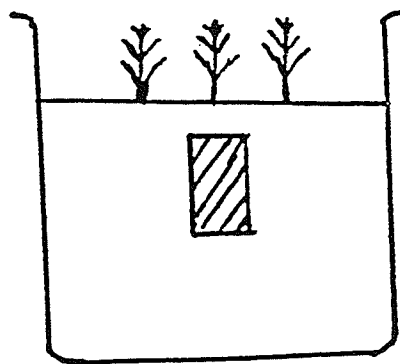
FUNNEL TREATMENTSNON FUNNEL TREATMENTS

Fig 5.1. Diagrammatic Representation of Funnelled and Non Funnelled Treatments

plants were watered using distilled deionized water. The soil also received an additional 150 ug g^{-1} of N as $(\text{NH}_4)_2\text{SO}_4$ applied in a split application; 100 ug g^{-1} of N was applied 28 d after emergence and the remaining 50 ug g^{-1} of N was applied 49 d after emergence.

The plants were grown under 16 h of artificial light and 8 h of darkness. The temperature was maintained at 22°C during the day and 16°C at night. The relative humidity in the growth chamber was kept at 40 % during the day and 70 % at night. The light intensity close to the plants canopy ranged from 500 to $550 \text{ umoles m}^{-2} \text{ s}^{-1}$.

5.2.3. Harvesting

The plants were harvested at the flowering stage by cutting the entire plant shoots at the soil surface level using a sharp knife. The samples were dried at 65°C and weighed. The cylinders in the pots were carefully removed by slicing off the soil and roots at the ends of the cylinders. The cylinders containing the soil and roots were then transferred to a 50 mesh sieve and the roots carefully separated from the soil by washing the soil through the sieve. When the roots were soil free they were dried at 65°C and weighed.

5.2.4. Plant Tissue Analysis

Plant shoot samples were ground in a Willey mill and then thoroughly mixed. A 1.0 g sample was pre-digested in 5 ml HNO_3 and $2.5 \text{ ml } 70 \% \text{ HClO}_4$ for 30 min and then digested on a digestion block at 230°C until the solution in the digestion tubes turned clear. The samples were cooled, transferred to 25 ml volumetric flasks and made up to

volume. The concentration of Zn in the digests was determined using an Atomic Absorption Spectrophotometer.

5.2.5. Calculations of Fertilizer Zn Uptake

The amount of Zn in plant shoots that was absorbed from the Zn fertilizer was calculated as follows:

$$\text{Fertilizer Zn Uptake (ug)} = \text{Zn Uptake in Fertilizer Treatment (ug)} - \text{Zn Uptake in Respective Control (ug)}.$$

Fertilizer Zn uptake per unit mass of roots recovered from the cylinders was calculated by dividing the amount of Zn absorbed from the Zn fertilizer by the mass of roots recovered from the respective cylinder.

5.3. Results and Discussion

5.3.1. Effect of Zn Fertilizer Treatments and Size of Fertilizer Band on Shoot and Root Dry Matter Yields

Analysis of variance indicated that the main effects were significant indicating that band size as well as zinc treatments significantly affected root growth in the fertilizer band as well as plant Zn content. The interaction between band size and zinc fertilizer treatments was also significant, and therefore the interaction effects are presented and discussed (Table 5.2).

Shoot dry matter yields were not significantly affected by application of either ZnCl_2 or ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$ to

Table 5.2. Effect of Zn fertilizer treatment and size of fertilizer band on shoot dry matter yield, root dry matter yield, plant Zn content and Zn uptake.

Size of Fertilizer Band	Zn Fertilizer Treatment	Shoot DM Yield (g pot ⁻¹)	Root DM Yield (mg cyl ⁻¹)	Shoot Zn Conc (ug g ⁻¹)	Soil + Fertilizer Zn Uptake (ug pot ⁻¹)
Band Size 1 (2.86 cm ²)	Control	34.0 ab ¹	113 c	11.5 e	391 c
	ZnCl ₂ Alone	33.9 ab	57 c	15.3 de	509 c
	ZnCl ₂ + (NH ₄) ₂ SO ₄	32.3 ab	75 c	18.0 de	582 c
Band Size 2 (15.89 cm ²)	Control	35.4 ab	963 b	10.8 e	384 c
	ZnCl ₂ Alone	34.7 ab	227 c	31.6 c	1095 b
	ZnCl ₂ + (NH ₄) ₂ SO ₄	35.4 a	219 c	32.4 cd	1148 b
Band Size 3 (32.15 cm ²)	Control	34.5 ab	1633 a	9.9 e	349 c
	ZnCl ₂ Alone	35.0 ab	287 c	45.3 b	1578 a
	ZnCl ₂ + (NH ₄) ₂ SO ₄	30.9 b	467 c	58.1 a	1777 a

¹Duncans Multiple Range Test. Means with the same letter within a column are not significantly different (P = 0.05).

the small or medium size fertilizer bands (Table 5.2). Shoot dry matter yield was significantly less with ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$ in the largest fertilizer band than with ZnCl_2 and $(\text{NH}_4)_2\text{SO}_4$ in the medium sized fertilizer band.

The amount of roots recovered from the medium and largest fertilizer bands was significantly less with ZnCl_2 alone and ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$ than without Zn fertilizer (Table 5.2). Root growth was also reduced when the Zn treatments were applied to the smallest fertilizer band, but the decreases were not significant. Since the same amount of roots should have entered the cylinders containing the Zn fertilizer as entered the cylinders without Zn, the results show that the Zn fertilizer bands were toxic to plant roots. No reports were found in the literature indicating that inorganic Zn fertilizers applied as fertilizer bands were toxic to roots.

Although no reports of toxicity of Zn to roots was found in the literature, other metals have been shown to reduce root growth. Al^{3+} toxicity, for example, to plant roots has been reported in many acid soils. Adams and Lund (1966) measured the growth rate of the primary roots of cotton plants grown in culture solution containing Al^{3+} and in acid soils of varying Al contents. They found that the growth of the cotton roots decreased as the molar activity of Al in the nutrient solution increased. Pavan et al. (1982) found that coffee root growth was inhibited progressively by increasing Al^{3+} levels. Reduction in root growth was best correlated to an increase in the activity of Al^{3+} . Brenes and Perason (1973) demonstrated that Al^{3+} activity was a good index of Al toxicity for corn, sorghum lucerne and subterranean clover.

According to Foy (1978) Al injured roots were characteristically stubby and brittle. Root tips and lateral roots became thickened, turned brown and lacked fine branching suggesting that such roots were very inefficient in the absorption of water and nutrients.

Different plant species and varieties differ in their tolerance to excess Al, and in several species it has been shown that the differences were genetically controlled (Reid 1971). Al tolerant cultivars of wheat, barley, rice, peas and beans as well as corn inbreds were found to increase the pH of their nutrient solution and thus decreased the solubility and therefore toxicity of Al (Clarkson 1965; Klimashevskii and Berezovskii 1973; Howeler and Cadavid 1976; Mugwira and Patel 1977; Foy and Fleming 1978). Bartlett and Riego (1972) noted that Al complexed with citrate, EDTA or soil organic matter extract was detoxified for maize whereas ionic Al severely injured the roots.

Mn and Fe toxicity to plants have also been reported in the literature. However, Mn toxicity affected the plant tops more severely than the roots Foy (1978). Millikan (1949) noted that excess Fe resulted in stunted root growth which showed large accumulations of organically bound phosphate. Plant species and genotypes within species were found to differ in tolerance to Mn and Fe toxicity.

The reduction in root growth in the Zn fertilizer band is in contrast to the results obtained with nutrients such as P and N. Strong and Soper (1974a), for example, found that roots of flax, wheat, rape and buckwheat proliferated extensively within the reaction zone of applied P. They also showed that the extent of root proliferation

in the reaction zone varied with plant species. Rape and buckwheat showed the greatest root proliferation in the fertilizer band. As a result, such crops recovered larger amounts of P from the fertilizer band. Marschner (1986) reported that root density of crops such as barley increased severalfold in zones where the concentration of nutrients especially N was high and this effect resulted in greater plant growth and higher yields. Thus, the results obtained in this study suggest that the toxicity effects of Zn to plant roots may be an important factor limiting utilization of Zn by plants from inorganic Zn fertilizer bands.

The amount of roots in the smallest and largest fertilizer bands was increased when $(\text{NH}_4)_2\text{SO}_4$ was added to the ZnCl_2 fertilizer band, but the differences were not significant (Table 5.2). The amount of roots recovered from the medium size fertilizer band was not significantly affected by addition of $(\text{NH}_4)_2\text{SO}_4$ to the fertilizer band. Therefore, application of $(\text{NH}_4)_2\text{SO}_4$ to the ZnCl_2 fertilizer band was generally not effective in stimulating root growth into the fertilizer band. Pumphrey et al. (1963) suggested that N fertilizers promoted greater root growth due to N nutrition, and that this effect was largely responsible for greater Zn uptakes from inorganic Zn fertilizers applied together with N fertilizers.

The amount of roots recovered from the fertilizer bands increased almost proportionately with increase in the size of the fertilizer band for treatments which did not receive Zn fertilizer (controls), as expected (Fig. 5.2). On the other hand, the mass of roots recovered from fertilizer bands treated with ZnCl_2 alone or ZnCl_2 in combination

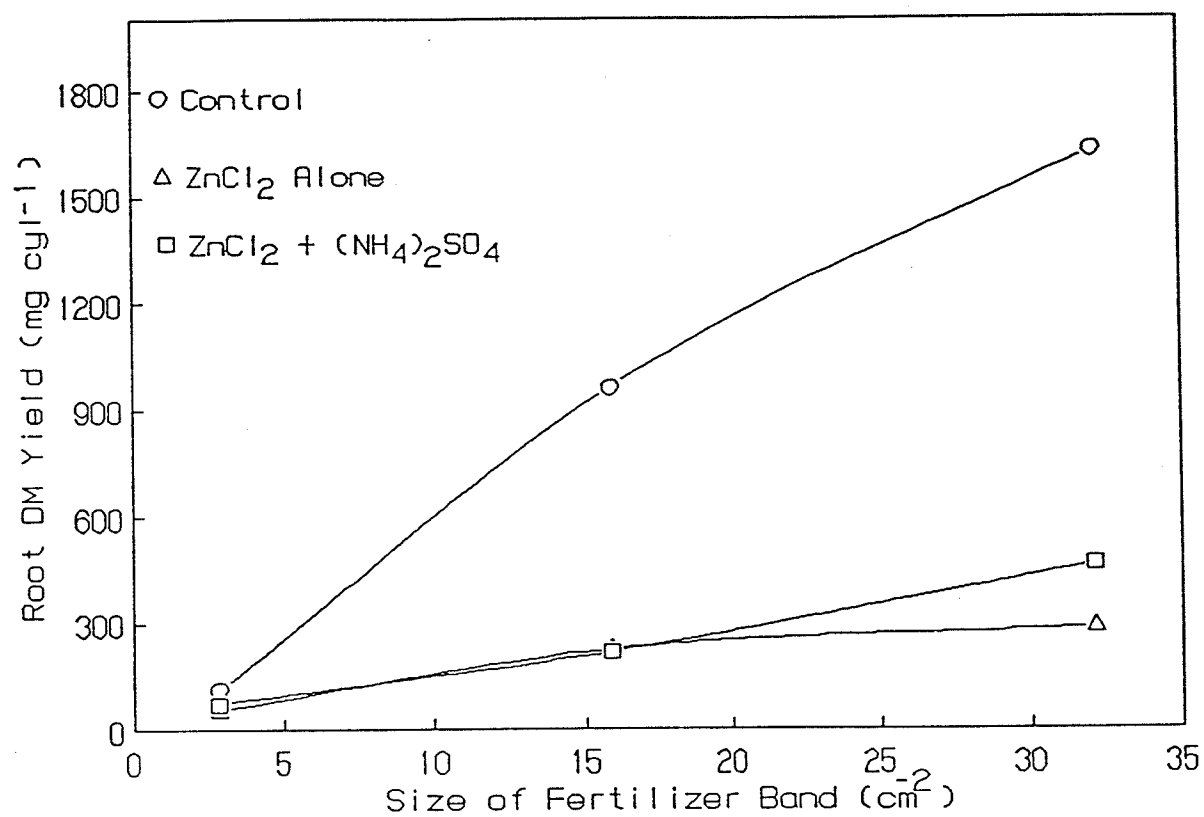


Figure 5.2. Effect of Zn fertilizer treatment and size of fertilizer band on root dry matter yield

with $(\text{NH}_4)_2\text{SO}_4$ did not increase proportionately with the size of the fertilizer band. In fact, the differences in the masses of roots recovered from the three band sizes were not significant when ZnCl_2 was added (Table 5.2). The lack of proportionate increases in root masses with increase in the size of the fertilizer band is likely due to retardation of root growth as a result of toxicity effects of Zn from the ZnCl_2 .

5.3.2. Effect of Zn Fertilizer Treatments and Size of Fertilizer Bands on Plant Zn Content and Zn Uptake

Concentrations of Zn in plant shoots as well as Zn uptake were significantly greater with ZnCl_2 or ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$ than without Zn (Table 5.2). However, the differences were not significant when the Zn treatments were applied to the smallest fertilizer band.

Concentrations of Zn in plant shoots were significantly greater with $(\text{NH}_4)_2\text{SO}_4$ in combination with ZnCl_2 than with ZnCl_2 alone for the largest fertilizer band size (Table 5.2). Concentration of Zn in plant shoots treated with ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$ was only slightly greater than with ZnCl_2 alone for the medium and small fertilizer bands. The higher Zn concentration in plants with $\text{ZnCl}_2 + (\text{NH}_4)_2\text{SO}_4$ than with ZnCl_2 alone was probably due in part to the greater solubility of the Zn fertilizer when $(\text{NH}_4)_2\text{SO}_4$ was added. Previous studies showed that $(\text{NH}_4)_2\text{SO}_4$ increased the solubility of Zn when applied to ZnCl_2 fertilizer bands. It should be noted, however, that increases in concentration of Zn in plant shoots when $(\text{NH}_4)_2\text{SO}_4$

was added to ZnCl_2 in the small and largest fertilizer bands was nearly proportional to increases in amount of roots between treatments with and without $(\text{NH}_4)_2\text{SO}_4$. Therefore, the higher concentrations of Zn in plant shoots treated with ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$ in the largest and smallest fertilizer bands may also in part be attributed to greater amounts of roots recovered from such treatments.

Zinc uptake by plants was consistently greater with ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$ than with ZnCl_2 only, regardless of the size of the fertilizer band. However, the differences were not significant (Table 5.2).

As expected, concentrations of Zn in plant shoots and Zn uptake were similar for all treatments without Zn fertilizer (Fig. 5.3). The concentration of Zn in plant shoots as well as Zn uptake were significantly increased by increasing the size of the fertilizer band when ZnCl_2 was applied with or without $(\text{NH}_4)_2\text{SO}_4$. Plant Zn content and Zn uptake increased almost proportionately with the size of the fertilizer band, particularly when results for the medium and largest fertilizer bands are compared (Table 5.2 and Fig. 5.3).

