

CHEMICAL AND PLANT AVAILABILITY OF ZINC SORBED
BY HYDROUS IRON OXIDES

A Thesis Submitted to
The Faculty of Graduate Studies and Research
University of Manitoba

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by



WAEEL A.M. ELMOSLY

JULY 1985

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To My Gracious Parents

For Their Patience and Praying For Me

ABSTRACT

Zinc deficiency is one of the most common micronutrient deficiencies in agricultural crops. Reduction of Zn availability in many soils is attributed mainly to the rapid fixation and sorption of labile Zn by different soil components. The hydrous oxides of Fe and Al are considered to be the major reactive solid phase constituents responsible for the unavailability and fixation of Zn against plant uptake in soils.

The retention of Zn by hydrated iron oxide from aqueous solution was studied. Sorption of Zn by hematite ($\alpha\text{-Fe}_2\text{O}_3$) was highly dependent upon the pH of the equilibrium solution and increased markedly with increasing pH. Continuing adsorption of Zn at high pH values at which precipitation of $\text{Zn}(\text{OH})_2$ was expected to take place suggested that Zn was probably precipitated as $\text{Zn}(\text{OH})_2$ on surfaces of the oxide as well as being adsorbed. Capacity of the hematite for Zn sorption was very high provided the pH of the equilibrium system was maintained at levels which favoured sorption. Hydrogen ions were released upon adsorption of Zn on surfaces of the iron oxide. Ambient temperature during equilibration over the range 17 to 30 C had no significant effect on Zn adsorption on surfaces of the hematite.

Reversibility of Zn sorbed by hematite ($\alpha\text{-Fe}_2\text{O}_3$) was investigated. Zinc adsorbed on surfaces of the oxide at pH values of 6 and 7 were successively extracted at room temperature using deionized H_2O , 1.0 M MgCl_2 and 0.005 M DTPA buffered solution. A

large portion of the sorbed Zn was released upon extraction. Most of the total extractable Zn was extracted in the first two successive extractions and then decreased markedly with subsequent extractions. The portion of total sorbed Zn extracted was about 85% for DTPA, 33 to 60% for $MgCl_2$ and 6 to 50% for deionized H_2O . The desorption studies showed that Zn, depending upon reversibility, sorbed by $\alpha-Fe_2O_3$ can be categorized into "readily desorbed", "less readily desorbed" and "occluded and/or fixed" zinc .

The effect of ambient temperature during equilibration on desorption of Zn from hematite ($\alpha-Fe_2O_3$) was also studied. Zinc sorbed by the oxide at pH 7 was extracted at 17, 20, 25 or 30 C. Amounts of Zn extracted increased markedly with increasing temperature during equilibration indicating that the desorption reaction(s) of Zn from the surfaces of $\alpha-Fe_2O_3$ was an endothermic type of reaction. Extractable Zn increased in the order: deionized H_2O , $MgCl_2$, DTPA at a given temperature.

The extractability and chemical availability of Zn chemically combined with hematite added to a sandy soil was estimated using DTPA buffered solution as an extractant. Non-treated and soil samples treated with $ZnCl_2$ or $Zn-Fe_2O_3$ at a rate of 5 ppm Zn (soil basis) were incubated for 1, 2, 4, and 6 weeks at room temperature after wetting to field capacity moisture content. DTPA-extractable Zn from soil treated with $Zn-Fe_2O_3$ was higher than that of soil treated with $ZnCl_2$ suggesting that Zn sorbed by the hematite was more available in soil than Zn added as $ZnCl_2$. One to six weeks of

incubation had no significant effect on the extractability of Zn from Zn-Fe₂O₃ or ZnCl₂ added to the Almasippi sandy soil. It was concluded that Zn-Fe₂O₃ would be a good inorganic source of plant available zinc in soil.

A plant growth study using soybean as a test crop was carried out to estimate the plant availability of zinc chemically combined with hematite (α -Fe₂O₃). The dry matter yield of soybeans increased significantly when the Zn-Fe₂O₃ was added at rate of 5 ppm Zn. The increase in dry matter yield was about 40% when Zn-Fe₂O₃ was mixed throughout the soil, and about 25% when banded below the seed compared to the yield of control plants. Soybeans did not respond to the addition of ZnCl₂ at rate of 5 ppm Zn either when mixed with the soil or banded below the seed. Zinc concentration in the aerial portions of Zn-Fe₂O₃ treated plants was relatively low but was higher than that of the control and ZnCl₂ treated plants, indicating that Zn sorbed by hematite was available for plant absorption and utilization.

