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THE EFFECT OF SOIL SALINITY ON ZINC
UTILIZATION BY WHEAT AND BLACK BEANS

BY

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ABSTRACT

The effect of adding manganese and zinc to wheat and black beans grown in salt-affected soils was studied under growth chamber conditions.

Increasing soil salinity by mixing various proportions of saline and nonsaline soil decreased the yield of wheat and black beans significantly with all micronutrient treatments. Adding zinc alone or with manganese had no significant effect on wheat yields at all salinity levels. However, black bean yields on nonsaline soils and at low salinity levels were increased significantly by zinc application. Zinc content and zinc uptake by wheat decreased with increasing salinity, whereas salinity had no significant effect on zinc content of black beans. Zinc uptake by black beans, however, decreased with increases in soil salinity.

The effectiveness of two zinc fertilizers, ZnSO_4 and ZnEDTA, in salt-affected soils was also studied. Zinc sulfate was more effective in increasing yield and zinc content at high salinity levels than was ZnEDTA. However, ZnEDTA on nonsaline and slightly saline soils was more effective than ZnSO_4 when added at equal concentrations.

Addition of various salts to a nonsaline soil decreased the yield of wheat with or without added zinc. The effectiveness of different salts in depressing yield was similar with and without zinc and followed the order NaCl (10.1 mmhos/cm) $>$ MgCl_2 (8.9 mmhos/cm) $>$ CaCl_2 (8.8 mmhos/cm) $>$ MgSO_4 (B) (8.7 mmhos/cm) $>$ MgSO_4 (A) (5.5 mmhos/cm). The chloride salts were more toxic to the plants than sulfate salts. Zinc content of plants decreased when the soil was treated with MgCl_2 , CaCl_2 or CaSO_4 and increased when the soil was treated with NaCl or MgSO_4 . However, the greatest increases occurred when MgSO_4 was added. Adding

zinc increased zinc content at all salinity levels. Zinc uptake decreased when salts were added except with MgSO_4 where the zinc uptake increased.

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INTRODUCTION

Numerous studies have been conducted to determine the uptake of macronutrients by field crops from soils adjusted to varying levels of salinity. In contrast, studies on the influence of soil salts on micronutrient uptake and the extent to which growth can be improved by adding various kinds of micronutrient fertilizers are limited. Soil salinity greatly affects plant growth by its effect on increasing the osmotic pressure of the soil solution causing a water stress. Excess soil salts may also interfere with nutrient uptake. High salt concentrations may produce nutritional imbalances by decreasing or increasing the uptake of essential nutrients as well as causing specific ion toxicities.

Zinc deficiencies have been noted in both saline and nonsaline soils. Several soils in many parts of the world are both saline and zinc deficient. Thus, in order to obtain a better understanding of zinc deficiency in saline soils, studies were conducted to determine:

1. The effect of soil salinity on the utilization of native and applied zinc.
2. The extent to which zinc fertilizer may improve plant growth under saline conditions.
3. The efficiency of ZnSO_4 and ZnEDTA as zinc fertilizers on saline and nonsaline soils.
4. The cations or anions responsible for altering zinc utilization on saline soils.

LITERATURE REVIEW

I. Soil Zinc

The total zinc content of soils varies from 10 to 300 ppm (Lindsay 1972). Hodgson et al. (1965) found the concentration of zinc in soil solution to vary from 10^{-6} to 10^{-8} M of which 30 to 70% was present as inorganic ions. Exchangeable zinc is usually less than 1.0 ppm (Lindsay 1972).

Total zinc content of surface soils is greater than for subsoils (Hibbard 1940; Thorne et al. 1942; Wright et al. 1955; Lindsay 1972; Swaine and Mitchell 1960; Follett and Lindsay 1970). Total zinc concentration is greatest in soils that have accumulated organic matter from leaf fall and other plant residues for long periods (Hibbard 1940; Wright et al. 1955). Zinc is enriched in the surface soil by vegetative residues and this may be a major factor in zinc deficiencies of deep-rooted plants. In general, zinc is not leached and soil accumulations are closely associated with residues of organic materials.