As indicated earlier, differences among the amount of roots in the various ZnCl_2 fertilizer bands were not significant, but greater amount of roots were always recovered from larger bands than from smaller bands. Fertilizer Zn uptake per unit mass of roots recovered from the cylinders was not significantly affected by increasing the size of the fertilizer band (Table 5.3). Fertilizer Zn uptake by plant shoots was nearly proportional to the amount of roots recovered from the fertilizer band (Fig. 5.4). Therefore, the higher concentrations of

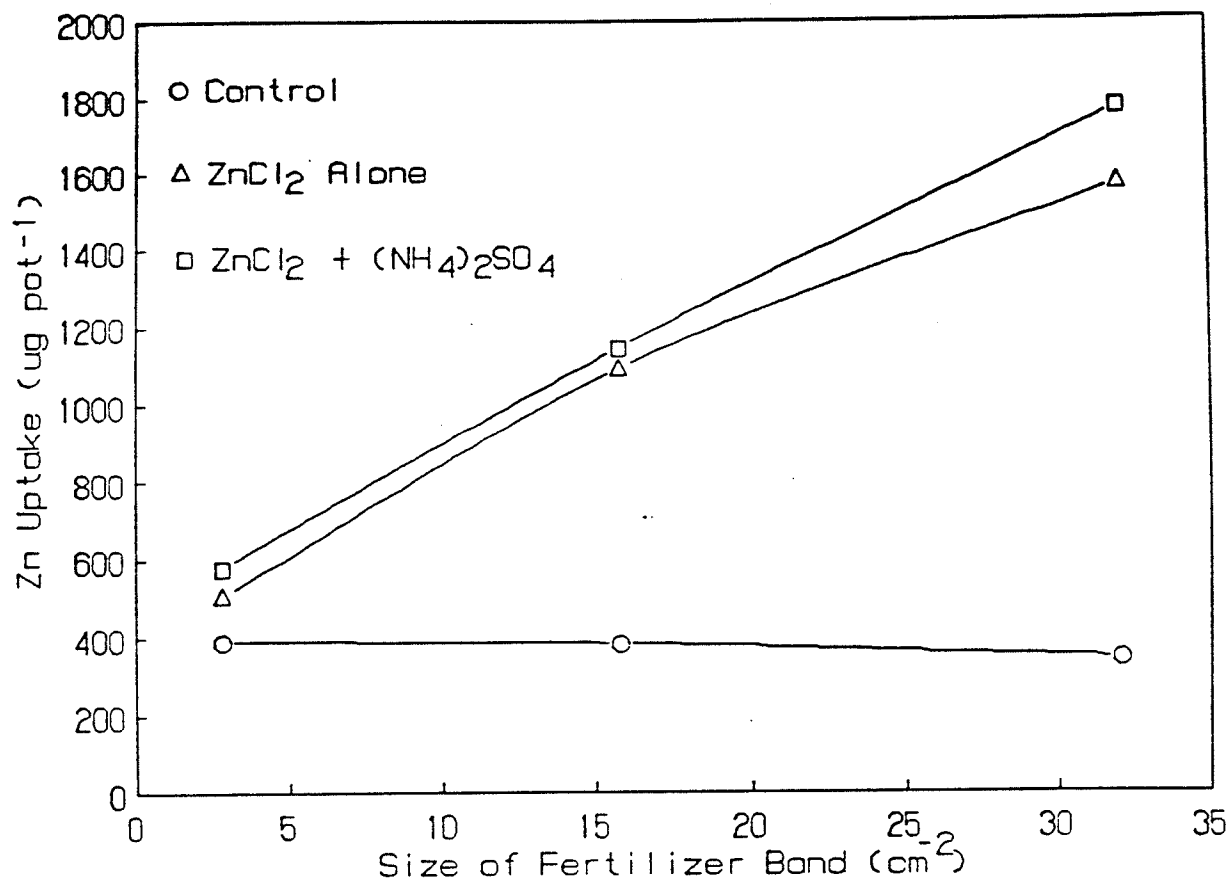


Figure 5.3. Effect of Zn fertilizer treatment and size of fertilizer band on Zn uptake

Table 5.3. Effect of Zn fertilizer treatment and size of fertilizer band on utilization of applied Zn fertilizer.

Size of Fertilizer Band	Zn Fertilizer Treatment	Fertilizer Zn Uptake ($\mu\text{g pot}^{-1}$)	Fertilizer Zn Uptake Per Unit Mass of Roots ($\mu\text{g mg}^{-1}$ root)
Band Size 1 (2.86 cm^2)	ZnCl ₂ Alone	118 c ¹	2.11 a
	ZnCl ₂ + (NH ₄) ₂ SO ₄	191 c	3.25 a
Band Size 2 (15.89 cm^2)	ZnCl ₂ Alone	711 b	3.07 a
	ZnCl ₂ + (NH ₄) ₂ SO ₄	764 b	4.23 a
Band Size 3 (32.15 cm^2)	ZnCl ₂ Alone	1229 a	4.31 a
	ZnCl ₂ + (NH ₄) ₂ SO ₄	1429 a	3.15 a

¹Duncans Multiple Range Test. Means with the same letter within a column are not significantly different ($P = 0.05$).

Zn and fertilizer Zn uptake by plants grown in the larger fertilizer bands was due to greater amounts of roots recovered from the vicinity of application of the Zn fertilizer. According to Soper et al. (1989) fertilizer Zn uptake from inorganic fertilizers increased markedly with increase in volume of soil treated with the Zn fertilizer even when the amount of Zn added remained the same. They suggested that greater fertilizer Zn uptakes from treatments in which the Zn fertilizer was mixed with larger volumes of soil was due to greater contact between plant roots and the Zn fertilizer. Therefore, it appears that the amount of roots in the fertilizer band was the most important factor affecting fertilizer Zn uptake by the plants.

5.3.3. Effect of Funnelling Plant Roots Through the Zn Fertilizer Bands on Shoot and Root Dry Matter Yields

Shoot dry matter yields were usually significantly lower when the roots were funnelled through the cylinders than when the roots were not funnelled (Table 5.4). Shoot dry matter yields were not significantly affected by application of ZnCl_2 , either alone or in combination with $(\text{NH}_4)_2\text{SO}_4$, regardless of whether or not the roots were funnelled through the fertilizer bands.

The mass of roots recovered from the fertilizer bands was increased 3 to 8 fold when the roots were funnelled through the fertilizer bands (Table 5.4). Therefore, funnelling the roots through the cylinders was very effective in increasing the amount of roots in contact with the Zn fertilizer.

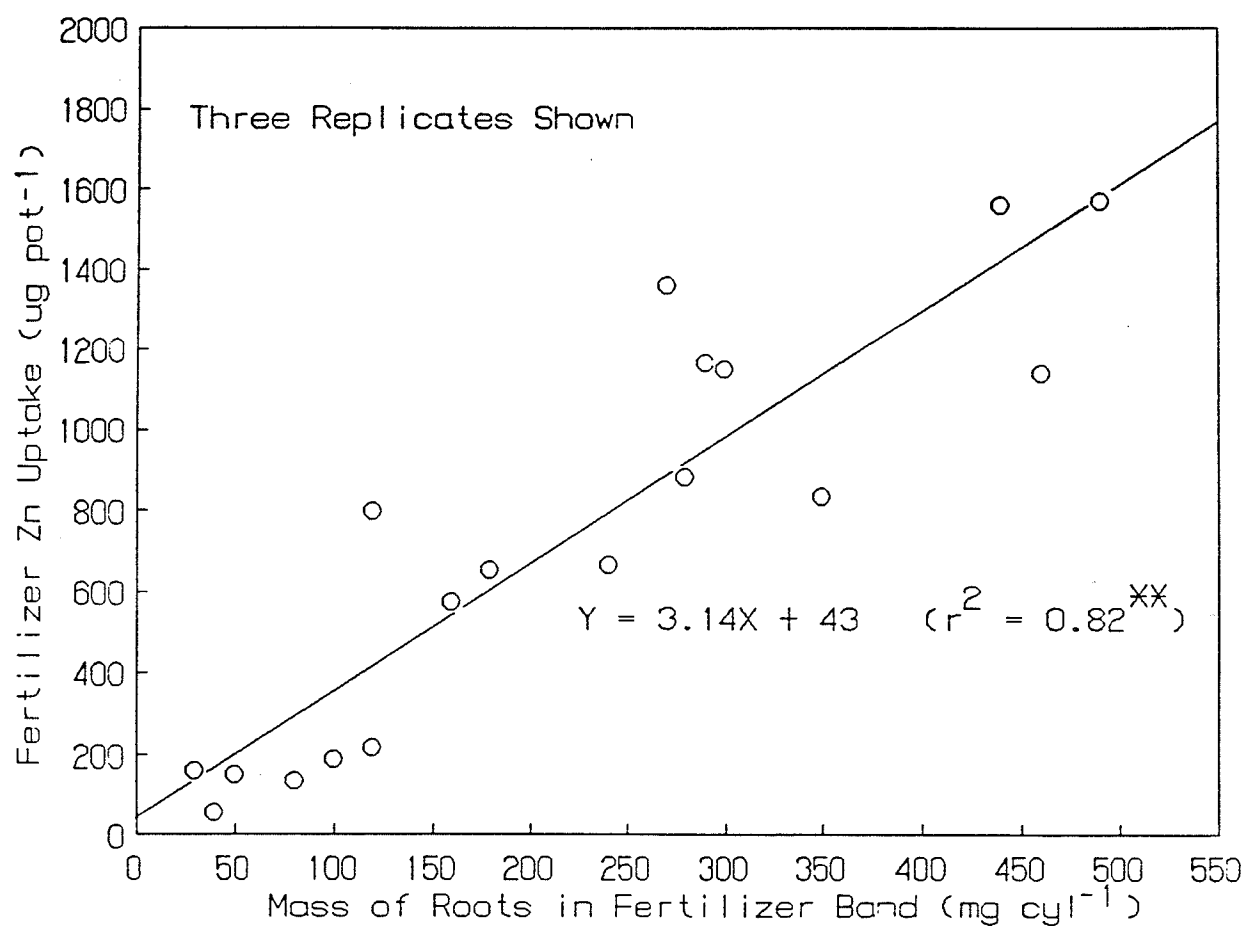


Figure 5.4. Effect of mass of roots in the ZnCl_2 fertilizer band on fertilizer Zn uptake

Generally, the mass of roots was not significantly affected by Zn treatments. Reductions in root mass did occur (not significant) with application of Zn, when roots were not funnelled through the fertilizer band, presumably due to toxicity of the Zn in the fertilizer band.

A visual examination of the roots recovered from the various treatments showed that roots recovered from the funnelled treatments, including the controls were usually very coarse when compared to the roots recovered from the non funnelled treatments. Thus, it was inferred that the surface area per unit mass of roots recovered from the fertilizer bands was decreased when the roots were funnelled through the fertilizer bands.

5.3.4. Effect of Funnelling Plant Roots Through the Zn Fertilizer Band on Shoot Zn Content and Zn Uptake

The concentration of Zn in plant shoots was similar for treatments without Zn (Table 5.4). On the other hand, the concentration of Zn in plant shoots treated with ZnCl_2 alone or ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$ was significantly greater than that of plants without Zn for both funnelled and nonfunnelled treatments. Plant Zn content was not significantly affected by the application of $(\text{NH}_4)_2\text{SO}_4$ to the ZnCl_2 fertilizer band whether or not the roots were funnelled through the fertilizer band. Concentrations of Zn in plant shoots treated with ZnCl_2 alone or ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$ were significantly increased when the roots were funnelled through the fertilizer band.

Table 5.4. Effect of enhanced root contact with a Zn fertilizer band on shoot dry matter yield, root dry matter yield, plant Zn content and Zn uptake.

Treatment		Shoot DM Yield (g pot ⁻¹)	Root DM Yield (mg cyl ⁻¹)	Shoot Zn Conc (ug g ⁻¹)	Soil + Fertilizer Zn Uptake (ug pot ⁻¹)
NON FUNNEL	Control	34.0 a ¹	113 b	11.5 e	391 c
	ZnCl ₂ Alone	33.9 a	57 b	15.3 cd	509 ab
	ZnCl ₂ + (NH ₄) ₂ SO ₄	32.3 ab	75 b	18.0 bc	582 a
FUNNEL	Control	23.4 b	316 a	12.3 de	290 d
	ZnCl ₂ Alone	23.0 b	426 a	21.2 ab	486 b
	ZnCl ₂ + (NH ₄) ₂ SO ₄	24.1 b	392 a	23.7 a	573 a

¹Duncans Multiple Range Test. Means with the same letter within a column are not significantly different (P = 0.05).

Zinc uptake by plant shoots was significantly increased when ZnCl_2 was applied alone, or in combination with $(\text{NH}_4)_2\text{SO}_4$ for both root treatments (Table 5.4). Zinc uptake by plant shoots was always higher with $(\text{NH}_4)_2\text{SO}_4$ in combination with ZnCl_2 than with ZnCl_2 only for both the funnelled and non funnelled treatments. But, the differences were significant only when the roots were funnelled through the fertilizer bands. The amount of roots in the funnelled treatments that received ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$ was slightly lower than amount of roots in treatments that received ZnCl_2 only. Thus, it appears that higher Zn uptakes by plant shoots in such treatments was likely a result of higher concentrations of Zn in soil solution due to the $(\text{NH}_4)_2\text{SO}_4$.

Zinc uptake was not significantly affected by funnelling the roots through the cylinders when Zn was applied even though concentration of Zn in the plants was positively affected by funnelling roots through the fertilizer band. The lack of an increases in Zn uptake was due to the lowering in yield of shoots when the roots were funnelled through the fertilizer bands (Table 5.4).

5.3.5. Effect of Funnelling Plant Roots Through the Zn Fertilizer Band on Utilization of the Zn Fertilizer

The proportion of total amount of Zn in plant shoots that was absorbed from the Zn fertilizer was approximately doubled when roots in treatments with ZnCl_2 only were funnelled through the fertilizer band (Table 5.5). The proportion of total amount of Zn in plant shoots derived from the Zn fertilizer was also increased from 33 % to 49 %

Table 5.5. Effect of enhanced root contact with a ZnCl_2 fertilizer band on utilization of Zn from the Zn fertilizer.

Treatment		Fertilizer Zn Uptake ($\mu\text{g pot}^{-1}$)	Percent ¹ of Total	Fertilizer Zn Uptake Per Unit Mass of Roots ($\mu\text{g mg}^{-1}$ root)
NON FUNNEL	ZnCl_2 Alone	118 b ²	(23.2 b)	2.11 ab
	$\text{ZnCl}_2 + (\text{NH}_4)_2\text{SO}_4$	119 ab	(32.8 ab)	3.25 a
FUNNEL	ZnCl_2 Alone	196 ab	(40.3 ab)	0.46 b
	$\text{ZnCl}_2 + (\text{NH}_4)_2\text{SO}_4$	281 a	(49.0 a)	0.72 b

¹Proportion of total amount of Zn in plant shoots that was derived from the Zn fertilizer.

²Duncans Multiple Range Test. Means with the same letter within a column are not significantly different ($P = 0.05$).

when the roots of plants treated with ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$ were funnelled through the fertilizer band.

Generally, the proportion of Zn in plant shoots derived from the Zn fertilizer increased when $(\text{NH}_4)_2\text{SO}_4$ was added to the fertilizer band. However, the increases in Zn uptake from the Zn fertilizer due to addition of $(\text{NH}_4)_2\text{SO}_4$ to the fertilizer band were not significant.

Fertilizer Zn uptake per unit mass of roots in the fertilizer band decreased approximately 5 fold when the roots were funnelled through the fertilizer band (Table 5.5). However, the differences were significant only in treatments with ZnCl_2 in combination with $(\text{NH}_4)_2\text{SO}_4$. These results show that the efficiency of the roots in the fertilizer band with respect to the utilization of the Zn fertilizer was greatly decreased by funnelling the roots through the fertilizer band.

5.4. Summary and Conclusions

Root growth was severely retarded within the zone of application of a ZnCl_2 fertilizer band. It was concluded therefore, that the Zn fertilizer band was toxic to plant roots.

Root growth into the fertilizer band was only slightly increased by application of $(\text{NH}_4)_2\text{SO}_4$ to the fertilizer band. Adding $(\text{NH}_4)_2\text{SO}_4$ to the ZnCl_2 fertilizer band usually slightly enhanced Zn uptake by the plant. The enhanced Zn uptake appeared to be due to slight increases in root growth and increased solubility of the Zn fertilizer with $(\text{NH}_4)_2\text{SO}_4$.

Utilization of Zn by wheat plants from the fertilizer band was largely controlled by the extent of root to Zn fertilizer contact.

Concentrations of Zn in plant shoots as well as Zn uptake from the Zn fertilizer were remarkably increased by increasing the size of the fertilizer band or funnelling the plant roots through the fertilizer band.

6.0. EFFECT OF CONCENTRATION OF ZINC IN ZnCl_2 and Zn-EDTA
FERTILIZER BANDS ON ROOT GROWTH AND ZINC UPTAKE BY WHEAT

6.1. Introduction

Results obtained from the previous plant growth study demonstrated that when ZnCl_2 was applied to wheat as a fertilizer band, root growth within the zone of application was severely reduced. It was concluded therefore, that the ZnCl_2 fertilizer band was toxic to roots. There was no information in the literature indicating that inorganic Zn fertilizers were toxic to plant roots when applied as fertilizer bands. There was also no information in the literature regarding root growth habits in zones of application of organically complexed Zn fertilizers such as Zn-EDTA.

Thus, studies were conducted on two Willowcrest fine sand soils and an Almasippi loamy fine sand soil to obtain additional information regarding the influence of organically complexed and inorganic Zn fertilizer bands on root growth and Zn uptake from the fertilizer bands. Perhaps, such information may be very useful in accounting for the large differences in Zn uptake by plants from organically complexed and inorganic Zn fertilizer bands.

The objectives of the studies were:

- (a) to determine the influence of concentration of Zn in ZnCl_2 and Zn-EDTA fertilizer bands on root growth and Zn uptake by wheat;
- (b) to determine the influence of ionic and complexed forms of Zn on root growth.

6.2. Materials and Methods

6.2.1. Plant Growth Studies

Three different experiments were conducted using three different soils which were all low in DTPA-extractable Zn (Table 6.1).

Table 6.1. Some physical and chemical characteristics of the soils used.