The effects of zinc source, rate and method of zinc application on soybean yield and Zn uptake were studied in a second growth chamber experiment. ZnCl₂, Zn-Fe₂O₃ and Zn-EDTA were used as sources of Zn for plants. Their effectiveness in increasing dry matter yield and Zn content of soybeans decreased in the order: Zn-EDTA, ZnCl₂, Zn-Fe₂O₃. Mixing fertilizer zinc as uniformly as possible with the total soil volume was much more effective than band application in increasing the yield and Zn concentration in the

plants. Increasing the rate of Zn added as $\text{Zn-Fe}_2\text{O}_3$ and ZnCl_2 from 5 to 10 ppm resulted in significant increases in Zn uptake and dry matter yield of soybeans. Concentration of Zn in plant tissues derived from the $\text{Zn-Fe}_2\text{O}_3$ was adequate suggesting that the "readily desorbed" and the "less readily desorbed" zinc, and perhaps the occluded fraction, were released from surfaces of the iron oxide and readily absorbed by plant roots. The results strongly indicated that zinc chemically combined with hematite was highly available for plant uptake and would be a good zinc fertilizer.

The plant availability and plant uptake of Zn from ZnCl_2 mechanically mixed with various amounts of hematite in a fertilizer band was also studied. Mechanically mixing 5 ppm Zn as ZnCl_2 with 0.1, 0.25, 0.5 or 1.0 g of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and banding it 2.5 cm below the seed resulted in highly significant increases in Zn uptake and dry matter yield of soybeans. This interesting fact suggested that application of an inorganic Zn fertilizer such as ZnCl_2 mixed with iron oxide in a fertilizer band would be more effective in increasing yield and zinc content of plants than band application of only the inorganic Zn fertilizer.

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I. INTRODUCTION

Zinc is an essential micronutrient for plant growth. Deficiency of zinc in agricultural crops is increasing in many parts of the world and it has now become one of the most frequently encountered micronutrient deficiencies. The zinc content of soils, according to rather extensive surveys, is generally in the range of 10-300 ppm. Certainly zinc, because of its low concentration, can be considered as a trace element in soil. Many studies have shown that zinc uptake by plants is not only dependent on soil content of zinc but is also greatly affected by soil temperature, soil texture, soil pH, CaCO_3 content, organic matter content, level of phosphorus, and plant species and varieties.

Fixation and adsorption of zinc by soils are often mentioned in the literature as chemical processes governing the concentration of ionic species of zinc in the soil solution. Clay minerals, carbonates, humic substances, and hydrous oxides of Fe, Al, and Mn have been suggested as possible constituents involved in the fixation (adsorption, co-precipitation and/or precipitation) of added zinc. This may induce Zn deficiency in plants and result in low efficiency of zinc fertilization.

Recently, soil chemists have paid much more attention to the adsorption of zinc by soil constituents, and the mechanisms by which hydrated iron and aluminum oxides adsorb zinc. More knowledge and a better understanding of the mechanisms of adsorption, bond strength, and the circumstances under which adsorption reaction(s) take place

are of extreme importance in determining the availability of zinc applied to soil and in improving the methods, rate and time of Zn fertilizer application. The research reported here was conducted to explore:

- (a) the factor(s) affecting the amount of zinc adsorbed on surfaces of iron oxide [hematite (α -Fe₂O₃)].
- (b) the reversibility of zinc adsorbed on surfaces of the hematite.
- (c) the chemical availability of zinc combined with the hematite added into a soil.
- (d) the plant availability of zinc adsorbed on surfaces of the hematite, and the uptake of zinc by plants from ZnCl₂ mixed with the hematite in a fertilizer band.

II. REVIEW OF LITERATURE

Iron Oxides in Soils

The hydrous metal oxides of iron, released upon weathering of many primary and secondary soil minerals, frequently form a considerable fraction of both temperate and tropical soils and markedly influence their chemical and physical properties. Schwertmann and Taylor (1977) reviewed the formation, crystal structure, and properties relevant to soils of different forms of iron oxides. They reported that the various crystalline iron oxides, oxyhydroxides, and hydroxides may occur in many forms in association with organic matter, as coatings on phyllosilicate clay minerals such as montmorillonite and vermiculite, or as discrete minerals. They may (i) determine soil color; (ii) promote aggregation and cementation; (iii) reflect some aspects of soil genesis; and (iv) create adsorption sites for various anions and cations, particularly those of importance in plant nutrition and environmental pollution.