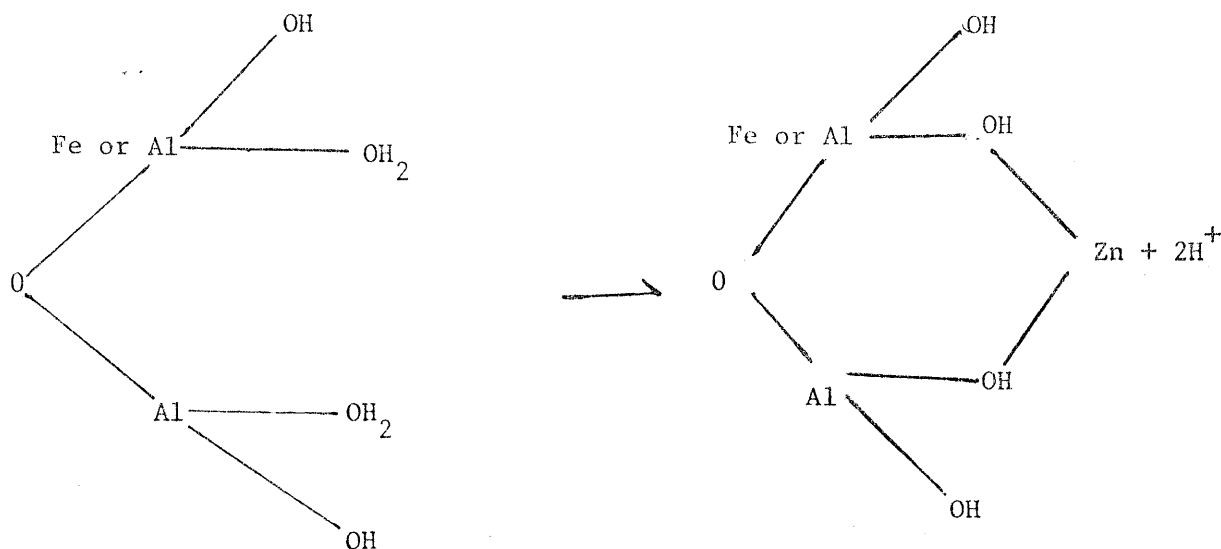
Zinc in soil is held by exchangeable sites and adsorbed to solid surfaces. Zinc in an active state in soil occurs either as the simple divalent cation (Zn^{2+}) or possibly as the monovalent $Zn(OH)^+$ ion (Russell 1973). Separation of zinc reactions into those of precipitation or adsorption is most difficult, and very few studies permit a clear conclusion on this point. One of the major problems in studying adsorption reactions of zinc has been the failure to consider which of the various hydrolysis and complex species of zinc in solution are adsorbed. Some workers have conjectured that retention of zinc in excess of the exchange capacity of soils may be due to precipitation of $Zn(OH)_2$, but the possibility of its precipitation has not been critically examined (DeMumbrum and Jackson 1956; Bingham and Sims 1964).

Most of the simple zinc compounds such as ZnO (zincite), ZnCO₃ (Smithsonite) are too soluble to persist in soils. Under reducing conditions where H₂S is produced, ZnS (Sphalerite) can form; but under normal oxidizing conditions the concentrations of S⁼ is too low for this mineral to be stable (Lindsay 1972). Kittrick (1976) examined the solubility of ZnS in the presence of H₂S and found the concentrations of H₂S actually found in the atmosphere are high enough to engender control of zinc in the soil solution of aerated soils by ZnS. However, these results contradict findings of McGregor (1972) who reported that adding ZnS maintained a higher zinc concentration in soil solution than for untreated soils. He concluded that ZnS did not control zinc concentration in soil solution. Kalbasi (1977) found that the zinc concentration in soil solution increased with time when ZnS was banded. In contrast, the zinc concentration in soil solution decreased with time when the soil was treated with ZnSO₄ and ZnEDTA. He attributed this difference to the partial oxidation of ZnS to less sparingly soluble compounds. He also found that the concentrations of zinc in extracts of soils treated with ZnEDTA were much higher than concentrations of zinc in extracts of soils treated with ZnSO₄. Zinc concentrations in soil solution were much lower when the soils were treated with ZnS than when they were treated with ZnSO₄ or ZnEDTA. His results indicated that when non-calcareous soils were treated with ZnSO₄, the reaction product was Zn(OH)₂ which persisted for only a few weeks. ZnSO₄ was precipitated as ZnCO₃ or Zn₅(CO₃)₂(OH)₆ in calcareous soils which persisted for 32 weeks or more. No solid-phase reaction products were found when ZnEDTA was banded in the soil. He suggested that this may be caused by zinc persisting in the soil as ZnEDTA resulting in low concentrations of ionic zinc in soil solution and therefore little or no