Soil Characteristics	Willowcrest FS	Willowcrest FS	Almasippi LFS
pH (1:1 soil : H ₂ O)	7.0	7.9	8.4
Inorganic Carbon (% CaCO ₃ Equiv.)	0.2	1.0	4.1
Organic Matter (%)	2.4	2.4	2.7
DTPA-Extr. Zn (ug g ⁻¹)	0.5	0.6	0.5
Field Capacity Moisture Content (%)	29.4	21.9	22.0

The first experiment was conducted using the Almasippi soil to determine the effect of ZnCl₂ and Zn-EDTA fertilizer bands and rate of Zn applied on root growth and Zn uptake by wheat when the fertilizer was banded into a calcareous soil. The soil was air dried and then sieved through a 2 mm sieve. A 5000 g sample of soil was then placed into each plastic pot. The soil in each pot was thoroughly mixed with N, P, K and Cu fertilizers as basal treatments. The rates of application based on soil weight were 100 ug g⁻¹ of N as (NH₄)₂SO₄, 50 ug g⁻¹ of P as KH₂PO₄, 200 ug g⁻¹ of K as KH₂PO₄ and KCl and 5 ug g⁻¹

of Cu as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The Zn treatments consisted of the two Zn fertilizers, ZnCl_2 and Zn-EDTA applied at rates of 0, 0.63, 1.26, 2.52, and 5.03 mg Zn cm^{-2} . The various rates of Zn were applied to the surface of soil contained in acrylic cylinders. The cylinders were 5 cm long and open at both ends, with an area of 32.2 cm^2 at the open ends. The cylinders were first closed on one end with parafilm and then filled with 200 g of soil which had been treated with N, P, K and Cu as described before. The various rates of Zn were applied in 40 ml of a ZnCl_2 or Zn-EDTA solution, which was uniformly spread over the entire surface of the soil in the cylinder.

The parafilm covering one end of the cylinders was carefully removed after application of the various Zn treatments, and the cylinders placed approximately in the middle of the pots such that the top surface of the cylinders was approximately 5 cm below the surface of the soil in the pot. This was achieved by removing 3500 g of soil from the pot, placing the cylinder containing the Zn treatments on the surface of the soil remaining in the pot and then replacing the soil that was removed from the pot. Seeding, maintenance of plants during the growing period, harvesting and handling of shoot and root samples was similar to the procedures used for the first plant growth study (Section 5.0).

The second experiment was conducted using a slightly calcareous Willowcrest fine sand soil to determine the effect of a wider range of rates of Zn on root growth and Zn uptake by wheat from ZnCl_2 and Zn-EDTA fertilizer bands. The experiment was conducted on growth

benches and all the Zn treatments were applied to a fertilizer band of area 15.89 cm^2 . The rates of Zn applied were 0, 0.16, 0.63, 2.52, 5.03, and $10.06 \text{ mg Zn cm}^{-2}$. The fertilizer band was formed using acrylic cylinders and using the same procedures as described for the first experiment. The soil was also prepared as described before. Applications of the basal treatments, seeding, maintenance of plants, harvesting and analysis of the plant samples were similar to those used for the first experiment. However, since the plants were grown on growth benches, the temperature, relative humidity and light conditions during the growing period were not as effectively controlled as in the first experiment.

The third experiment was conducted using a noncalcareous Willowcrest fine sand soil to evaluate the effect of limited incorporation of the ZnCl_2 and Zn-EDTA fertilizers into the soil on root growth and Zn uptake from the fertilizer bands. Incorporation of the Zn fertilizers into a limited volume of soil was done in an attempt to provide for a wider range of concentrations of Zn in the fertilizer band, since results from the plant growth study conducted on the slightly calcareous soil showed that when ZnCl_2 or Zn-EDTA were applied to the surface of the soil in the cylinders, rates of Zn as low as $0.16 \text{ mg Zn cm}^{-2}$ were still high enough to significantly reduce root growth into the fertilizer band. The experiment was conducted in the growth chamber in a completely randomized design. The procedures used in the preparation of the soil, application of the basal treatments, maintenance of the plants, harvesting and digestion of the plant samples were similar to the ones described for the first experiment.

All the Zn fertilizer treatments were also applied to acrylic cylinders, but instead of applying the Zn solution to the surface of the soil in the cylinders the solution was mixed throughout the 200 g of soil contained in the cylinders. In this experiment the cylinder with an area of 32.15 cm^2 at the open end was used and the rates of Zn applied were 0.02, 0.05, 0.10, 0.20, 0.40, 0.80, 1.60, and $3.20 \text{ mg Zn cm}^{-3}$.

6.2.2. Determination of Complexed and Ionic Zn in Soil Solution

Soil samples with the same treatments as those used in the plant growth studies described above were incubated at field capacity moisture content for a period of 14 d and then the concentrations of complexed and ionic forms of Zn in soil solution determined. For the soils used in the first two plant growth studies, 460 g of soil was placed in columns formed by fitting together two acrylic rings, each 2.5 cm high and 9.5 cm internal diameter using standard electrician tape. One end of the column was closed using parafilm. The columns had an area of 76.02 cm^2 at the open end. Before the Zn treatments were applied to the cylinders, 56.2 and 55.7 ml of distilled deionized water were added to the calcareous and slightly calcareous soils respectively. ZnCl_2 and Zn-EDTA, each at rates of 0, 0.63, 1.26, 2.51, and $5.03 \text{ mg Zn cm}^{-2}$ contained in 45 ml of Zn solution were uniformly spread on the surface of the soil used in the first plant growth study and rates of Zn equivalent to 0, 0.16, 0.63, 2.52, 5.03, and $10.06 \text{ mg Zn cm}^{-2}$ were applied to the soil used in the second plant growth study. The additional 45 ml of solution increased moisture content of the

soils to field capacity moisture content. The top ends of the columns were then covered with perforated parafilm to prevent rapid evaporation at the soil surface as well as ensure adequate aeration at the soil surface.

After 13 d of incubation at room temperature the moisture content of the samples for both soils was further raised to 27.0 %. Additional water was added to ensure that sufficient water would be present in the soils to provide an adequate amount of soil solution when the soils were centrifuged. The samples were then incubated for one more day and a 1.5-cm slice of soil was obtained from the surface of the column, transferred to 250 ml centrifuge bottles and centrifuged at 10,000 rpm (13,000 G) for 40 min. The supernatant collected at the surface of the soil was decanted. The complexed as well as ionic form of Zn in the supernatant were determined as follows: The supernatant was filtered and an aliquot taken and analyzed for total Zn concentration using an Atomic Absorption Spectrophotometer. A separate aliquot of the supernatant was treated with NaOH and the precipitated inorganic Zn removed by filtration. The concentration of complexed Zn was then determined in the filtrate using an Atomic Absorption Spectrophotometer. The concentration of ionic Zn was then obtained by subtraction of the concentration of complexed Zn from concentration of total Zn. This procedure was found to quantitatively separate ionic Zn and Zn complexed with EDTA (Appendix A).

The same procedure as outlined above was used to obtain the amount of ionic and complexed Zn in soil solution for the noncalcareous soil used in the third plant growth study. However, for this soil the

various rates of Zn (0, 0.02, 0.05, 0.10, 0.20, 0.40, 0.80, 1.60 and 3.20 mg Zn cm⁻³) were applied in 40 ml of ZnCl₂ or Zn-EDTA solution, and instead of applying the solution to the surface of soil in acrylic cylinders it was thoroughly mixed with 200 g of soil contained in 250 ml centrifuge bottles. An additional 18.8 ml of distilled deionized water was added to bring the soil close to field capacity moisture content. The moisture content was further raised to 35 %, 24 h before the samples were centrifuged.

6.3. Results and Discussion

6.3.1. Shoot and Root Dry Matter Yields

Shoot dry matter yield for wheat was not significantly affected by any of the treatments on any of the soils studied (Tables 6.2, 6.3, and 6.4). In contrast, the amount of roots in the fertilizer bands was affected by treatments in many instances. The amount of roots in the fertilizer band was not affected when ZnCl₂ was applied to the calcareous soil, regardless of the rate of Zn applied (Table 6.2). However, root growth in the fertilizer band was significantly less with Zn-EDTA at a rate of 5.03 mg Zn cm⁻³ than without Zn. Root dry matter yield was also less with 5.03 mg Zn cm⁻² as Zn-EDTA than with ZnCl₂ at rates of 2.52 mg Zn cm⁻² or less. Thus, Zn-EDTA was toxic to roots when the highest rate of Zn was applied to the calcareous soil.

Both Zn fertilizers reduced root growth in the fertilizer bands when applied to the slightly calcareous soil even at rates of Zn as low as 0.16 mg cm⁻² (Table 6.3). Amount of roots in the fertilizer band tended to decrease with amount of Zn added, particularly for the ZnCl₂

Table 6.2. Effect of source and rate of Zn applied on shoot and root dry matter yield and plant Zn content - Almasippi LFS (calcareous soil).

Zn Fertilizer	Rate of Zn Applied (mg cm ⁻²)	Shoot DM Yield (g pot ⁻¹)	Root DM Yield (mg cyl ⁻¹)	Shoot Zn Conc. (ug g ⁻¹)
Control	0	37.5 a	626 a ¹	7.7 f
ZnCl ₂	0.63	36.5 a	558 a	8.4 f
	1.26	37.8 a	625 a	10.1 ef
	2.52	39.4 a	540 a	10.3 ef
	5.03	39.6 a	524 ab	12.0 e
Zn-EDTA	0.63	40.3 a	522 ab	15.9 d
	1.26	37.2 a	539 a	23.0 c
	2.52	37.7 a	511 ab	31.1 b
	5.03	38.9 a	403 b	39.7 a

¹Duncans Multiple Range Test. Means with the same letter within a column are not significantly different (P = 0.05).

Table 6.3. Effect of source and rate of Zn applied on shoot and root dry matter yield and plant Zn content - Willowcrest FS (slightly calcareous soil).

Zn Fertilizer	Rate of Zn Applied (mg cm ⁻²)	Shoot DM Yield (g pot ⁻¹)	Root DM Yield (mg cyl ⁻¹)	Shoot Zn Conc. (ug g ⁻¹)
Control	0	19.5 a	208 a ¹	9.2 e
ZnCl ₂	0.16	16.8 a	135 bc	13.3 e
	0.63	16.5 a	118 bc	15.1 e
	2.52	16.1 a	125 bc	14.6 de
	5.03	18.1 a	102 bc	14.8 de
	10.06	16.5 a	84 c	21.8 d
Zn-EDTA	0.16	17.4 a	125 bc	9.8 e
	0.63	- ²	- -	- -
	2.52	19.3 a	162 ab	31.5 c
	5.03	15.8 a	92 c	46.4 b
	10.06	17.5 a	143 bc	69.0 a

¹Duncans Multiple Range Test. Means with the same letter within a column are not significantly different (P = 0.05).

²Data for treatment not available.

Table 6.4. Effect of source and rate of Zn applied on shoot dry matter yield - Willowcrest FS (noncalcareous soil).

Zn Fertilizer	Rate of Zn Applied (mg cm ⁻³)	Shoot DM Yield (g pot ⁻¹)
Control	0	40.3 a ¹
ZnCl ₂	0.02	43.4 a
	0.05	41.0 a
	0.10	40.3 a
	0.20	44.4 a
	0.40	40.5 a
	0.80	44.5 a
	1.60	43.3 a
	3.20	43.7 a
Zn-EDTA	0.02	41.2 a
	0.05	42.3 a
	0.10	42.4 a
	0.20	40.6 a
	0.40	42.2 a
	0.80	42.7 a
	1.60	41.5 a
	3.20	37.7 a

¹Duncans Multiple Range Test. Means with the same letter within a column are not significantly different (P = 0.05).

treatments. The large reductions in amount of roots in the ZnCl_2 fertilizer band was not evident in the calcareous soil when similar rates of Zn were applied to the fertilizer band (Table 6.2). Thus, the data shows that root growth in Zn fertilizer bands can vary considerably with the source of Zn fertilizer used as well as the soil type.

The effect of incorporating the Zn fertilizers into a limited volume of soil on masses of roots recovered from the Zn fertilizer bands is represented in Fig. 6.1 (Experiment 3). The amount of roots recovered from the fertilizer bands varied considerably with the source as well as rate of Zn applied. The two Zn fertilizers varied considerably in the extent to which they affected root development in the Zn fertilizer reaction zone. Zn-EDTA was more detrimental to root growth in the fertilizer band than ZnCl_2 applied at similar rates for virtually all rates of applied Zn.

Application of Zn-EDTA at rates as low as $0.02 \text{ mg Zn cm}^{-3}$ resulted in a considerable reduction in root growth in the fertilizer band when compared to the control treatment. The amount of roots in the Zn-EDTA fertilizer band initially decreased very rapidly with amount of Zn added and then remained relatively constant when more than $0.8 \text{ mg Zn cm}^{-3}$ were applied (Fig. 6.1). Application of Zn-EDTA at rates greater than $0.8 \text{ mg Zn cm}^{-3}$ resulted in about a 75 percent reduction in root growth in the fertilizer band.

In contrast to the data obtained with Zn-EDTA, plants treated with 0.2 to $0.8 \text{ mg Zn cm}^{-3}$ as ZnCl_2 showed a slight root proliferation in the fertilizer band when compared to the control treatment (Fig. 6.1). Maximum root growth in the ZnCl_2 fertilizer band occurred at about the

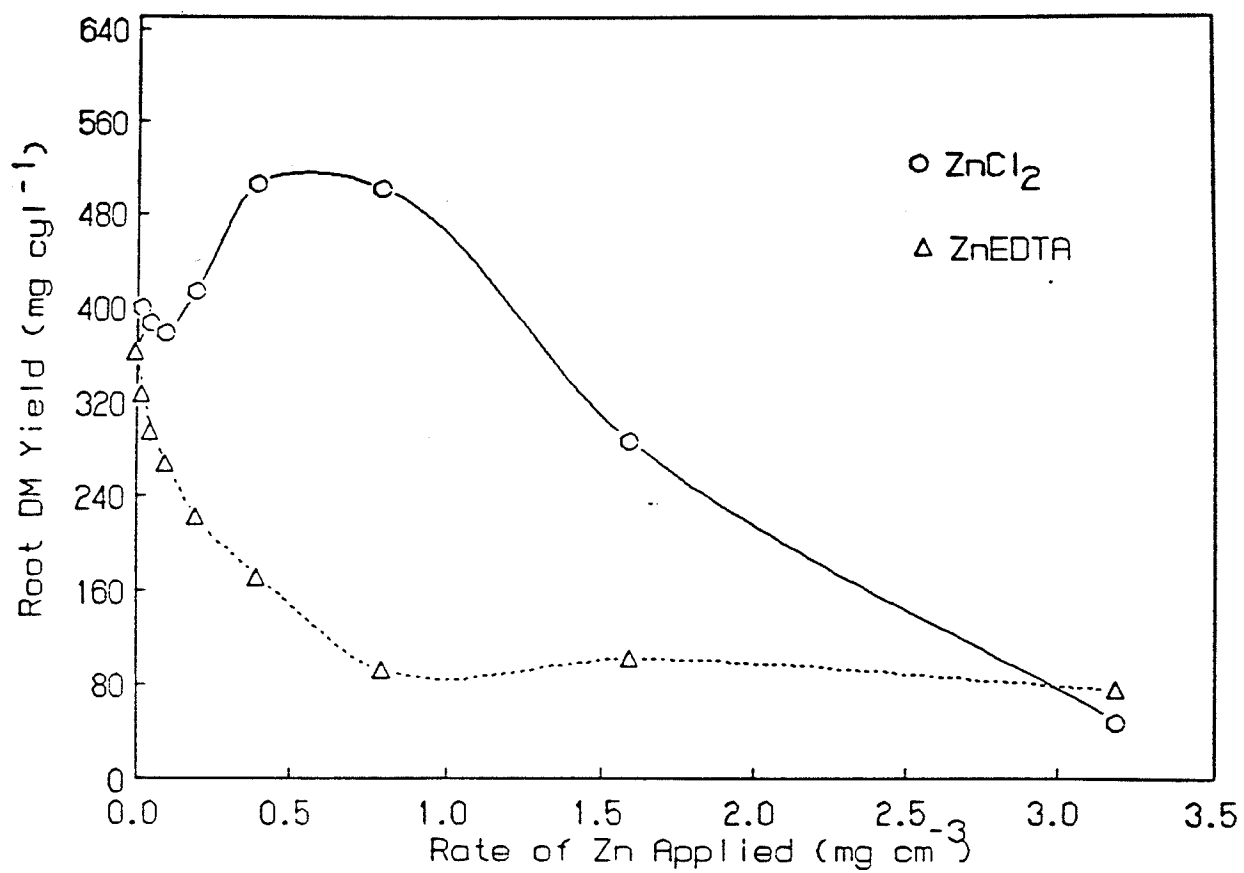


Figure 6.1 Effect of source and rate of Zn applied on root dry matter yield - Willowcrest FS (noncalcareous soil)

0.63 mg Zn cm⁻³ rate. A sharp decrease in root growth in the ZnCl₂ fertilizer band occurred when more than 0.8 mg Zn cm⁻³ was applied.