Goethite and hematite are the most frequently occurring forms of iron oxides in soils followed by lepidocrocite, maghemite, ferrihydrite, and other forms such as akaganeite and limonite. Goethite is apparently not restricted to given climatic regions. It occurs in almost every soil type and climate region and is responsible for the yellowish-brown color of many soils, but hematite appears to be absent in soils recently formed under a humid

temperate climate. Hematite has a greater pigmenting effect than goethite and causes the red color of reddish soils. Schwertmann and Taylor (1977) also reported that even at low concentrations in a soil, iron oxides have a high pigmenting power and determine the color of many soils. Thus, soil color, as determined by the type and distribution of iron oxides within a profile, is helpful in explaining soil genesis and is also an important criterion for naming and classifying soils. Iron oxides also affect soil structure and fabric, often being responsible for the formation of aggregates and cementation of other major soil components, giving rise to granules, nodules, pipe-stems, or bog iron ores.

Many investigators have reported that goethite is the more strongly crystalline form of iron oxides and, thermodynamically, is the only stable oxide under most soil conditions. However, Schwertmann and Taylor (1977) concluded from different studies that under specific environmental conditions, the unstable crystalline forms of iron oxides such as lepidocrocite, ferrihydrite, hematite and maghemite will transform to goethite. Ferrihydrite will transform to goethite in the presence of high concentrations of organic compounds and highly oxidative conditions. The introduction of CO_2 into the system induces the transformation of lepidocrocite to goethite, and may account for the absence of lepidocrocite in calcareous soils. However, this transformation appears to be a very slow process in soils due to the low solubility of soil lepidocrocite and dissolution rate.

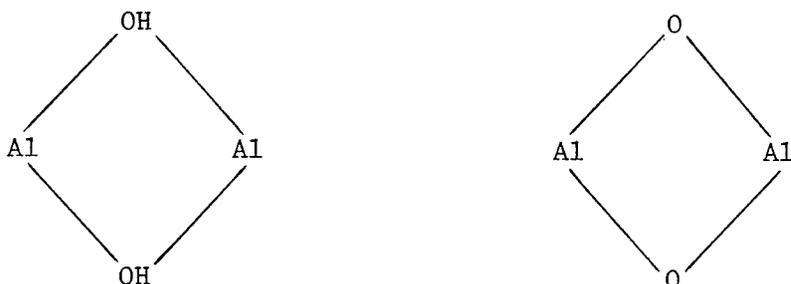
Schwertmann (1971) reported that hematite in sediments exposed to a subsequent cool and wet climate can frequently transform to goethite. The hematite is dissolved by reduction and/or complex formation, and the subsequent oxidation and/or precipitation causes the neo-formation of goethite. Also under the influence of organic matter supplied from the roots, hematite is transformed to goethite, as evidenced by the occurrence of a yellow zone adjacent to recent roots in a red soil. However, such transformations from amorphous or less crystalline materials to a more crystalline state change the surface properties of the colloids.

Characteristics of Fe and Al Oxides as Adsorbents

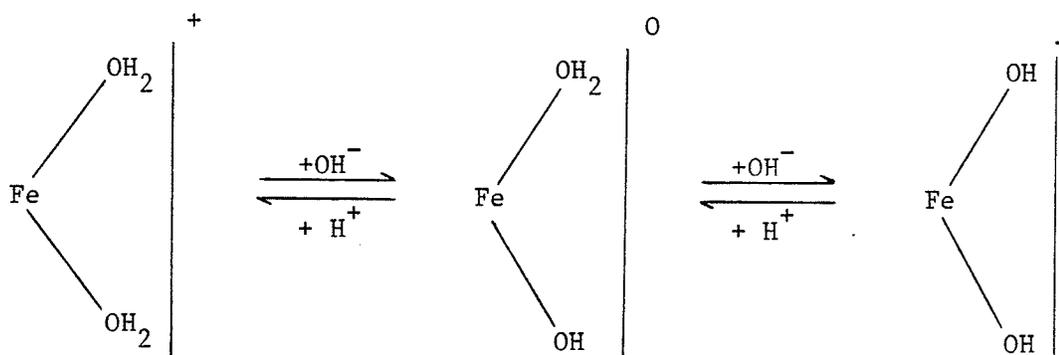
(a) Surface Charge:

It is postulated that hydrous oxides of Fe and Al play a significant role in controlling the concentrations of various ions in soil solutions and natural water systems. The reactions between these oxides and components of the soil solution take place at the solid-solution interface. Therefore, the structure and reactivity of this surface is an important property of iron and aluminum oxides.