precipitation of zinc compounds near the ZnEDTA band. He also found that ZnS dissolved very slowly such that ZnS persisted in the soils at all sampling dates. He concluded that when very large amounts of zinc were applied to soil or when microregions in soil were saturated with zinc, such as a band or point source of application, the formation of new zinc solid phases, in addition to adsorption and fixation were very likely.

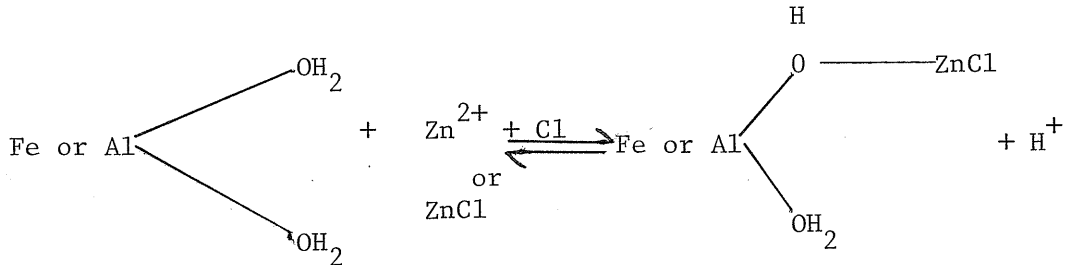
Jenne (1968) proposed that zinc, along with several other heavy metal ions, may be occluded and coprecipitated with hydrous oxides of manganese and iron and that these oxides form the principal matrix in which the less abundant heavy metals are held. Tillar (1967) concluded that the interaction between zinc and silicic acid is probably due to adsorption rather than formation of a separate zinc silicate phase. Nelson and Malsted (1955) studied the reaction of zinc with montmorillonite and concluded that strongly bound zinc was desorbed according to first-order chemical kinetics. Kalbasi (1977) postulated two mechanisms for zinc adsorption by oxides of Fe and Al (Fe_2O_3 and Al_2O_3):

1 - Specific zinc adsorption which involved adsorption of Zn^{2+} and the release of two H^+ ions for each mole of zinc adsorbed:



Adsorption by this mechanism accounted for 60 to 90% of zinc absorbed by Fe and Al oxides (Kalbasi 1977).

2 - Nonspecific zinc adsorption which involved adsorption of $ZnCl^+$ or Zn^{2+} plus Cl^- , and the release of one H^+ ion for each mole of zinc adsorbed:



Adsorption of zinc by this mechanism accounted for 10 to 40% of total zinc adsorbed and decreased markedly with increasing pH.

Udo et al. (1970) found that the adsorption of zinc by calcareous soils could be explained by the Langmuir adsorption equation and the solubility of zinc in calcareous soils corresponded to the solubility of zinc hydroxide or carbonate when the amount of added zinc exceeded the adsorption maximum. Algabaly and Jenny (1943) concluded that some adsorbed zinc becomes non-extractable by entering the octahedral layer of montmorillonite. Later, Elgabaly (1950) suggested that zinc might be fixed in holes normally occupied by Al^{3+} in the octahedral layer. Zn^{2+} with an ionic radius of (0.83Å) was found to substitute to some extent for Mg^{2+} (0.78Å) and Fe^{2+} (0.83Å) due to their ionic radii similarity (Goldschmidt 1954). Thorne (1957) indicated that zinc was adsorbed on the crystal surfaces of dolomite and magnesite at sites in the lattice that were normally occupied by Mg^{2+} . Zinc formed a silicate mineral (Souconite) when zinc substituted for Mg in montmorillonite (Lindsay 1972).