A visual inspection of roots from all treatments was conducted using a microscope (Figs 6.2a and 6.2b). Root branching was severely reduced by all rates of Zn-EDTA, with decrease in branching being more evident at the high rates of Zn. Plants treated with ZnCl₂ showed a reduced branching only at the high rates of applied Zn. In addition to reduced root branching, roots recovered from treatments receiving high rates of Zn as ZnCl₂ or Zn-EDTA consisted of thick roots only and thus the surface area per unit weight of roots in the fertilizer band would be reduced substantially.

6.3.2. Concentrations of Zinc in Plant Shoots

Zinc concentration in wheat plants grown on the calcareous soil was increased by application of ZnCl₂ and Zn-EDTA fertilizers (Table 6.2). The concentration of Zn in the plant shoots usually increased with amount of Zn added for both Zn fertilizers. The Zn content of plants was significantly greater when plants were treated with 5.03 mg Zn cm⁻² as ZnCl₂ than for untreated plants and plants treated with 0.63 mg Zn cm⁻² (Table 6.2). Plant Zn content was significantly increased by all rates of Zn applied as Zn-EDTA when compared to concentrations of Zn in untreated plants. Plant Zn content was significantly higher in plants treated with Zn-EDTA than plants treated with ZnCl₂, regardless of the rate of Zn applied.

Both Zn fertilizers increased the concentration of Zn in plant shoots, when they were applied to the slightly calcareous soil

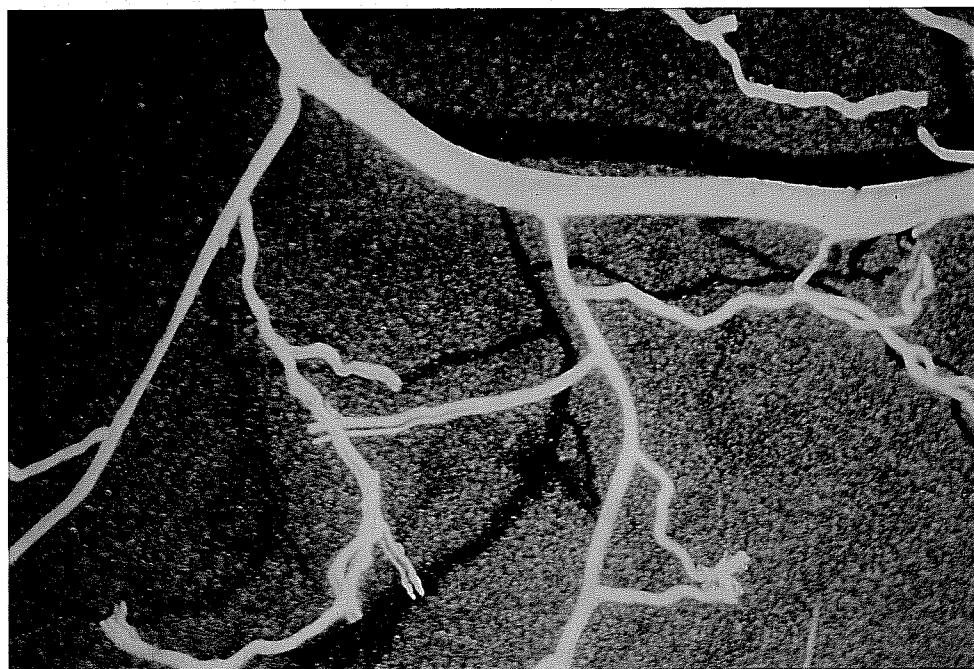


Fig. 6.2a. Root growth in control treatment (no Zn added)
(magnification 28X)



Fig. 6.2b. Root growth in ZnCl_2 and Zn-EDTA fertilizer bands
treated with the $3.20 \text{ mg Zn cm}^{-3}$ rate (magnification 28X)

(Table 6.3). However, some of the increases were not statistically significant. Plant Zn content also increased when ZnCl_2 or Zn-EDTA were applied to the noncalcareous soil (Fig. 6.3). Zinc content of plants grown on the slightly calcareous and noncalcareous soils increased with amount of Zn added. It is also quite evident from the results that Zn concentrations in the plant shoots were much greater with Zn-EDTA than with ZnCl_2 on the slightly calcareous soil.

At very low rates of Zn application both Zn fertilizers were equally effective in supplying Zn to the plant when applied to the noncalcareous soil (Fig 6.3). However, in contrast to results obtained on the calcareous and slightly calcareous soils, ZnCl_2 was more effective than Zn-EDTA in supplying Zn to the plants grown on the noncalcareous soil when the higher rates of Zn were applied.

6.3.3. Concentrations of Complexed and Ionic Forms of Zn in the ZnCl_2 and Zn-EDTA Fertilizer Bands

The concentrations of total Zn in the Zn-EDTA fertilizer bands were remarkably higher than concentrations of Zn in the ZnCl_2 fertilizer bands for all the three soils, when the Zn fertilizers were applied at equivalent rates of Zn (Tables 6.5, 6.6 and 6.7).

Virtually all the water soluble Zn in the ZnCl_2 fertilizer bands existed in the ionic form whereas considerable amounts of both the ionic as well as complexed forms of Zn were present in fertilizer bands treated with Zn-EDTA. The total amount of Zn in soil solution increased with amounts of ZnCl_2 or Zn-EDTA applied for all three soils. The amounts of Zn in the ionic and complexed forms both increased with

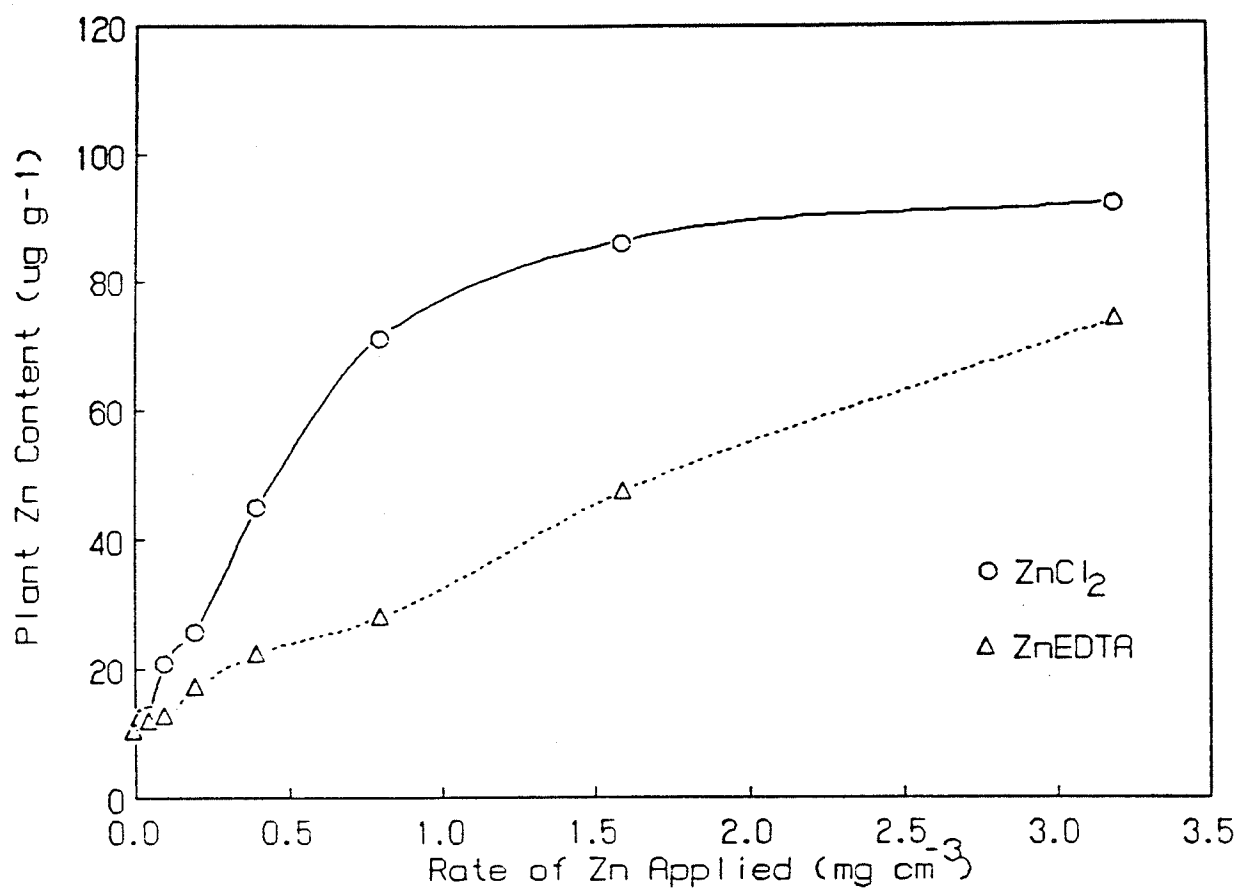


Figure 6.3. Effect of source and rate of Zn applied on plant Zn content - Willowcrest FS (noncalcareous soil)

Table 6.5. Effect of source and rate of Zn applied on concentration of Zn in soil solution - Almasippi LFS (calcareous soil).

Rate of Zn Applied (mg cm ⁻²)	ZnCl ₂			Zn-EDTA		
	Total Zn (ug ml ⁻¹)	Complexed Zn (ug ml ⁻¹)	Ionic Zn (ug ml ⁻¹)	Total Zn (ug ml ⁻¹)	Complexed Zn (ug ml ⁻¹)	Ionic Zn (ug ml ⁻¹)
0	0.15	0.04	0.11	0.15	0.40	0.11
0.63	0.27	0.08	0.19	320	176	144
1.26	0.54	0.07	0.47	664	352	312
2.52	2.40	0.01	2.39	1256	752	504
5.03	33.0	0.02	32.9	2624	1656	968

Table 6.6. Effect of source and rate of Zn applied on concentration of Zn in soil solution - Willowcrest FS (slightly calcareous soil).

Rate of Zn Applied (mg cm ⁻²)	ZnCl ₂			Zn-EDTA		
	Total Zn (ug ml ⁻¹)	Complexed Zn (ug ml ⁻¹)	Ionic Zn (ug ml ⁻¹)	Total Zn (ug ml ⁻¹)	Complexed Zn (ug ml ⁻¹)	Ionic Zn (ug ml ⁻¹)
0	0.08	0.01	0.07	0.08	0.01	0.07
0.16	0.40	0.04	0.36	49.2	40.2	2.00
0.63	0.73	0.05	0.68	280	264	16.0
2.52	24.0	0.10	23.9	1024	984	40.0
5.03	184	6.60	177	1752	1704	48.0
10.06	648	17.2	631	3064	2872	192

Table 6.7. Effect of source and rate of Zn applied on concentration of Zn in soil solution - Willowcrest FS (noncalcareous soil).

Rate of Zn Applied (mg cm ⁻³)	ZnCl ₂			Zn-EDTA		
	Total Zn (ug ml ⁻¹)	Complexed Zn (ug ml ⁻¹)	Ionic Zn (ug ml ⁻¹)	Total Zn (ug ml ⁻¹)	Complexed Zn (ug ml ⁻¹)	Ionic Zn (ug ml ⁻¹)
0	0.04	0.02	0.02	0.04	0.02	0.02
0.02	0.09	0.02	0.07	23.0	7.40	15.6
0.05	0.25	0.03	0.22	66.4	36.4	30.0
0.10	0.50	0.02	0.48	192	112	80.0
0.20	2.20	0.20	2.00	378	250	128
0.40	13.2	2.20	11.0	776	604	172
0.80	120	8.00	112	1616	1288	328
1.60	460	29.40	431	4240	3520	720
3.20	1820	100	1720	6000	4960	1040

amounts of Zn-EDTA applied to the fertilizer band for all three soils and tended to co-vary with amount of Zn-EDTA added.

It should be noted that the concentration of Zn in soil solution of the calcareous soil treated with ZnCl_2 was lower than the concentration of Zn in the soil solution of the slightly calcareous soil treated with similar amounts of ZnCl_2 (Tables 6.5 and 6.6). The low concentration of Zn in soil solution of the calcareous soil was likely caused by the high pH and larger amounts of CaCO_3 in the calcareous soil (Table 6.1). According to results obtained in studies reported earlier, the solubility of Zn in ZnCl_2 fertilizer bands was lower in a calcareous soil than in a noncalcareous soil. Kalbasi et al. (1978b) also showed that the solubility of Zn applied as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was greater in noncalcareous than in calcareous soils.

Concentrations of Zn in the Zn-EDTA fertilizer bands were also affected by soil type. Concentration of Zn in soil solution was greater for the slightly calcareous soil than for the calcareous soil when equivalent rates of Zn-EDTA were applied. The results suggest that Zn-EDTA was slightly more stable in the slightly calcareous soil than in the calcareous soil. These results are also consistent with results obtained by Lindsay and Norvell (1969) and the results obtained in studies reported in a previous section.

6.3.4. Relations Among Root Growth, Concentrations of Zn in Plant Shoots and Concentrations of Zn in Soil Solution

(a) Almasippi Loamy Fine Sand Soil (Calcareous)

The amount of roots in the ZnCl_2 fertilizer band was not significantly correlated to the concentration of Zn in soil solution for the calcareous soil. A linear regression analysis of the data obtained showed that only 39 % of the variation in the mass of roots in the fertilizer band could be attributed to variations in the concentration of Zn in soil solution. It should be noted that the concentration of Zn in soil solution was generally very low for virtually all rates of Zn applied except when the rate of Zn applied to the fertilizer band was $5.03 \text{ mg Zn cm}^{-2}$. Thus, the lack of a significant response in root growth to varying concentrations of Zn in soil solution was probably due to the low concentrations of Zn in soil solution.

In contrast to results obtained with ZnCl_2 , the amount of roots recovered from fertilizer bands treated with Zn-EDTA decreased linearly with total amount of Zn in soil solution according to the relation

$$\text{Root DM Yield (mg cyl}^{-1}) = 590 - 0.07 \text{ Total Zn (ug ml}^{-1}) \quad (r^2 = 0.86^{**})$$

Therefore, high concentrations of Zn in the Zn-EDTA fertilizer bands were toxic to roots. It should be noted however, that the concentration of ionic and complexed Zn in soil solution co-varied considerably with amount of Zn-EDTA applied to the fertilizer band.

Therefore, it was difficult to determine whether decreases in root growth with amounts of Zn-EDTA applied were caused by the high concentrations of ionic, complexed or both forms of Zn.

The amount of roots in the Zn-EDTA fertilizer bands were generally slightly lower than amount of roots recovered from the ZnCl_2 fertilizer bands when equivalent rates of Zn were applied to the calcareous soil (Table 6.2). Yet, concentrations of Zn in plants treated with Zn-EDTA were remarkably higher than concentrations of Zn in plants treated with ZnCl_2 at equivalent rates of Zn. Zn-EDTA maintained a remarkably higher concentration of Zn in soil solution than ZnCl_2 . Thus, the results clearly suggest that the large differences in plant Zn content with the two Zn fertilizers were due to the large differences in the solubility of the Zn fertilizers.

(b) Willowcrest Fine Sand Soil (Slightly Calcareous)

The amount of roots in the ZnCl_2 fertilizer bands was very poorly correlated with concentration of Zn in soil solution for the slightly calcareous soil ($r^2 = 0.38$ NS). However, in contrast to results obtained with the calcareous soil, all concentrations of Zn resulting from application of the various rates of Zn were equally toxic to roots. Therefore, although the concentration of Zn in soil solution increased with amounts of ZnCl_2 applied, the amount of roots recovered from the fertilizer band was not significantly changed (Table 6.3). Thus, it is not surprising that the amount of roots recovered from the fertilizer band was poorly correlated with concentration of Zn in soil solution.

The amount of roots recovered from the Zn-EDTA fertilizer band was also very poorly correlated with concentration of Zn in soil solution ($r^2 = 0.48$ NS). This effect is also probably due to the fact that all concentrations of Zn in soil solution resulting from application of the various rates of Zn-EDTA were equally toxic to roots. However, it should also be noted that in this experiment large variations in plant growth resulted from the lack of adequate control of environmental conditions during the growing period. These variations may have affected the results obtained.

The amount of roots recovered from fertilizer bands treated with ZnCl_2 was not significantly different from the amount of roots recovered from treatments that received Zn-EDTA regardless of the rate of Zn applied (Table 6.3). Yet, there were marked differences in the concentration of Zn in plant shoots when the two Zn fertilizers were applied at equivalent rates of Zn. Concentrations of Zn in plant shoots treated with Zn-EDTA were always higher than concentrations of Zn in plants treated with ZnCl_2 . Therefore, as indicated earlier, the results strongly suggest that high concentrations of Zn in soil solution are essential for high uptakes of Zn from Zn fertilizer bands. Zn-EDTA maintained a remarkably higher concentration of Zn in soil solution than ZnCl_2 when equivalent amounts of Zn were applied to the soil used in this study (Table 6.6).