Hydrous oxides of Fe and Al have a structure in which Fe and Al atoms are linked by (OH) and (O) groups as follows: (Hsu, 1968)



At the surface of the polymeric structure the co-ordinate positions of the terminal atoms are occupied by aquo ($\text{Al-H}_2\text{O}$) and hydroxo (Al-OH) groups. The relative proportion of the aquo and hydroxo groups is determined by suspension pH and this in turn determines the surface charge, i.e. the surface charge is created by an adsorption or desorption of H^+ (or a desorption or adsorption of OH^- , respectively) in the potential determining layer consisting of surface O, OH, and OH_2 groups. The H^+ and OH^- ions which establish the surface charge are therefore called potential determining ions (PDI). The following model has been proposed by Parks and de Bruyn (1962):



Concentrations of the potential determining ions and the net surface charge of the hydrous oxide are obviously pH dependent and thus, at any pH value, there will be present on the surface three types of sites: positive, negative and neutral. The pH value at which the number of positive sites equals the number of negative sites and the whole surface will be electrically neutral is termed the isoelectric point (IEP) or zero point of charge (ZPC) (Parks 1965). Various criteria have been used to distinguish between ZPC and IEP. Breeuwsma and Lyklema (1973) defined ZPC as the pH value at which the net surface charge is equal to zero but the IEP is the pH where the electrokinetic potential is zero. Isoelectric point is often taken as identical to the pH where the diffuse double-layer charge is zero.

The pH of the ZPC for a given oxide will depend on the relative basic and acidic properties of the solid. Strongly amphoteric oxides such as Fe_2O_3 and Al_2O_3 should have ZPC's near neutral pH while an acid oxide such as SiO_2 should have a ZPC at low pH values since it is a proton donor (Parks, 1965; Parks and de Bryun, 1962). The ZPC of complex mixtures of oxides and hydrous oxides, as might be found in soils, will be a complex function of all the various components involved. Values reported for the ZPC of synthetic hematite lie in the range of pH 7.5-9.3 (Atkinson et al., 1967). Parks (1965) reported that the ZPC values are generally lower for natural samples than those found for the synthetic ones. However, since the net charge on such a surface is dependent on the H^+ or OH^-

activity, it can be made positive or negative by raising or lowering the pH.

(b) Ion Adsorption:

Fe or Al atoms do not participate directly in charge development on the surface of their oxides. The charge is developed by association or dissociation of H^+ or OH^- ions on oxide surfaces. This surface charge is balanced by an equivalent amount of anions or cations (counter ions) present in ambient solution.

The adsorption of ions by sesquioxides has been classified by chemists into two types of adsorption. Schwertmann and Taylor (1977) reported that adsorption was termed "nonspecific" when the adsorbed ion is electrostatically held in the outer diffuse electric double layer. In contrast, the type of adsorption in which the counter ion is held much more strongly by the oxide surface through physical or chemical forces is termed "specific" adsorption. They further suggested that the specifically adsorbed ions penetrate the coordination shell of the Fe or Al atom, exchange their OH and OH_2 ligands and are bound by covalent bonds directly via their O and OH groups to the structural cation. However, the amount of a particular ion specifically or nonspecifically adsorbed by Fe or Al hydrous oxides depends mainly on its concentration in, and the pH of the equilibrium solution. Schwertmann and Taylor (1977) also reported that at a given pH, adsorption of a particular ion increases with increasing concentration in solution.

Adsorption of Ions on Surfaces of Sesquioxides

The chemical nature and generally high specific surface area of sesquioxides, in particles and as coating on other particles make them efficient sinks for anions such as phosphate, sulphate, molybdate, and silicate as well as trace elements like Cu, Ni, Co, Pb, Cr, and Zn, some of which are essential for plant growth. The adsorption capacity of these oxides arises from the existence of a pH-dependent surface charge.