High levels of organic matter in the upper horizon of soil are believed to be important in keeping zinc more available in the surface horizon of soil. Numerous studies have demonstrated a high correlation between organic matter and chemically extractable or plant available zinc (Follett and Lindsay 1970; Martens et al. 1966). Apparently organic matter can interact with zinc in three important ways: -

1. Organic zinc can be mineralized and made available to plant.
2. Organic matter constituents can form mobile and labile complexes with zinc.
3. Zinc can be bound into organic constituents that are immobile in soils and constitute a fixation mechanism by which zinc is not readily released.

The presence of soluble zinc-organic complexes in soils was demonstrated by Hodgson et al. (1966). They concluded that on the average about 60% of the soluble zinc in soils was complexed with organic matter. The degree of complexing of zinc was correlated with soluble organic matter ($r = 0.88$). Stevenson and Ardakani (1972) reviewed the reactions of organic matter with micronutrients. They concluded that insoluble metal combinations were most likely bound to the humic fraction, particularly humic acid, while soluble metal complexes were mainly associated with individual biochemical molecules such as organic acids and amino acids. Metal complexes with fulvic acid were found to have high water solubilities.

Randhawa (1965a,b) studies the adsorption of zinc by humic acid. The least stable fraction that accounted for most of the zinc was believed to be associated with phenolic-OH and weakly acidic-COOH groups. The more stable fraction of zinc was bound by strongly acid-COOH groups. In his studies, strongly bound zinc represented less than 1% of the

total zinc retained.

II. Zinc in the Plant

Lack of zinc in plants results in distinctive plant symptoms associated with retardation of normal growth and a lack of chlorophyll. An abnormal shape of palisade cells and an almost complete absence of chloroplast and starch were also observed in zinc-deficient plants such as corn, tomato, buckwheat and mustard (Thorne 1957). Zinc plays an important role in auxin formation and in other enzyme systems. Zinc is recognized as an essential component in several dehydrogenases, proteinases, and peptidases (Vallee and Walker 1970).

Skoog (1940) investigated the relationship between Zn deficiency and auxin production. He could find no auxin activity in stems of zinc deficient tomato and sunflower plants and a very reduced activity in the leaves. When zinc was added to severely affected plants, auxin content increased greatly in one to a few days. He postulated that auxin destruction in deficient plants resulted from an increase in peroxidase activity. The role of zinc in auxin production of plants has been further clarified by Tsui (1948a). He confirmed the findings of Skoog with respect to the reduction in auxin content of zinc-deficient plants and further showed that the decrease in auxin applied to bound auxin as well as to free auxin. Tsui (1948b) found that within two days after zinc was added to deficient plants, the water content of the plants increased and growth resumed. The osmotic pressure of the sap of the tops of zinc-deficient plants ranged from 5 to 9 atmospheres, whereas that of the controls varied from 5 to 6 atmospheres. The changes in water content were directly related in time to changes in auxin content. These findings are consistent with the report of Skoog et al.(1939). He found the application

of indoleacetic acid (auxin) to decapitated stems increased uptake of water and salt. Van Overbeek (1944) also showed that auxin increased the uptake of distilled water by potato discs. Apparently the increased water in tissues in the presence of auxin did not result from water moving against a concentration gradient, but resulted from the action of auxin under aerobic conditions in causing a loosening of the cell wall which allowed the cell to absorb water and expand osmotically (Orden et al. 1956; Cleland and Bonner 1956).

Kessler and Monselise (1959); Brown and Hayward (1966); and Prask and Plocke (1971) found that RNA and ribosome levels decreased in zinc deficient plants.

The findings noted above show that zinc plays a role in production or functioning of several enzyme systems. However, the interrelationships involved have not been clarified.