(c) Willowcrest Fine Sand Soil (Noncalcareous)

Root growth in ZnCl_2 and Zn-EDTA fertilizer bands was closely associated with concentrations of Zn in soil solution, when the Zn

fertilizers were applied to the noncalcareous soil (Fig. 6.4).

A marked root proliferation occurred in the ZnCl_2 fertilizer band when the concentration of Zn in soil solution was approximately 300 ug ml^{-1} or less. Maximum root proliferation occurred when the concentration of Zn in soil solution was approximately 50 to 150 ug ml^{-1} . A rapid decrease in the amount as well as quality of roots recovered from the fertilizer band occurred when the concentration of Zn in soil solution was higher than 300 ug ml^{-1} , when compared to the amount as well as quality of roots recovered from the control treatments. Thus, the results show that high concentrations of ionic Zn in soil solution were toxic to roots since virtually all the Zn in soil solution was in the ionic form when ZnCl_2 was applied to the fertilizer band (Table 6.7).

Root growth was reduced by virtually all concentrations of Zn in soil solution in treatments that received Zn-EDTA, when compared to the amount of roots recovered from the control treatments (Fig. 6.4). The amount of roots recovered from the Zn-EDTA fertilizer band decreased very rapidly initially with increase in concentration of Zn in soil solution and then remained relatively constant when concentrations of Zn in soil solution were higher than 1600 ug ml^{-1} . Root growth into the fertilizer band was reduced by approximately 75 % when the concentration of Zn in soil solution was 1600 ug ml^{-1} or greater. The quality of roots recovered from such treatments was also remarkably deteriorated (Fig. 6.2b).

It should also be noted that when the concentration of Zn in soil solution was neither too high nor too low, the amount of roots

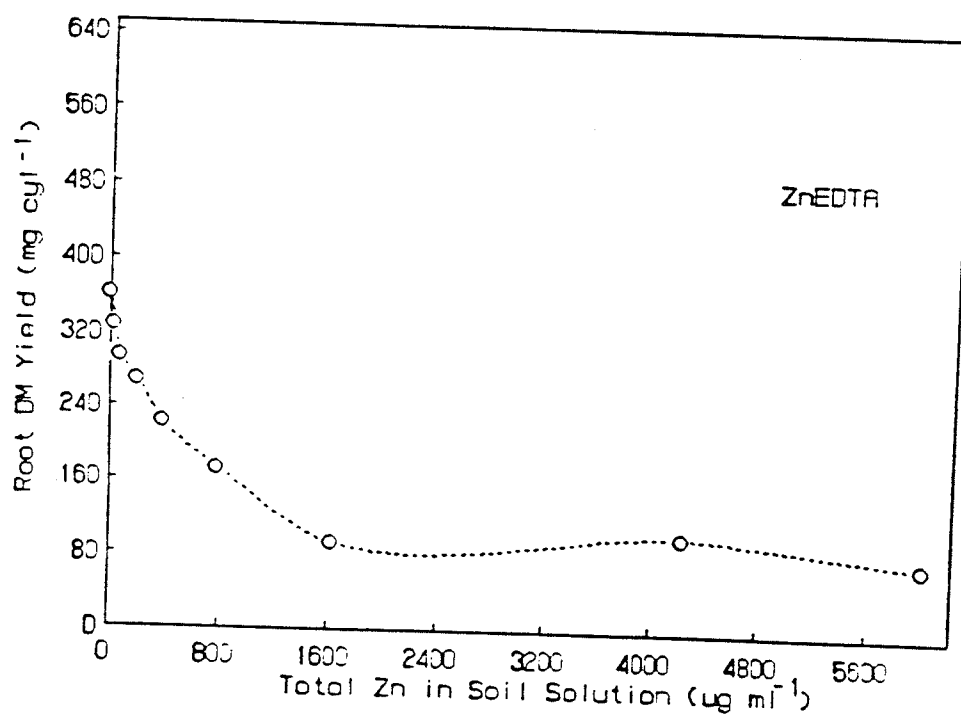
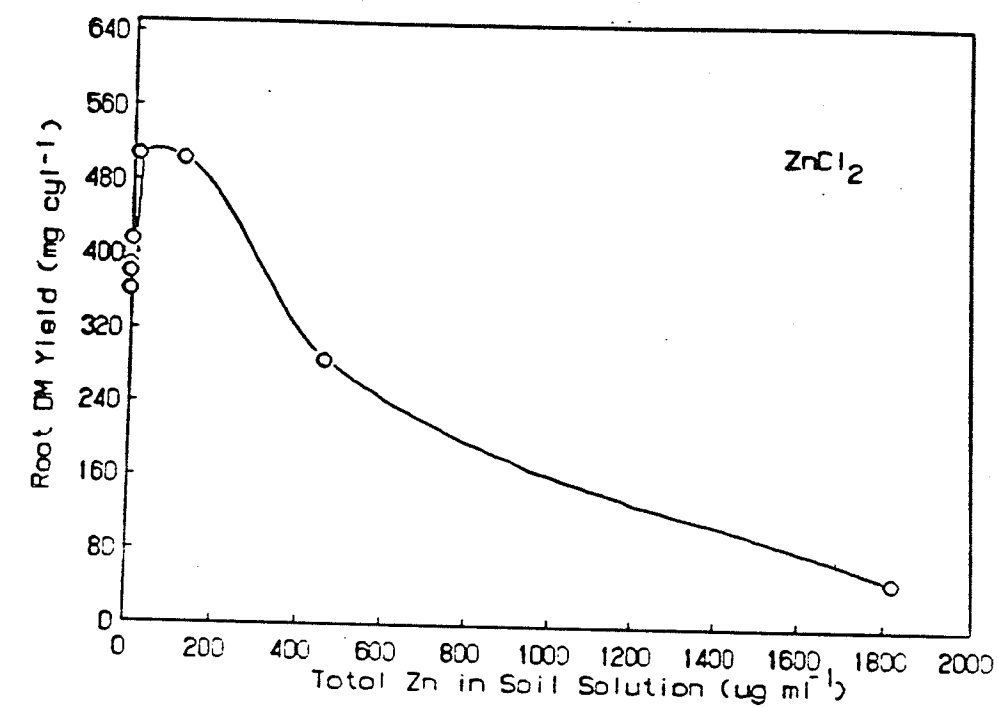


Figure 6.4. Effect of total amount of Zn in soil solution on root dry matter yield - Willowcrest FS (noncalcareous soil)

recovered from the ZnCl_2 fertilizer bands was consistently higher than the amount of roots recovered from the Zn-EDTA fertilizer bands (Fig. 6.4). Therefore, it appears that in such instances Zn-EDTA was more toxic to root growth than ZnCl_2 . It is also quite evident from results presented in Table 6.7 that considerable amounts of Zn in soil solution were present in the ionic as well as complexed form when Zn-EDTA was applied to the fertilizer band. But, it was difficult to determine whether the decrease in root growth that occurred in the Zn-EDTA fertilizer bands was associated with the ionic, complexed or both forms of Zn since the two forms of Zn co-varied considerably.

Concentrations of Zn in plant shoots increased with increase in concentration of Zn in soil solution for both Zn fertilizers, again indicating that high concentrations of Zn in soil solution were required for high Zn uptakes by the plants (Fig. 6.3 and Table 6.7). It is also important to note that in most instances concentrations of Zn in plant shoots treated with ZnCl_2 were consistently higher than concentrations of Zn in plant shoots treated with Zn-EDTA even when the concentration of Zn in soil solution was the same for both Zn fertilizers. As indicated earlier, the amount as well as quality of roots recovered from the ZnCl_2 fertilizer band in such instances was also greater than the amount as well as quality of roots recovered from the Zn-EDTA fertilizer bands. Thus, the results suggest that large amount of roots and high concentrations of Zn in the fertilizer band were essential for high Zn uptakes by the plants.

The results of experiments reported in section 6.0 confirmed results obtained in section 5.0 that root growth in Zn fertilizer bands

can be reduced. Both ZnCl_2 and Zn-EDTA when applied to small volumes of soil at high rates (simulated fertilizer band) reduced root growth as well as root quality. It should be noted that only two methods of Zn application were used in these studies. Therefore, other methods of application should be investigated to determine if Zn limits root growth in other types of fertilizer bands.

Root growth in fertilizer bands has been studied by Strong and Soper (1974a) as well as Racz et al. (1964) using P fertilizers. They found that various crop species varied in their ability to proliferate roots in the fertilizer band. Similar results were obtained in zones of application of high levels of N (Marschner 1986). Since various crops varied in their abilities to proliferate roots in P as well as N fertilizer bands it is reasonable to assume that various plant species may also vary in their ability to promote root growth in Zn fertilizer band. Thus, additional studies should be conducted to determine the response in root growth of various plant species in Zn fertilizer bands. Reports in the literature also showed that different plant species varied in their tolerance to excess Al (Reid 1971; Howeler and Cadavid 1976; Mugwira and Patel 1977).

It is also important to note that results obtained in this study showed that Zn complexed as Zn-EDTA as well as ionic Zn were both toxic to roots when present in high concentrations. In contrast, results reported in the literature indicate that only the ionic form of Al (Al^{3+}) was toxic to roots. Bartlett and Riego (1972), for example, noted that Al complexed with citrate, EDTA or soil organic matter extract was detoxified whereas ionic Al severely injured plant roots.

6.4. Summary and Conclusion

The extent of root growth in ZnCl_2 and Zn-EDTA fertilizer bands was controlled by the concentration of Zn in soil solution. High concentrations of Zn in the fertilizer bands were toxic to roots regardless of the source of Zn used.

Factors which affect the solubility of the Zn fertilizers in soils (soil type, source and rate of Zn applied as well as method of application) had a considerable influence on the extent of root growth in the Zn fertilizer bands.

The concentration of Zn in plant shoots was remarkably increased by high concentrations of Zn in soil solution. Increases in amount of roots also increased Zn uptake by plants. Thus, both the amount of roots and concentration of Zn in the fertilizer band were important factors in the utilization of Zn by plants from fertilizer bands.

7.0. EFFECT OF CONCENTRATIONS OF IONIC AND COMPLEXED ZINC IN
SOIL SOLUTION ON ROOT GROWTH AND ZINC UPTAKE FROM ZINC
FERTILIZER BANDS

7.1. Introduction

Results obtained from the previous plant growth studies clearly demonstrated that the extent of root growth as well as the quality of roots recovered from ZnCl_2 and Zn-EDTA fertilizer bands were significantly decreased by high concentrations of Zn in soil solution. Chemical studies conducted in conjunction with the plant growth studies revealed that virtually all the Zn in soil solution in fertilizer bands treated with ZnCl_2 was in the ionic form. It was therefore quite evident from the analysis of the data obtained that limited root growth into inorganic Zn fertilizer bands was closely associated with high concentrations of the ionic form of Zn in soil solution.

On the other hand, when Zn-EDTA was applied as a fertilizer band both the ionic as well as complexed forms of Zn were present in soil solution in significant amounts, and co-varied with increasing rates of Zn applied. According to results obtained so far high concentrations of Zn in the Zn-EDTA fertilizer bands also resulted in significant reductions in root growth into the fertilizer band. However, there was no conclusive evidence to associate the reductions in root growth in the fertilizer band to high concentrations of either the complexed or ionic form of Zn in soil solution or both.

Therefore, an additional plant growth study was conducted in conjunction with another chemical study to obtain additional information regarding the influence of amount of ionic and/or complexed forms of Zn in soil solution on root growth and Zn uptake from Zn fertilizer bands. The amount of complexed and ionic Zn in soil solution was varied by adding varying amounts of Na_2EDTA to ZnCl_2 fertilizer bands.

7.2. Materials and Methods

7.2.1. Plant Growth Study

A Willowcrest fine sand soil, low in DTPA-extractable Zn was used for the study (Table 7.1).

Table 7.1. Some of the physical and chemical characteristics of the soil used.

Soil Characteristics	Willowcrest (Gleyed Black)
pH (1:1 Soil:Water)	7.0
Inorganic Carbon (% CaCO_3 Equivalent)	0.2
Organic Matter (%)	2.5
DTPA-Ext. Zn ($\mu\text{g g}^{-1}$)	0.5
Field Capacity Moisture Content (%)	29.4
Texture	FS

The soil was air dried and sieved through a 2 mm sieve. 5000 g of the sieved soil was then weighed into 5 kg plastic pots. Prior to application of the Zn treatments the entire 5000 g of soil was uniformly mixed with 25 ml of each of four different nutrient solutions containing N, P, K, and Cu which were applied to the soil as basal treatments. The respective rates of application were 100 ug g^{-1} of N as $(\text{NH}_4)_2\text{SO}_4$, 50 ug g^{-1} of P as KH_2PO_4 , 200 ug g^{-1} of K as KH_2PO_4 and KCl and 5 ug g^{-1} of Cu as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The experiment was conducted as a completely randomized design. The treatments consisted of fertilizer bands at two rates of Zn as ZnCl_2 (6.12×10^{-6} and 4.89×10^{-5} moles Zn cm^{-3}), each rate of Zn uniformly mixed with five different rates of Na_2EDTA . (The low rate of Zn was found to stimulate root growth in the fertilizer band, while the high rate of Zn was found to be toxic to roots, when applied alone in a previous study). The amounts of Na_2EDTA added to the low rate of Zn were 0, 1.90×10^{-6} , 3.80×10^{-6} , 7.60×10^{-6} , 1.52×10^{-5} and 3.04×10^{-5} moles $\text{Na}_2\text{EDTA cm}^{-3}$, and the amounts of Na_2EDTA added to the high rate of Zn were 0, 1.52×10^{-5} , 3.04×10^{-5} , 6.08×10^{-5} , 1.22×10^{-4} and 2.43×10^{-4} moles $\text{Na}_2\text{EDTA cm}^{-3}$.

The required amounts of Na_2EDTA were weighed into large plastic weighing boats and uniformly mixed with 40 ml of a ZnCl_2 solution containing the required amount of Zn to be applied. The mixture was then incorporated in 200 g of soil which was then placed into acrylic cylinders of dimensions 5 cm high and an area of 32.15 cm^2 at the open ends. One end of the cylinders was closed using parafilm and the soil containing the various treatments placed into the cylinders. The

parafilm was then carefully removed, and the cylinders placed in the centre of the pot 5 cm below the soil surface. This was achieved by first removing about 3500 g of soil from the pot, placing the acrylic cylinders on the surface of the soil remaining in the pot and then replacing the soil that was removed from the pot.

Seeding, maintenance of the plants during the growing period, harvesting and handling of shoot and root samples was carried using the same procedures as described for previous plant growth studies. However, in this study in addition to recovering the roots from the fertilizer bands the amount of roots in the rest of the soil in each pot was also removed and weighed.

7.2.2. Determination of Ionic and Complexed Zn in Soil Solution

In conjunction with the plant growth study an incubation study was conducted to determine the concentration of ionic and complexed forms of Zn in the fertilizer bands with time.

A 200 g sample of soil was treated with N, P, K and Cu as outlined for the plant growth studies and placed in 250 ml centrifuge bottles. The rates of Zn and rates of Na_2EDTA applied in the plant growth study were used as treatments. The mixture was uniformly incorporated into the 200 g of soil in the centrifuge bottles using the same procedure as described for the plant growth studies, and water added to raise the moisture content to field capacity. Four sets of each treatment was prepared and each set of samples were incubated for a different time period i.e. 3, 14, 28 or 56 d. The incubation periods were selected to include the period of time from seeding to harvesting for the plant

growth study.

The soil solution from the incubated samples was obtained by centrifuging the samples at 10,000 rpm (13,000G) for 40 min. About 24 h before the samples were centrifuged the moisture content was increased to about 35 percent. The supernatant was filtered through Whatman #42 filter paper, the pH of the supernatant determined, and then the samples analysed for ionic and complexed Zn using the same procedure as described previously. Incubations were conducted in duplicate.

7.3. Results and Discussion

7.3.1. Total Shoot and Root Dry Matter Yields

Shoot dry matter yields with ZnCl_2 alone, were not significantly different from yields obtained in the control treatments (Table 7.2). Generally, shoot dry matter yields increased with amounts of Na_2EDTA applied to the low rate of Zn and then decreased when amounts of Na_2EDTA applied to the band were greater than 7.60×10^{-6} moles cm^{-3} . However, in most instances the differences were not significant. Shoot dry matter yield was not significantly affected by the amount of Na_2EDTA applied to the high rate of Zn when rates of Na_2EDTA were maintained at 1.22×10^{-4} moles cm^{-3} or less. A reduction in shoot yield occurred when Na_2EDTA was added at a rate of 2.43×10^{-4} moles cm^{-3} to the high rate of Zn.

The total amount of roots for plants treated with ZnCl_2 only was not significantly different from the amount of roots recovered from the

Table 7.2. Effect of rates of Na₂EDTA and Zn on shoot dry matter yield, root dry matter yield, and plant Zn content.