The adsorption of anions, particularly phosphate, by hydrous metal oxides of Fe and Al has been extensively studied. These oxides adsorb extremely large amounts of phosphate and thus affect plant available P particularly in acid soils. Hingston et al. (1967; 1972; 1974) found that the adsorption of different anions such as phosphate, selenite, and fluoride on surfaces of goethite and gibbsite was highly dependent on suspension pH. Changing the pH alters the surface charge of the oxide. Hingston et al. (1967) reported that the maximum adsorption of phosphate occurred at low pH. They suggested that phosphate was adsorbed specifically by metal hydrous oxides by effecting a ligand exchange, displacing H_2O and/or OH that are co-ordinated to the metal atoms on the surface. Rajan et al. (1974) concluded that at low phosphate adsorption which corresponded to low phosphorus concentration, adsorption took place mainly by displacing aquo groups ($Al-H_2O$). With an increase in phosphorus concentration, hydroxo groups ($Al-OH$) became the predominant sites of adsorption. The increase in phosphate

adsorption with decreasing pH was explained by an increasing ratio of OH_2 to OH surface groups. Bowden et al. (1980) described the adsorption of phosphate, citrate, and selenite on the surface of goethite. They reported that the adsorption of these anions by goethite depended on several factors. These included pH, the concentration of adsorbing ions, and the concentration and properties of the electrolyte. Similar observations and conclusions were obtained by different investigators using sulphate, silicate, and molybdate as the adsorbates and iron and aluminium oxides as adsorbents (Hsu, 1977).

Convincing information was also obtained which indicated that the hydrous metal oxides of Fe, Al, and Mn, especially in their amorphous form, adsorb low quantities of different cations, particularly heavy metals, and may play a significant role in controlling the concentrations of these heavy metals in soils and water. Jenne (1968) proposed that in very many situations the level of Co, Ni, Cu, and Zn (heavy metals) in soils and fresh water is controlled by adsorption on the surface of oxides, particularly those of Fe and Mn. He further believed that sorption or desorption of these heavy metals occurs in response to the aqueous concentration of the metal in question; aqueous concentration of other heavy metals; pH; and amount and strength of organic chelates and inorganic complex ion formers present in solution. Quirk and Posner (1975) believed that Jenne's suggestions would likely be true for many soils of Australia.

Kalbasi and Racz (1978a.) found that large quantities of Zn were extracted along with the amorphous and organic complexed Fe and Al from a number of Manitoba soils indicating that Zn was in some manner associated with oxides of Fe and Al in Manitoba soils. They concluded that hydrous Fe and Al oxides are the principal solid phase components controlling the labile fraction of Zn in some Manitoba soils. Shuman (1979) reported that about 20% of native soil Zn in 10 Georgia soils was associated with crystalline and noncrystalline iron oxides. Similar results were found by Iyengar et al. (1981). They reported that most of the total Zn, on an average about 25%, in 19 different soils in eastern United States was present in a form bound with Al- and Fe-oxide. This form of Zn was correlated more closely with free Al than with free Fe content in these soils. They also found that about 2% of the total Zn in the same soils was associated with Mn-oxide. This fraction of Zn increased with an increase in both soil pH and free Mn content.

McKenzie (1977) reported that the manganese oxide minerals have large surface areas and carry a high negative charge in all soil environments except under extremely acid conditions. The negative charge results in a high sorption capacity, particularly for heavy metals, and thus manganese oxides may accumulate large amounts of these elements. This accumulation is particularly pronounced in the case of Co, and can lead to Co deficiency in pastures, and to fixation of Co applied as fertilizer. In a study conducted by McKenzie (1980), he found that large amounts of Pb, Cu, Zn, Co, Ni,

and Mn were accumulated by nine synthetic manganese oxides and three synthetic iron oxides. This adsorption was a function of pH. Kinniburgh et al. (1976) found that freshly precipitated Fe and Al gels strongly specifically adsorbed divalent cations of the alkaline earth cations (Ca, Mg, Ba, Sr), and the transition and heavy metal cations (Zn, Cu, Pb, Ni, Co, Cd) from 1.0 M NaNO_3 solutions. The ability of the gels to adsorb divalent cations specifically, suggests that they play a role in determining the plant availability and movement of some of these cations in the soil. They may also affect the distribution of trace elements in rivers, lakes, oceans, and reactor fuel wastes. The adsorbed amounts of these cations increased markedly with increasing suspension pH.