III Factors Which Affect the Availability of Zinc in Soil

1. Soil pH

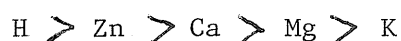
Plant uptake of zinc decreases as pH increases (Thorne 1957; Lindsay 1972). Lindsay (1972) found the solubility of zinc decreased 100-fold for each unit increase in pH. Lott (1938) showed that zinc toxicity was eliminated by the addition of CaCO_3 to a soil when the pH was increased to 6.0 or above. He found the minimum uptake of zinc by oat seedlings occurred at a pH of 6.5. Peech (1941) found Zn extracted with one normal NaCl increased with decreasing soil pH. Sharpless et al. (1969) suggested the decrease in availability of zinc with increasing pH was due in part to formation of Zn-hydroxide and Ca-zincate which have low solubility. Kalbasi (1977) felt that the decreasing availability of zinc with increasing pH was due to the adsorption of zinc by iron and aluminum oxides which increased with increasing pH. At low pH values,

some Zn^{2+} may be present on the exchange complex of soils, but at high pH values the level of Zn^{2+} in solution is so low that very little Zn^{2+} is held on the exchange complex (Lindsay 1972).

2. Soil Texture

Soils with a high proportion of clay retain or contain more zinc than soils with a high proportion of sand. Sandy soils are often deficient in available zinc since quartz is generally low in total zinc (Lucas and Kneezek 1972). Martens et al. (1966) found the amount of zinc extracted by 0.2 M $MgSO_4$ varied inversely with clay content.

Udo et al. (1970) found a good correlation between zinc content and organic matter and clay contents, suggesting that these two soil components are primarily responsible for retention of native zinc in some Arizona calcareous soils. The fixation of zinc in clay lattices was reported by Nelson and Melsted (1955). Zn^{65} was added to soils and clays with different exchangeable cations and measured zinc adsorption. The data indicated that zinc retention by soils in relation to other cations followed the order:



The low availability of zinc in soils with a high clay content may be due to two processes:

1. Adsorption on clay particles as Zn^{2+} or $Zn(OH)^+$
2. Precipitation of zinc as zinc hydroxide

It has been found that the strongest adsorption of zinc on crystal lattices was associated with surfaces that contain the Mg^{2+} ion (Thorne 1957).

3. CaCO₃ Content

The amount of $CaCO_3$ in the soil has an important effect on the availability of soil zinc to plants and zinc deficiencies are common

on calcareous soils (Thorne 1957). Calcareous soils have pH values of 7.4 or higher; the high pH values lower the availability of zinc; thus, zinc deficiencies would be expected on calcareous soils.

Leeper (1952) postulated that CaCO_3 may act as a strong adsorbent for heavy metals. Ravikovitch et al. (1968) found the zinc content of six crops grown on highly calcareous soils with a mildly alkaline reaction to be low; the zinc content of plants decreased with increases in the CaCO_3 level in the soil. Navrot and Ravikovitch (1969) used twenty-one calcareous soils and found an inverse relationship between native zinc absorption (content and uptake) by tomato plants and soil CaCO_3 content.

4. Organic Matter

Soil organic matter forms very stable complexes with zinc (Ellis and Kneezek 1972). Thorne (1957 and Baughman (1956) reported that zinc retained by organic matter was in two forms, chelated zinc and complexed zinc. Chelated zinc was defined as the portion of zinc that was extractable with copper acetate, whereas complexed zinc was designated as that portion which was not extractable by either copper or ammonium acetate, but which was released by oxidation of the organic matter with hydrogen peroxide. Thorne (1957) suggested that chelation and complexing of zinc by organic matter may be a significant factor in reducing zinc availability in soil. Several workers found that the Zn-organic matter complex supplied zinc in plant available form after it decomposed. Follet and Lindsay (1970) found a high correlation between organic matter content and DTPA extractable zinc. Martens et al. (1966) found that an increase in organic matter content at a constant level of clay increased the amount of zinc bound by the organo-clay complex, thereby resulting in increased extractability of soil zinc by 0.1 N HCl.