Rate of Zn Applied	Rate of Na ₂ EDTA Applied	Shoot DM Yield	Total Root DM Yield	Band Root DM Yield	Shoot Zn Conc.	Zn Uptake
(moles cm ⁻³)	(moles cm ⁻³)	(g pot ⁻¹)	(g pot ⁻¹)	(mg cyl ⁻¹)	(ug g ⁻¹)	(ug pot ⁻¹)
0	0	48.5 abc ¹	7.03 a	555 bc	11.5 f	558 e
6.12 x 10 ⁻⁶ (Low Rate)	0	46.1 bcd	7.79 a	675 a	31.9 e	1472 d
	1.90 x 10 ⁻⁶	42.5 d	5.79 b	613 ab	34.4 de	1464 d
	3.80 x 10 ⁻⁶	48.5 abc	7.15 a	520 c	26.4 e	1282 d
	7.60 x 10 ⁻⁶	51.0 a	5.79 b	247 d	24.3 e	1230 d
	1.52 x 10 ⁻⁵	50.2 ab	5.57 bc	133 efg	26.3 e	1316 d
	3.04 x 10 ⁻⁵	46.9 abc	4.61 cd	93 fgh	26.3 e	1230 d
4.89 x 10 ⁻⁵ (High Rate)	0	49.1 abc	6.82 a	79 ghi	56.6 b	2757 b
	1.52 x 10 ⁻⁵	47.1 abc	5.38 bc	180 de	74.7 a	3514 a
	3.04 x 10 ⁻⁵	48.1 abc	5.32 bc	159 ef	80.8 a	3887 a
	6.08 x 10 ⁻⁵	49.1 abc	5.66 b	44 hij	43.1 cd	2109 c
	1.22 x 10 ⁻⁴	45.5 cd	4.21 de	15 ij	43.3 cd	1975 c
	2.43 x 10 ⁻⁴	38.5 e	3.51 e	0 j	52.7 bc	2042 c

¹Duncan Multiple Range test. Means with the same letter within a column are not significantly different (P = 0.05).

control treatments (Table 7.2). The total amount of roots recovered from plants treated with the low rate of Zn were generally greater than the total amount of roots obtained in treatments that received the higher rate of Zn, and in some instances the differences were significant. The total amount of roots generally decreased as rate of Na_2EDTA applied was increased. Highest rates of Na_2EDTA substantially decreased the total amount of roots for both rates of Zn.

7.3.2. Root Dry Matter Yield From the Fertilizer Bands

The amount of roots recovered from fertilizer bands treated with 6.12×10^{-6} moles Zn cm^{-3} were generally much greater than the amount of roots obtained in treatments that received 4.89×10^{-5} moles Zn cm^{-3} (Table 7.2). A slight stimulation in root growth occurred in treatments with 6.12×10^{-6} moles Zn cm^{-3} but only when the plants were treated with ZnCl_2 only and with the lowest rate of Na_2EDTA . The amount of roots recovered from the fertilizer band then decreased gradually with amount of Na_2EDTA applied, and in most instances the decreases were significant when rates of Na_2EDTA were greater than 1.90×10^{-6} moles cm^{-3} . Root growth in the fertilizer band initially decreased fairly rapidly with amounts of Na_2EDTA applied and then remained relatively constant when rates of Na_2EDTA added to the band were greater than 7.60×10^{-6} moles cm^{-3} .

The amount of roots recovered from fertilizer bands treated with 4.89×10^{-5} moles Zn cm^{-3} were all significantly lower than the amount of roots recovered from untreated plants. Thus, all the fertilizer bands that received the high rate of Zn either alone or in combination

with Na_2EDTA were toxic to roots (Table 7.2). The amount of roots in fertilizer bands treated with 4.89×10^{-5} moles Zn cm^{-3} initially increased with amounts of Na_2EDTA applied, reaching a maximum in treatments with 1.52×10^{-5} to 3.04×10^{-5} moles $\text{Na}_2\text{EDTA cm}^{-3}$. Application of higher rates of Na_2EDTA to the fertilizer band resulted in significant reductions in root growth in the fertilizer band. In fact, no roots were found in fertilizer band that received 2.43×10^{-4} moles $\text{Na}_2\text{EDTA cm}^{-3}$.

7.3.3. Plant Zn Content and Zn Uptake

The concentration of Zn in plant shoots was significantly higher with ZnCl_2 , either alone or in combination with Na_2EDTA , than without Zn fertilizer (Table 7.2). Plant Zn content was greater when 4.89×10^{-5} moles Zn cm^{-3} was added than when 6.12×10^{-6} moles Zn cm^{-3} was added.

The concentration of Zn in plant shoots treated with the low rate of Zn was not significantly affected by the rate of Na_2EDTA applied to the fertilizer band. According to studies reported earlier (Section 6.0), Zn uptake by plants increased with increases in root growth as well as increases in concentrations of Zn in soil solution. Thus, it appears that in this study even though increasing the rates of Na_2EDTA increased concentration of Zn in soil solution the decreases in root growth with increasing rates of Na_2EDTA countered the effect of increasing Zn concentration (Table 7.2). The highest concentration of Zn in plant shoots treated with the low rate of Zn occurred in plants that received ZnCl_2 alone or very low rates of Na_2EDTA , suggesting that

the best combination between root growth and concentration of Zn in soil solution probably occurred in these treatments.

Plant shoot Zn content increased with amount of Na_2EDTA applied to the high rate of Zn, reaching a maximum when 3.04×10^{-5} moles $\text{Na}_2\text{EDTA cm}^{-3}$ were applied to the fertilizer band. The concentration of Zn in the plant shoots remained relatively constant as the amount of Na_2EDTA applied to the fertilizer band was increased further (Table 7.2). The greatest plant Zn content coincided with treatments that had the greatest amount of roots in the fertilizer band, again indicating that increased root to Zn fertilizer contact was very important for greater Zn uptake from the fertilizer bands. The results also show that despite the large reductions in root growth in the fertilizer bands that received the high rate of Zn the concentration of Zn in plants from such treatments was greater than concentration of Zn in plants treated with the lower rate of Zn (Table 7.2). Thus, high concentrations of Zn in the fertilizer bands was also very important for greater Zn uptake from the fertilizer band.

Zinc uptake by the wheat plants in response to the various treatments followed trends similar to that noted for plant Zn content (Table 7.2).

7.3.4. Concentration of Water Soluble Zn in Soil Solution

The total amount of Zn in soil solution was greater in fertilizer bands treated with 4.89×10^{-5} moles Zn cm^{-3} than with 6.12×10^{-6} moles Zn cm^{-3} (Figs 7.1 and 7.2). The concentration of Zn in soil solution increased with amount of Na_2EDTA added to the fertilizer band

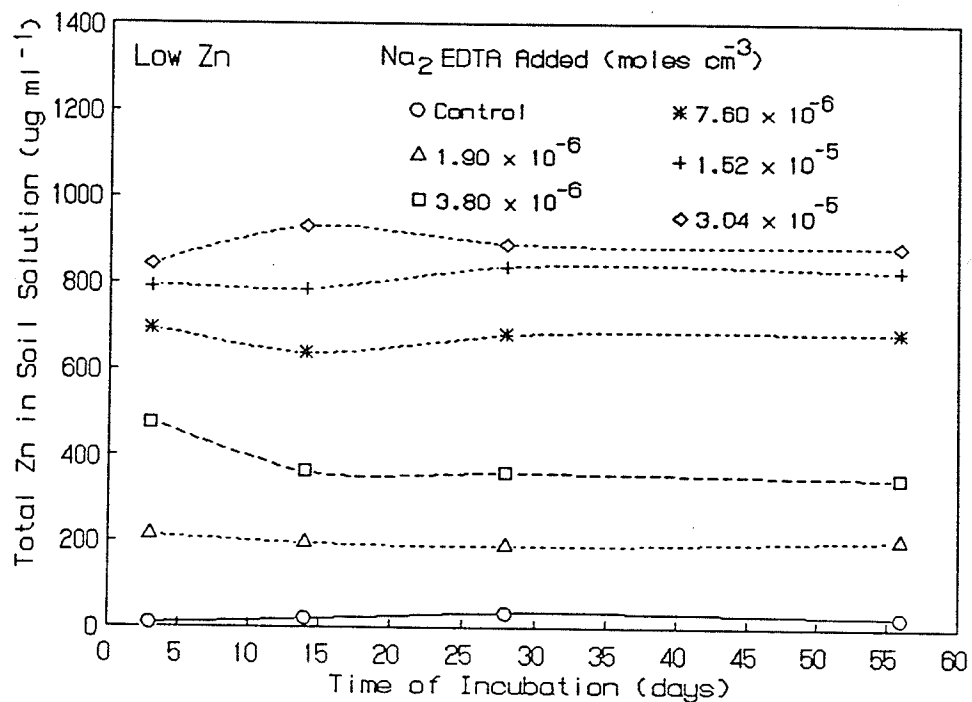


Figure 7.1. Effect of amount of Na₂EDTA and time of incubation on total Zn concentration - Low Zn rate

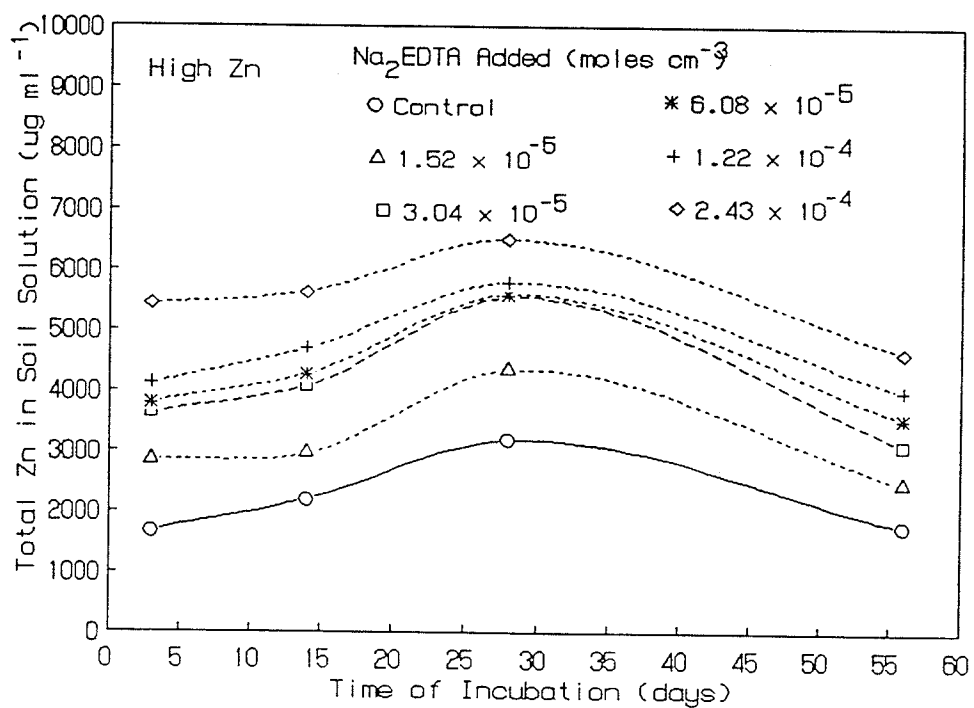


Figure 7.2. Effect of amount of Na₂EDTA and time of incubation on total Zn concentration - High Zn rate

suggesting that Na_2EDTA was quite effective in complexing the ionic form of Zn in soil solution and preventing precipitation and/or adsorption of Zn by soil constituents.

Concentration of Zn in soil solution remained relatively constant with time for the low rate of Zn, and also for the high rate of Zn except at 28 d. Concentrations of Zn in soil solution for treatments which were incubated for 28 d was slightly higher than concentration of Zn in treatments that were incubated for 3, 14, or 56 d (Fig. 7.2).

The concentrations of ionic Zn in fertilizer bands treated with 4.89×10^{-5} moles Zn cm^{-3} were always higher than the concentrations of ionic Zn in treatments that received 6.12×10^{-6} moles Zn cm^{-3} (Figs 7.3 and 7.4). The large difference in the concentration of ionic Zn in the two fertilizer bands can probably be attributed to the large differences in the pH of the soil solution for the two fertilizer bands as well as the amount of Zn applied. The pH of the soil solution in soils treated with the high rate of Zn varied from 5.55 to 3.64 whereas the pH of the soils treated with the low rate of Zn varied from 7.01 to 4.84 (Appendix B).

Application of Na_2EDTA to treatments with 6.12×10^{-6} moles Zn cm^{-3} increased the concentration of ionic Zn in soil solution above that with ZnCl_2 only. The amount of ionic Zn in soil solution increased with amount of Na_2EDTA added to the band, except for treatments that received the highest amount of Na_2EDTA which resulted in a sharp decrease in the amount of ionic Zn in soil solution (Fig 7.3).

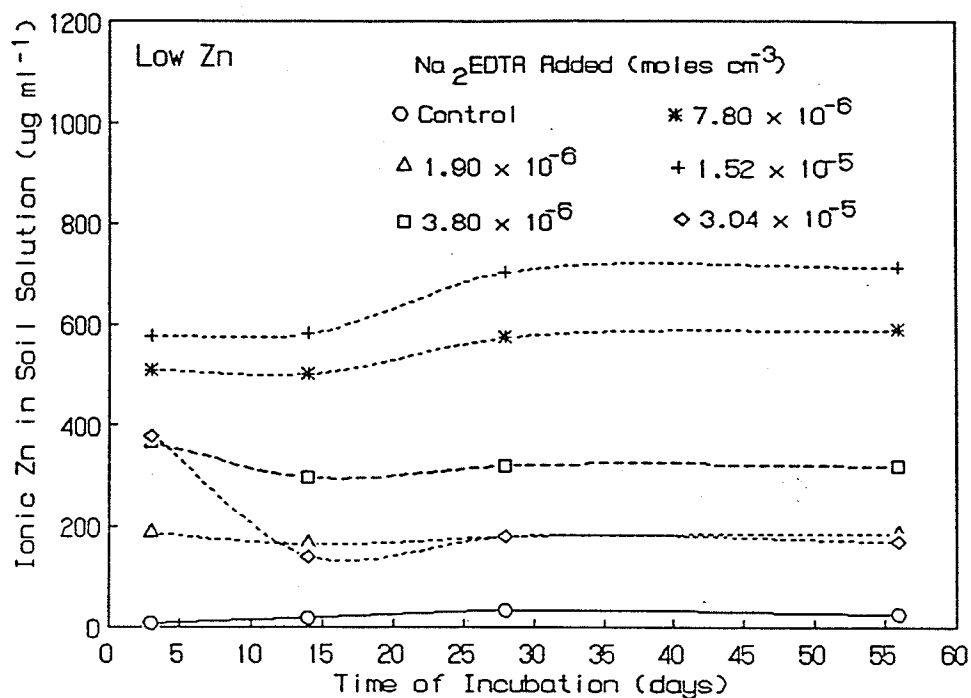


Figure 7.3. Effect of amount of Na₂EDTA and time of incubation on ionic Zn concentration - Low Zn rate

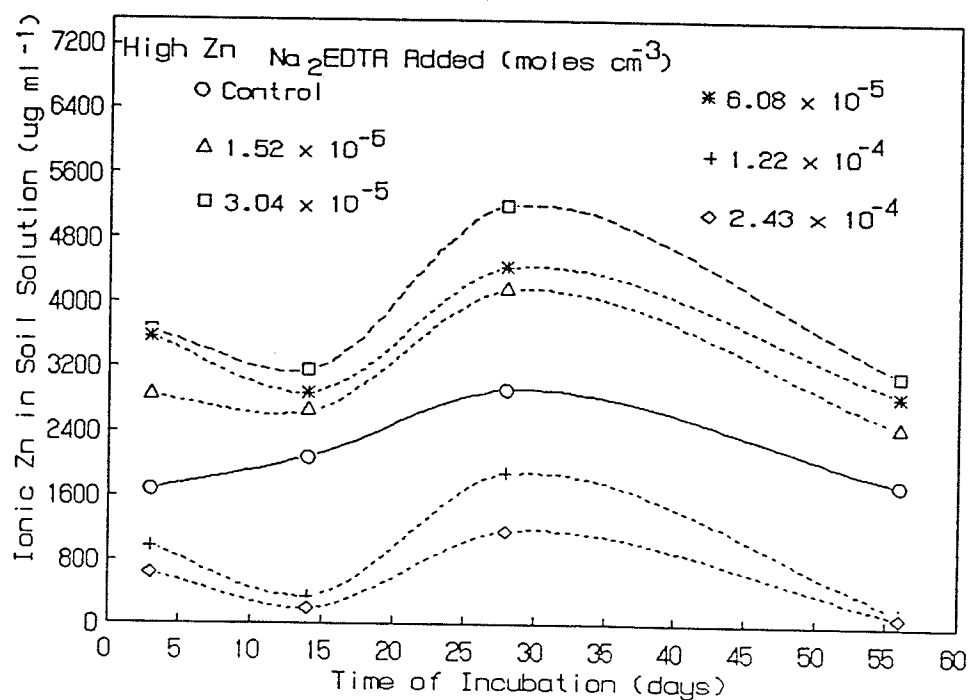


Figure 7.4. Effect of amount of Na₂EDTA and time of incubation on ionic Zn concentration - High Zn rate

The concentration of ionic Zn in soil solution for treatments that received 4.89×10^{-5} moles Zn cm^{-3} also increased with amount of Na_2EDTA added to the band. However, when the amount of Na_2EDTA applied was greater than 6.08×10^{-5} moles Zn cm^{-3} the concentration of ionic Zn in soil solution decreased sharply (Fig 7.4).