Therefore, it can be concluded that the hydrous metal oxides of Fe, Al, and Mn control the concentrations of anions as well as cations, some of which are essential for plant growth and others which behave as pollutants, in soils and fresh waters. The adsorption of these ions by hydrous oxides arises from the existence of a pH-dependent surface charge, otherwise these oxides do not possess a permanent electrical charge; instead their surface charge responds to the type and activity of the ions in the ambient solution. For example, the hydrous metal oxides may possess either a net positive or negative surface charge depending on the solution pH. This surface charge is normally balanced by the adsorption of counter ions of opposite charge.

Zinc Sorption by Sesquioxides

An understanding of the reactions which control the concentration of metals in natural waters and soil solutions is of great importance in maintaining and improving the fertility of soils and in developing pollution control procedures. The hydrous oxides of Fe, Al, and Mn have been suggested as possible constituents which control the concentrations of heavy metals in soil solutions and fresh waters. The role of these oxides in controlling heavy metal levels in soil can be satisfactorily understood only in terms of the factors which influence the sorption and desorption of the heavy metals by these oxides. Jenne (1968) proposed that pH, concentration of the metal ion of interest, concentration of competing metals, concentration of organic chelates and inorganic complex ion formers present in solution were the major factors affecting the adsorption and desorption of the heavy metals (Mn, Fe, Co, Ni, Cu, Zn) by sesquioxides of Fe and Mn. Chu 1968 (as found in Kalbasi 1977) reported that the retention of Zn on Al and Fe hydroxides was highly dependent on pH and on anion present in the solution. The amounts of Zn adsorbed by the hydroxides increased with increasing pH and more Zn was adsorbed by the hydroxides from a sulfate solution than from a chloride or acetate solution.

Kalbasi and Racz (1978a) found that the $\text{HNO}_3 + \text{HClO}_4^-$ extractable soil Zn concentration was highly correlated with Fe and Al concentrations and with clay content in a number of Manitoba soils varying in texture and Great Soil Group and Subgroup. Zinc

content was also significantly correlated with Fe and Al concentration when the clay size fraction was very small. They also found that relatively large quantities of Zn were extracted along with Fe and Al by an acid-oxalate solution. According to these observations, they suggested that the Fe and Al oxides were the major matrices for zinc in soils and the reaction between iron and aluminum oxides and zinc would play a significant role in determining the plant availability of Zn in Manitoba soils. This observation was supported by results of a laboratory study which showed that Zn was adsorbed by hydrated Fe_2O_3 and Al_2O_3 from aqueous solutions of ZnCl_2 (Kalbasi et al. 1978b.). The adsorption was highly pH-dependent and increased markedly with increasing pH. They concluded that specific adsorption of Zn by Al_2O_3 and Fe_2O_3 may be at least partially responsible for fixation and unavailability of added Zn in soils.

Stanton and Burger (1967; 1970) found that Zn was adsorbed on Fe and Al oxides by a mechanism involving polyvalent phosphate ions which may be important in soil systems when P is applied as a fertilizer. The adsorption of Zn on these oxides was affected by pH. They also showed that the more crystalline hydrated Fe oxides, such as goethite, fix Zn against plant uptake. Shuman (1977) found that Zn was adsorbed by aged and fresh iron and aluminum oxides. The adsorption capacities for the aged Fe oxide (goethite) and the aged Al oxide (gibbsite) were the same, but for both of the fresh oxides (amorphous) adsorption was about 10 times that for the aged

oxides which corresponded to a 10-fold difference between their respective CEC's and surface areas. He also found that the adsorption of Zn on all these oxides was greatly affected by pH. Studies of Zn affinity for oxides and hydroxides of Fe and Al (McBride et al., 1979; Kuo et al., 1980; Kinniburgh et al., 1982) showed a pronounced adsorption and a strong dependence of adsorption on pH.

(a) Influence of pH on Zn Sorption by Fe and Al Oxides:

Information obtained from the literature showed that adsorption of Zn on surfaces of hydrous oxides of Fe and Al is strongly dependent on the pH of the equilibrium solution. The surface charge of these oxides is determined by the activity of H^+ and OH^- ions in solution and by lowering or raising the pH, the net charge can be made positive or negative. At low pH the surface charge tends to be positive due to adsorption of protons (or loss of hydroxyls), at high pH it tends to be negative due to loss of protons (or adsorption of hydroxyls). This net charge is balanced by adsorption of anions or cations from the ambient solution.