It was expected that concentrations of ionic Zn would decrease with increasing amounts of EDTA added. However, as noted above, ionic Zn concentrations increased with amounts of EDTA added except at very high levels of EDTA. It is highly possible that due to the low pHs encountered (Appendix B), Fe and other cations in solution increased due to dissolution of solid phases. Thus, the EDTA may have complexed with these dissolved cations rather than the applied Zn. Norvell and Lindsay (1969) showed that at low pH Fe^{++} would compete more effectively than Zn for EDTA. This would result in higher concentrations of ionic Zn than expected. Increases in ionic Zn concentration would be expected until sufficient EDTA was added to complex all dissolved cations that compete more favourably than Zn for the EDTA. Large decreases in ionic Zn concentration would thus occur only when very large amounts of EDTA were added. This was observed only for the highest rate of EDTA applied to the low rate of Zn and the two highest rates applied to the high rate of Zn.

The concentration of ionic Zn in treatments with 6.12×10^{-6} moles Zn cm^{-3} did not change appreciably with time of incubation (Fig 7.3). Ionic Zn concentration in treatments with 4.89×10^{-5} moles Zn cm^{-3} was also reasonably similar at 3, 14 and 56 d of incubation (Fig. 7.4). Ionic Zn concentration at the 28 sampling day period was higher than

for other incubation times. The experiment was not repeated to confirm whether or not the values obtained for the 28 d incubation period was due to error or soil reactions.

7.3.5. Relationships Among Concentrations of Total, Complexed and Ionic Zn

The reason for varying the rates of Zn as well as the rates of Na₂EDTA applied was to obtain different ratios of complexed and ionic forms of Zn in soil solution at different concentrations of total Zn. This was required in order to determine if complexed Zn was toxic to plant roots, since in previous studies concentrations of complexed Zn co-varied with concentrations of ionic Zn. It is evident that at both the low and high rates of Zn applied, fertilizer bands contained low to high concentrations of complexed Zn when ionic Zn concentrations remained constant at a relatively low concentration (Table 7.3). Thus, elucidation of the effects of complexed Zn on root growth in the fertilizer band was made possible.

7.3.6. Relations Among Ionic Zn, Complexed Zn and Mass of Roots in the Fertilizer Band

Since the concentrations of the various forms of Zn in soil solution remained relatively constant with time the concentrations measured at various times of incubation were averaged for each treatment (Table 7.4). The corresponding amount of roots recovered from the fertilizer band is also shown.

Table 7.3. Effect of rates of Na₂EDTA and Zn and time of incubation on concentration of total and ionic Zn in soil solution.

Rate of Zn Applied	Rate of Na ₂ EDTA Applied	Time of Incubation (Days)					
		3	14	28	56		
		<u>Total</u>	<u>Ionic</u>	<u>Total</u>	<u>Ionic</u>	<u>Total</u>	<u>Ionic</u>
(moles cm ⁻³)	(moles cm ⁻³)	(ug ml ⁻¹)	(ug ml ⁻¹)	(ug ml ⁻¹)	(ug ml ⁻¹)	(ug ml ⁻¹)	(ug ml ⁻¹)
6.12 x 10 ⁻⁶ (Low Rate)	0	9.7	8.7	20.5	19.8	35.2	26.2
	1.90 x 10 ⁻⁶	214	188	196	164	188	204
	3.80 x 10 ⁻⁶	476	366	362	296	360	348
	7.60 x 10 ⁻⁶	696	510	638	502	682	574
	1.52 x 10 ⁻⁵	714	578	786	582	840	704
	3.04 x 10 ⁻⁵	846	380	932	140	892	180
4.89 x 10 ⁻⁵ (High Rate)	0	1680	1680	2200	2080	3200	2920
	1.52 x 10 ⁻⁵	2840	2840	2960	2640	4360	4160
	3.04 x 10 ⁻⁵	3640	3640	4080	3160	5560	5200
	6.08 x 10 ⁻⁵	3800	3560	4280	2880	5600	4440
	1.22 x 10 ⁻⁴	4120	960	4700	340	5800	1880
	2.43 x 10 ⁻⁴	5440	640	5640	200	6520	1160
Control		0.22	0.03	0.34	0.12	0.50	0.00
						0.40	0.02

Table 7.4. Effect of rates of Na_2EDTA and Zn on root dry matter yield, concentration of ionic and complexed Zn in soil solution.

Rate of Zn Applied	Rate Na_2EDTA Applied	Ionic Zn	Complexed Zn	Root DM Yield
(moles cm^{-3})	(moles cm^{-3})	($\mu\text{g ml}^{-1}$)	($\mu\text{g ml}^{-1}$)	(mg cyl^{-1})
0	0	0.04	0.32	555
6.12×10^{-6} (Low Rate)	0	22.3	0.58	675
	1.90×10^{-6}	180	21.0	613
	3.80×10^{-6}	326	61.0	520
	7.60×10^{-6}	544	132	247
	1.52×10^{-5}	354	148	133
	3.04×10^{-5}	218	694	93
4.89×10^{-5} (High Rate)	0	2110	100	79
	1.52×10^{-5}	3030	130	180
	3.04×10^{-5}	3780	320	159
	6.08×10^{-5}	3440	870	44
	1.22×10^{-4}	840	3815	15
	3.42×10^{-4}	530	5030	0

The concentration of ionic Zn in soil solution was very poorly correlated with the concentration of complexed Zn in soil solution ($r^2 = 0.01$ NS). Thus, the covariance between the two forms of Zn was virtually eliminated in this study.

Multiple regression analysis of the data showed that the amount of roots in the fertilizer band was most closely correlated to the concentration of complexed Zn in soil solution. Root dry matter yield in the fertilizer band decreased with increases in concentration of complexed Zn in soil solution according to the relation:

$$\text{Root DM Yield (mg cyl}^{-1}\text{)} = 597 - 73.4 \ln (\text{Complexed Zn (ug ml}^{-1}\text{)})$$

$$(r^2 = 0.76^{**})$$

Thus, the results obtained in this study show that complexed Zn in soil solution is toxic to roots and toxicity increases with concentration.

7.4. Summary and Conclusions

The studies conducted conclusively showed that Zn complexed as Zn-EDTA as well as ionic Zn severely restricted root growth in fertilizer bands when the concentration of Zn was high.

Total root growth in the pots (in the fertilizer band + remaining soil in the pot) also appeared to be lower at high rates of Zn application than without Zn or with low rates of Zn.

Plant Zn content and uptake increased with amount of Zn applied. Increasing the rate of Na₂EDTA added to ZnCl₂ fertilizer bands increased the amount of total Zn in soil solution. Total amount of Zn in soilsolution remained relatively constant with time of incubation (3 to 56 d).

8.0. UTILIZATION OF ZINC BY WHEAT FROM ZnCl_2 FERTILIZER AS
AFFECTED BY METHODS OF PLACEMENT AND ADSORBING MATERIALS

8.1. Introduction

Results obtained from previous plant growth studies showed that the concentration of Zn in plant shoots usually increased with increasing concentrations of Zn in soil solution in the fertilizer band. Unfortunately, the amount as well as the quality of roots in the fertilizer band were reduced when the concentration of Zn in soil solution was very high. It was also shown that a low density of roots in the fertilizer band resulted in less Zn uptake than when the root density was high and increasing the size of the fertilizer band (increasing root to fertilizer contact) increased uptake when the concentration of Zn in the band remained constant. Thus, in order to maximize Zn uptake from a Zn fertilizer band, root growth into the band, fertilizer band size, and concentration of Zn in soil solution have to be balanced such that maximum utilization occurs. Therefore, a plant growth study was conducted in which a single rate of Zn was applied to various sizes of fertilizer bands as ZnCl_2 either alone or in combination with adsorbing materials (Fe_2O_3 or zeolite) to determine the optimum conditions for increasing the utilization of Zn from ZnCl_2 fertilizer bands. The adsorbing materials were added in an attempt to

reduce Zn concentration in the fertilizer band but hopefully to maintain it in a plant available form.

8.2. Materials and Methods

The study was conducted in the growth chamber using a Willowcrest fine sand soil (Table 8.1). The treatments were arranged in a completely randomized design and replicated three times.

Table 8.1. Some of the physical and chemical characteristics of the soil used.

Soil Characteristic	Willowcrest (Gleyed Black)
pH (1:1 soil : H ₂ O)	7.0
Inorganic Carbon (% CaCO ₃ Equivalent)	0.2
Organic Matter (%)	2.5
DPTA-Extr. Zn (ug g ⁻¹)	0.5
Field Capacity Moisture Content (%)	29.4
Texture	FS

Prior to application of the various treatments the soil was air dried, sieved through a 2 mm sieve and treated with N, P, K, and Cu using the same procedure as outlined for previous plant growth studies. 5000 g of soil was placed in each pot.

The treatments used in this study consisted of three sizes of fertilizer bands to which ZnCl₂ was applied either alone or in

combination with Fe_2O_3 or Chabazite (zeolite). An absolute control as well as a treatment in which the various Zn treatments were mixed throughout the soil were also included. The adsorbing materials were selected based on their differences in adsorption characteristics. Fe_2O_3 has been shown to adsorb significant amounts of Zn in soil solution both specifically as well as nonspecifically (Kalbasi et al. 1978a). On the other hand, Chabazite, a zeolite with the formula $\text{Ca}[\text{Al}_2\text{SiO}_4\cdot\text{O}_{12}]\cdot 6\text{H}_2\text{O}$ is considered to have a very large C.E.C. Grim (1968) reported that most zeolites have a C.E.C. in the order of 1000-3000 mmol kg^{-1} . The three sizes of fertilizer bands used were: (1) a narrow band, which was 0.63 cm wide (2) a wide band which was 2.54 cm wide and (3) a wide band (2.54 cm wide) which was incorporated to a depth of 1 cm. 1500 g of soil was removed from each pot, the fertilizer band applied, and then the soil was replaced. All the fertilizer bands were located approximately 4 cm below the surface of the soil and extended to a distance of 18 cm across the centre of the soil in the pots. A single rate of Zn, 5 $\mu\text{g g}^{-1}$ of soil based on 5000 g of soil, or 6.25 mg of Zn was applied in a volume of 1 ml as ZnCl_2 solution. Fe_2O_3 or zeolite was mixed with 1 ml of ZnCl_2 solution in ratios to obtain mixtures which contained 10 % Zn prior to application to the fertilizer band.

Ten wheat seeds were placed 2.5 cm deep and directly above the various fertilizer bands. Ten d after emergence the plants were thinned to 5 plants in each pot. The remaining plants were grown to the flowering stage which occurred about 65 d after seeding. Maintenance of the plants during the growing period, harvesting and

handling of the shoot samples were carried out using the same procedure as described for previous plant growth studies conducted in the growth chamber.

8.3. Results and Discussion

8.3.1. Shoot Dry Matter Yields

Shoot dry matter yields were not significantly affected by any of the treatments (Table 8.2).

8.3.2. Concentrations of Zn in Plant Shoots and Zn Uptake

Concentrations of Zn in plant shoots treated with ZnCl_2 alone was greater than in plants without ZnCl_2 (Table 8.2). However, the differences were significant only when the Zn fertilizer was applied as a narrow band or a wide band which was incorporated into the soil to a depth of 1 cm. In most instances concentrations of Zn in plants treated with ZnCl_2 in combination with Fe_2O_3 were less than that in plants with ZnCl_2 alone and only slightly higher than without Zn. Concentrations of Zn in plant shoots treated with ZnCl_2 in combination with zeolite were generally higher than concentrations of Zn in untreated plants (Table 8.2). The increases in plant Zn content were significant only when the ZnCl_2 and zeolite were applied as a wide band or mixed with the entire soil volume. The concentration of Zn in plant shoots when the ZnCl_2 + zeolite was mixed throughout the soil was higher than the Zn content of plants with all other treatments except for the treatment with ZnCl_2 applied in a wide band and incorporated into the soil to a depth of 1 cm.

Table 8.2. Effect of placement method of Zn fertilizer and adsorbing material on shoot dry matter yield, plant Zn content and Zn uptake.

Zn Treatment	Method of Application	Shoot DM Yield (g pot ⁻¹)	Shoot Zn Conc (ug g ⁻¹)	Zn Uptake (ug pot ⁻¹)
Control		40.9 a ¹	11.8 de	481 dc
ZnCl ₂ Alone	Narrow Band	40.4 a	14.0 bc	566 bc
	Wide Band	41.9 a	13.3 cde	513 dc
	Wide Band (Inc.)	41.6 a	15.8 ab	658 ab
	Mixed Throughout Soil	40.6 a	13.1 cd	532 c
ZnCl ₂ + Fe ₂ O ₃	Narrow Band	39.7 a	12.8 cd	502 dc
	Wide Band	40.4 a	10.6 e	428 d
	Wide Band (Inc.)	42.8 a	13.3 cd	569 bc
	Mixed Throughout Soil	42.1 a	12.3 cde	517 cd
ZnCl ₂ + Chabazite	Narrow Band	42.4 a	13.6 cd	576 bc
	Wide Band	39.1 a	13.9 c	543 c
	Wide Band (Inc.)	42.6 a	13.5 cd	573 bc
	Mixed Throughout Soil	41.8 a	16.3 a	678 a

¹Duncans Multiple Range Test. Means with the same letter within a column are not significantly different (P = 0.05)

Generally, the effect of various treatments on Zn uptake by plant shoots was similar to effects of treatments on Zn concentration in tissue since yields were not affected by treatment (Table 8.2).

Increasing the size of the fertilizer band or volume of soil fertilized above that of the narrow band did not increase fertilizer Zn uptake except when ZnCl_2 + zeolite was mixed with the entire volume of soil. Zn concentrations in plants was highest when ZnCl_2 + zeolite was mixed throughout the entire volume of soil. ZnCl_2 alone, applied in a wide band and incorporated to a depth of 1 cm also proved to be a highly effective treatment in increasing Zn concentration in plants.

The results obtained in this study suggest that the differences in plant Zn content among the various treatments applied can be attributed to the extent to which a balance between the concentration of Zn in soil solution and root growth into the fertilizer bands (root to fertilizer contact) was achieved.

Both the narrow and wide band treatments of ZnCl_2 were not highly effective in increasing Zn uptake into the plant shoots most likely due to toxicity effects of the fertilizer bands to plant roots. Application of the 6.25 mg Zn as narrow bands and wide bands resulted in rates of Zn equivalent to 0.55 and 0.14 mg Zn cm^{-2} , respectively. Previous studies, conducted on a slightly calcareous soil, showed that rates of Zn as low as 0.16 mg Zn cm^{-2} were detrimental to root growth. Thus, it is quite likely that the rates of Zn applied to the narrow and wide band treatments were toxic to roots and Zn utilization may have been restricted due to poor root growth in the fertilizer band.

The results obtained in this study also showed that incorporation of ZnCl_2 alone into a limited volume of soil was very effective in increasing the concentration of Zn in the plant. The higher plant Zn contents obtained in such treatments was likely a consequence of achieving a greater balance between the concentration of Zn in soil solution and root growth into the fertilizer band. Incorporation of the Zn into the soil to a depth of 1 cm resulted in rates of Zn equivalent to $0.14 \text{ mg Zn cm}^{-3}$. Previous studies conducted on the same soil showed that rates of Zn equivalent to $0.63 \text{ mg Zn cm}^{-3}$ resulted in maximum root growth into the fertilizer band (Fig. 6.1). Thus, concentrations of Zn in soil solution resulting from application of Zn at a rate of 0.14 mg cm^{-3} were obviously not high enough to retard root growth into the fertilizer band. The concentrations of Zn in the fertilizer band was also fairly high, at least when compared to treatments in which the Zn fertilizer was mixed throughout the soil. Thus, the required conditions for greater utilization of the Zn fertilizer i. e. greater root growth and relatively high concentrations of Zn in soil solution were probably almost achieved in this treatment.

Lack of significant increases in plant Zn content in treatments that received Fe_2O_3 and the Zn fertilizer suggest that some of the Zn applied was probably specifically adsorbed to the Fe_2O_3 . Kalbasi et al. (1978a) reported that Fe_2O_3 specifically adsorbed Zn and that specifically adsorbed Zn was not exchangeable with respect to Ca, Mg or Ba and thus probably not very plant available.