McBride et al. (1979) studied the effect of pH and competing cations on Zn and Cu solubility in an acid mineral soil. The effect of suspension pH on the solubility of Zn in the presence of 0.015 M Ca^{2+} was shown on a pH-pZn curve. Changes in the slope of the pH-pZn curve occurred at three pH ranges; 4-5.4, 5.4-7.2, and > 7.2, respectively. The pH range of 4-5.4 showed a gradual increase in

the curve slope as a result of decreased Zn solubility. Between a pH of 5.4 and 7.2, the slope was essentially constant. At pH values higher than 7.2, a slope reversal occurred as a result of increased Zn solubility. They concluded that Zn solubility in soils with pH > 5.5 seemed to be determined by a nucleation or specific adsorption process, possibly involving Al and Fe oxides. At lower pH values, adsorption of Zn was reduced by competing cations, while at high pH (> 7.5) soluble Zn increased as organic complexes in soil solution became more evident. They further concluded that a single reaction mechanism probably cannot account for Zn and Cu solubility over a wide range of pH. The adsorption on hydrous oxide surfaces in soil is a more important mechanism for Zn than for Cu, since the results showed a great tendency of Cu to remain in organic complex form over a wide pH range. Kuo et al. (1980) found that the sorption of Zn, Cu, and Cd by three acid soils was a function of pH. Sorption of Zn occurred at pH levels below the zero point of charge of each soil used in the study and increased markedly with increasing pH. The maximum percent of Zn sorbed occurred in the pH range 6.3 to 7.1, depending on soil type. It was greater for the silty clay loam soil than for the silty loam and sandy loam soils, indicating that not only hydrous oxides of Fe and Al were responsible for the reduction of Zn concentration in soil solution but also the clay content and organic matter may have had some effect. Kinniburgh, et al. (1976) found that the divalent cations of the alkaline earth, transition, and heavy metal elements were

specifically adsorbed by freshly precipitated Fe and Al gels from 1.0 M NaNO_3 solution. The adsorption was strongly pH dependent. It occurred at pH values lower than the zero point of charge of Fe and Al gels. Although the pH at which adsorption started differed from element to element, the adsorption of ions of all elements used in the study increased markedly with increasing pH values from 6 to 8. They also concluded that the adsorption was highly selective at low pH values, since the divalent transition and heavy metal cations were adsorbed by Fe and Al gels at a considerably lower pH than were the alkaline earth cations. Kinniburgh and Jackson (1982) found that Zn concentration in, and the pH of the equilibrium solution were the primary variables controlling Zn adsorption by Fe gels. At equilibrium concentrations above about 10^{-5} M Zn, adsorption increased by roughly a factor of ten times between pH 5.5 and 6.5. At trace concentrations ($< 10^{-7}$ M), Zn adsorption was even more strongly pH-dependent, increasing by about 45 times for each unit rise in pH. Bar-Yosef et al. (1975) found that the initial pH value of the suspension was a very important factor determining the rate of Zn diffusion in goethite pastes. The diffusion rate at pH 5 was about five times higher than at pH 6 when all other conditions (electrolyte concentration, bulk density of the paste, and time) were equal. Quirk and Posner (1975) reported that Zn adsorption on goethite was strongly pH dependent and increased markedly with pH in the region of pH 5-7. More Zn was adsorbed from chloride solution than nitrate solution. Kalbasi et al. (1978b) found that the