Zeolites retain Zn in exchangeable forms. The zeolite proved ineffective in enhancing Zn utilization above that with ZnCl_2 alone

when applied as bands. Thus, concentration of Zn in soil solution and root growth into the fertilizer band must have been similar to that with ZnCl_2 alone. Zn uptake with ZnCl_2 + zeolite was greater than with ZnCl_2 alone when the Zn fertilizer and the zeolite were mixed throughout the entire soil volume. In this treatment it appears, therefore, that Zn adsorbed on the zeolite was more plant available than Zn which was allowed to react with all soil constituents.

8.4. Summary and Conclusions

Application of ZnCl_2 fertilizer in a narrow or wide band was generally not highly effective in increasing plant Zn content probably due to limited root growth into the fertilizer as a result of Zn toxicity.

Concentrations of Zn in plant shoots was significantly increased when the ZnCl_2 fertilizer alone was incorporated into a limited volume of soil. It appeared that the greatest balance between the concentration of Zn in soil solution and root growth into the fertilizer band was achieved in this treatment.

Plant Zn content was also remarkably increased when the Zn fertilizer and zeolite were mixed throughout the soil. It appeared that the zeolite decreased the extent of retention of the Zn fertilizer by other soil constituents, making it more available to the plants. Mixing the Zn fertilizer throughout the soil either alone or in combination with Fe_2O_3 was not effective in increasing plant Zn content.

9.0. SUMMARY AND CONCLUSIONS

Utilization of Zn by plants from inorganic Zn fertilizers applied as narrow bands has been shown to be very limited. In contrast, Zn uptake by most plants was usually satisfactory when organically complexed Zn fertilizers were applied to soils as narrow bands. Studies were conducted using simulations of fertilizer bands to determine the causes for the large differences in Zn uptake by plants from organically complexed and inorganic Zn fertilizer bands. The simulated fertilizer bands consisted of small volumes or areas of soil treated with varying rates of ZnCl_2 or Zn-EDTA.

Studies were conducted, using sectioned soil columns to compare the solubility and extent of Zn movement from ZnCl_2 and Zn-EDTA fertilizer bands when applied to a calcareous and a noncalcareous soil. Concentrations of Zn in Zn-EDTA fertilizer bands were much greater than concentrations of Zn in ZnCl_2 bands for both soils, indicating that the Zn-EDTA fertilizer was more soluble than ZnCl_2 . Solubility of Zn in the Zn-EDTA bands was similar for both soils when it was applied alone. Solubility of Zn in the ZnCl_2 bands was much lower in the calcareous than in the noncalcareous soil.

The influence of macronutrient fertilizers on solubility of Zn in the fertilizer bands was studied. $(\text{NH}_4)_2\text{SO}_4$, Urea and $\text{NH}_4\text{H}_2\text{PO}_4$ increased the solubility of Zn-EDTA in the calcareous soil but decreased its solubility in the noncalcareous soil. $(\text{NH}_4)_2\text{SO}_4$ increased solubility of Zn in the ZnCl_2 bands in both soils. In contrast, $\text{NH}_4\text{H}_2\text{PO}_4$ decreased the solubility of Zn in the ZnCl_2 bands in both soils. Urea decreased the solubility of Zn in the ZnCl_2 bands in the

noncalcareous soil but increased its solubility in the calcareous soil.

Zinc movement from Zn-EDTA fertilizer bands was greater than Zn movement from ZnCl_2 bands. Movement of Zn from Zn-EDTA bands was greater in the calcareous than in the noncalcareous soil. $\text{NH}_4\text{H}_2\text{PO}_4$ was most effective in promoting greater movement of Zn from the Zn-EDTA fertilizer bands when Zn-EDTA + $\text{NH}_4\text{H}_2\text{PO}_4$ were applied to the calcareous soil. $(\text{NH}_4)_2\text{SO}_4$ promoted greater movement of Zn from ZnCl_2 bands in both soils. Thus, greater solubility of Zn in the fertilizer bands resulted in greater movement of Zn from the bands.

This study showed that the greater uptake of Zn by plants from Zn-EDTA fertilizer bands is probably due at least in part to greater solubility and movement of Zn from Zn-EDTA fertilizer bands. This study also showed that addition of other fertilizer salts such as $(\text{NH}_4)_2\text{SO}_4$, urea and $\text{NH}_4\text{H}_2\text{PO}_4$ can alter plant availability of Zn from both Zn-EDTA and ZnCl_2 fertilizer bands due to their effect on solubility and movement of Zn from the fertilizer bands.

A plant growth study was conducted to determine the influence of the extent of root to Zn fertilizer contact on utilization of Zn by plants from a ZnCl_2 fertilizer band. The amount of roots in the fertilizer band was varied by varying the size of the fertilizer band or funnelling the plant roots through the band. Root growth into the Zn fertilizer bands was severely retarded indicating that the fertilizer bands were toxic to roots. Fertilizer Zn uptake by plant shoots increased almost linearly with increase in the amount of roots in the fertilizer band ($r^2 = 0.82^{**}$). Thus, increasing the root to Zn fertilizer contact increased Zn uptake from the fertilizer band.

Addition of $(\text{NH}_4)_2\text{SO}_4$ to the fertilizer band resulted in a slight stimulation in root growth. Thus, Zn uptake from such treatments was also slightly higher than Zn uptake in treatments that received ZnCl_2 alone. Funnelling the roots through the fertilizer band was also effective in increasing the concentration of Zn in the plants.

Following the establishment of the fact that inorganic Zn fertilizer bands were toxic to roots, studies were conducted to compare the extent of root growth and Zn uptake by wheat from ZnCl_2 and Zn-EDTA fertilizer bands when the Zn fertilizers were applied to calcareous, slightly calcareous and noncalcareous soils. Various rates of Zn were applied in order to study the effect of concentration of Zn in soil solution on root growth and Zn uptake. For the calcareous and slightly calcareous soil the Zn fertilizers were applied to the surface of the soil contained in acrylic cylinders and for the noncalcareous soil the Zn fertilizers were mixed with a limited volume of soil (200 g). Incubation studies were also conducted to determine the concentration of Zn in the fertilizer bands. The total amount of Zn in soil solution was also separated into the ionic and complexed fractions.

Root growth was not affected by any of the rates of ZnCl_2 applied to the calcareous soil. Root growth was equally retarded by all rates of ZnCl_2 applied to the slightly calcareous soil. Root growth was stimulated considerably when low rates of ZnCl_2 were applied to the noncalcareous soil. However, when the rates of ZnCl_2 applied were high the amount as well as quality of roots recovered from the fertilizer band was severely reduced. Zn-EDTA reduced root growth in the fertilizer bands in all the three soils for most of the rates of Zn

applied.

Concentrations of Zn in the ZnCl_2 fertilizer bands were generally much lower in the calcareous than in the slightly calcareous soil when similar rates of Zn were applied. Concentrations of Zn in the fertilizer bands were quite low when low rates of ZnCl_2 were applied to the noncalcareous soil but when the rates of Zn applied were high concentration of Zn in soil solution were very high. Concentrations of Zn in Zn-EDTA fertilizer bands were much higher than concentrations of Zn in ZnCl_2 bands applied at equivalent rates of Zn for all three soils. Thus, these studies showed that the extent of root growth into the fertilizer bands was closely related to the concentration of Zn in soil solution. Root growth into the fertilizer bands was not adversely affected by low concentrations of Zn in soil solution. However, when concentrations of Zn in soil solution were high the Zn fertilizer bands were toxic to roots. Virtually all the Zn in soil solution in the ZnCl_2 fertilizer bands was in the ionic form. Thus, high concentrations of ionic Zn in the fertilizer bands were toxic to roots. On the other hand, significant amounts of ionic as well as complexed Zn were present in soil solution when Zn-EDTA was applied to the fertilizer band and both forms of Zn co-varied considerably. Thus, it was difficult to determine at this stage if high concentrations of complexed Zn were also toxic to roots.

Concentrations of Zn in plant shoots increased with rates of Zn applied. It was also quite evident that concentrations of Zn in plant shoots were much greater with Zn-EDTA than with ZnCl_2 when equivalent rates of Zn were applied to the calcareous and slightly calcareous soil

even though Zn-EDTA was more toxic to roots than ZnCl_2 in the calcareous soil. Thus, the studies showed that Zn-EDTA was likely more effective than ZnCl_2 in increasing plant Zn content at least in part due to its ability to maintain higher concentrations of Zn in soil solution at equivalent rates of applied Zn.

Concentrations of Zn in plant shoots were greater with ZnCl_2 than with Zn-EDTA when the Zn fertilizers were applied to the noncalcareous soil, although the concentration of Zn in soil solution was greater in the Zn-EDTA fertilizer bands than in the ZnCl_2 bands. However, the amount of roots in the ZnCl_2 bands was much greater than the amount of roots in the Zn-EDTA fertilizer bands. Thus, as indicated earlier greater amounts of roots in Zn fertilizer bands were very important for greater Zn uptake. These studies also showed that in order to maximize the utilization of Zn from Zn fertilizer bands the concentration of Zn in soil solution and root growth into the fertilizer bands have to be balanced.

In order to determine whether high concentrations of Zn complexed as Zn-EDTA were also toxic to roots, incubation studies were conducted to determine if the covariance between ionic and complexed Zn could be eliminated. Various rates of Na_2EDTA were applied to a low (non toxic) and a high (toxic) rate of Zn in ratios which were intended to vary the amount of ionic Zn complexed with EDTA. The effect of time of incubation (3 to 56 d) on concentration of Zn in soil solution was also studied. A plant growth study was also conducted in which the treatments used in the incubation study (except time of incubation) were used as treatments. The extent of root growth and Zn uptake from

the fertilizer bands was investigated.

The total amount of Zn in soil solution increased with amount of Na₂EDTA applied for both rates of Zn applied and remained relatively constant with time of incubation. Concentrations of ionic Zn increased with Na₂EDTA applied but when the rates of Na₂EDTA applied were quite high the concentration of ionic Zn decreased sharply. Concentrations of ionic Zn in soil solution were very poorly correlated with concentrations of complexed Zn in soil solution ($r^2 = 0.01$ NS). Thus, the covariance between complexed Zn and ionic Zn was virtually eliminated.

Root dry matter yields in the fertilizer band was most closely correlated to concentrations of complexed Zn in the fertilizer band. Root dry matter yield in the fertilizer band was decreased by high concentrations of complexed Zn in soil solution ($r^2 = 0.76^{**}$). Thus, the study showed that Zn complexed with EDTA as well as ionic Zn were toxic to roots when concentrations of Zn in the fertilizer band was high. Plant Zn content and Zn uptake increased with amounts of Zn applied.

Lastly, a plant growth study was conducted in which an attempt was made to balance the concentration of Zn in soil solution and root growth into the fertilizer in order to promote greater utilization of Zn from a ZnCl₂ fertilizer band. Zn fertilizer, at a rate of 5 ug of Zn g⁻¹, was applied either alone or in combination with adsorbing materials (Fe₂O₃ or zeolite) as follows: (1) a narrow band (2) a wide band (3) a wide band incorporated into a limited volume of soil (45 g) (4) mixed throughout 5000 g of soil.

The concentration of Zn in the plant was not increased by increasing the size of the fertilizer band suggesting that the narrow band as well as the wide bands were probably equally toxic to roots. Incorporation of the ZnCl_2 fertilizer alone into a limited volume of soil was very effective in increasing the concentration of Zn in the plants as well as Zn uptake. The results suggest that a greater balance between the concentration of Zn in soil solution and root growth into the fertilizer band was probably achieved in this treatment.

Incorporation of the Zn fertilizer throughout the soil with a zeolite was very effective in increasing the concentration of Zn in plant shoots. Thus, it appears that Zn adsorbed onto zeolite is more plant available than Zn allowed to react with all the other soil constituents. Mixing the Zn fertilizer throughout the soil either alone or in combination with Fe_2O_3 was not effective in increasing plant Zn content.

The major conclusion which can be drawn from the studies reported in this manuscript is that high concentrations of Zn in the fertilizer band as well as root to fertilizer contact are important in Zn uptake by plants from Zn fertilizer bands. Root growth in the Zn fertilizer band was shown to be greatly impaired when Zn concentrations in the band are high. Thus, in order to maximize Zn uptake a balance between root growth (or root to fertilizer contact) and Zn concentrations must be obtained.

10.0. BIBLIOGRAPHY

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APPENDIX A.

A QUANTITATIVE METHOD DEVELOPED TO SEPARATE IONIC ZINC FROM ZINC COMPLEXED WITH EDTA.

Background Theory

The solubility product of Zn(OH)_2 at a pH of 7.0 is given as 1.20×10^{-17} . Therefore, assuming equilibrium with Zn(OH)_2 the concentration of Zn in solution at various pH values can be calculated from the relation

$$(\text{Zn}^{++})(\text{OH}^-)^2 = 1.20 \times 10^{-17}.$$

Example

At a pH of 7.0 $(\text{H}^+) = 10^{-7.0}$ and $(\text{OH}^-) = 10^{-7.0}$.

$$\begin{aligned} \text{Thus,} \quad (\text{Zn}^{++}) &= \frac{1.20 \times 10^{-17}}{(\text{OH}^-)^2} \\ &= 1.20 \times 10^{-3} \text{ moles Zn L}^{-1} \\ &= 78.4 \text{ mg Zn L}^{-1} \\ &= 78.4 \text{ ppm.} \end{aligned}$$

Similarly, it can be shown that at a pH of 9.0 the concentration of ionic Zn in equilibrium with Zn(OH)_2 is 0.0078 ppm. Thus, at a pH of 9.0 virtually all the ionic Zn in solution is precipitated as Zn(OH)_2 . Based on the above theory, a method was developed to separate ionic Zn in solution from Zn complexed with EDTA.

Materials and Methods

Five different amounts of a 0.061 M Na_2EDTA solution were added to 50 ml portions of a 0.061 M ZnCl_2 solution in order to complex

different amounts of ionic Zn in solution as Zn-EDTA (Table A.1). The total concentration of Zn in the mixture (complexed + ionic) was first measured using an Atomic Absorption Spectrophotometer. The ionic form of Zn was then precipitated as $\text{Zn}(\text{OH})_2$ by treating the mixture with NaOH. The pH of the mixture was slowly raised to 9.0 using the NaOH in order to precipitate virtually all the ionic Zn in solution. The precipitate formed was filtered using Whatman No. 42 filter paper and then the concentration of Zn in the filtrate (complexed Zn) measured using the Atomic Absorption Spectrophotometer. The measured concentrations were then correlated with the expected values.

Results

The measured concentrations of complexed Zn were closely correlated to the expected values ($r^2 = 0.99^{**}$), in a ratio of almost 1:1. Therefore, the method was used to separate ionic Zn from complexed Zn in supernatants obtained from fertilizer bands treated with ZnCl_2 or Zn-EDTA.

Table A.1. Summary of procedure used to separate ionic Zn from Zn complexed with EDTA.

Sample No.	Volume 0.061 M Zn ml	Volume 0.061 M Na ₂ EDTA ml	Total [Zn] in the mixture (Measured) ug ml ⁻¹	Complexed [Zn] (pH = 9.0) (Measured) ug ml ⁻¹	Expected Complexed [Zn] ug ml ⁻¹
1	50	10	2730 ¹	470 ¹	550 ¹
2	50	20	2210	850	880
3	50	30	2170	1290	1290
4	50	40	2020	1650	1620
5	50	50	1850	1820	1850

¹Average of 2 replicates.

Appendix B. Effect of rates of Na₂EDTA and Zn and time of incubation on pH of the soil solution.

Rate of Zn Applied	Rate of Na ₂ EDTA Applied	pH			
		Time of Incubation (Days)			
(moles cm ⁻³)	(moles cm ⁻³)	3	14	28	56
6.12 x 10 ⁻⁶ (Low Rate)	0	7.01	6.58	4.65	4.87
	1.90 x 10 ⁻⁶	6.58	4.98	4.84	4.84
	3.80 x 10 ⁻⁶	6.70	5.01	5.02	5.18
	7.60 x 10 ⁻⁶	6.38	5.16	5.05	5.16
	1.52 x 10 ⁻⁵	5.93	5.37	5.18	5.32
	3.04 x 10 ⁻⁵	5.13	5.53	5.58	5.49
4.89 x 10 ⁻⁵ (High Rate)	0	5.55	4.33	4.55	4.72
	1.52 x 10 ⁻⁵	4.60	4.57	4.88	4.93
	3.04 x 10 ⁻⁵	4.08	4.24	4.53	4.64
	6.08 x 10 ⁻⁵	3.83	3.83	4.00	4.16
	1.22 x 10 ⁻⁴	3.64	3.81	3.99	4.23
	2.43 x 10 ⁻⁴	3.76	3.75	3.86	4.03
Control		7.54	6.42	5.19	5.03