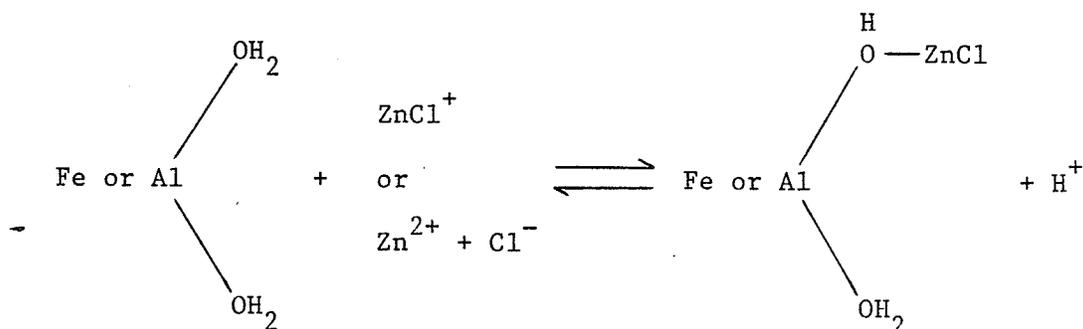
sorbing capacity of Fe and Al oxides was a function of the initial pH of the equilibrium solution. Values for pH varied from 6.42 to 6.92 for adsorption of Zn by Al_2O_3 , and from 5.93 to 6.96 for Zn adsorption by Fe_2O_3 in their study. Adsorption increased markedly with pH for both Fe_2O_3 and Al_2O_3 . The amount of Zn adsorbed (mmole/100 g) increased from 3.63 to 18.52 as suspension pH increased from 6.42 to 6.92 for Al_2O_3 and increased from 6.38 to 29.06 mmole/100 g as suspension pH increased from 5.93 to 6.96 for Fe_2O_3 . Release of H^+ ions upon Zn adsorption was an aspect of Zn adsorption by these oxides suggesting that surface aquo ($-\text{OH}_2$) and hydroxo ($-\text{OH}$) groups were involved in Zn adsorption. The molar ratio of H^+ released to Zn adsorbed increased with pH from 1.53 to 1.96. The results also showed that iron oxide adsorbed Zn at a lower pH than Al_2O_3 and had a higher adsorption capacity than Al_2O_3 at equal pH values. They attributed that to the lower isoelectric pH of Fe_2O_3 as compared to Al_2O_3 . Similar results were obtained by McKenzie (1980). He found that adsorption of Zn and other heavy metal ions (Pb, Cu, Ni, Co) increased markedly with increasing pH of the equilibrium solution. The results for the iron oxides showed that an increase of two pH units resulted in an increase in adsorption of the metal ions from a low value to 100% of the amount added. Moles of H^+ released per mole of metal ion adsorbed varied from 1.3 to 2.0. He concluded from this observation that the most likely forms of the adsorbed ions were M^{2+} and MOH^+ . Shuman (1977) studied the influence of aging and pH on the adsorption of Zn by Fe

and Al hydrous oxides. He found that Zn adsorption on the surfaces of both fresh and aged Fe and Al hydrous oxides, used in the study, occurred at a pH value (pH 4) lower than the points of zero charge which were pH 8.5 for the Fe oxide and 6.7 for the Al oxide. Adsorption increased markedly with increasing pH from 4 to 8. Maximum Zn adsorption by both fresh and aged Fe and Al hydrous oxides was at a pH value about 7 to 8 and decreased markedly at pH above 8. He concluded that Zn probably precipitated as $Zn(OH)_2$ at pH values above 8 causing reduction in Zn concentration in the equilibrium solution and hence low adsorption. He also found that the adsorption capacity of the aged Fe oxide was slightly less than that for the Al oxide, but that of the fresh Fe oxide was slightly higher than that of the Al oxide.

(b) Mechanism(s) of Zn Adsorption by Fe and Al Oxides:

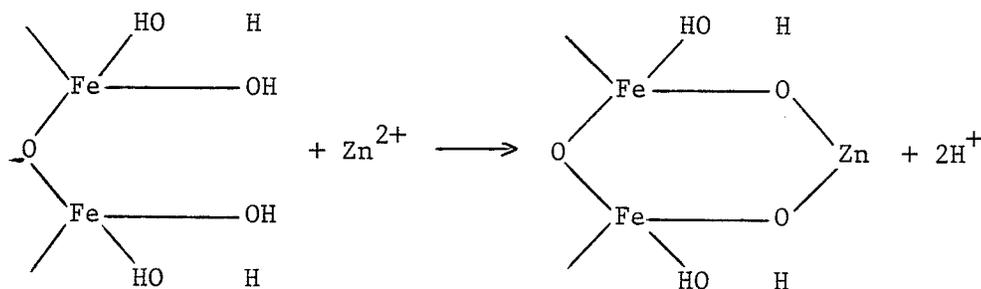
A strong association between Zn and the hydrated oxides of iron and aluminum was found to exist in different soils. This association may be the reason for both the unavailability of native Zn forms and fixation of applied Zn into a plant unavailable form. Although such an association exists, the mechanism(s) involved are not fully understood and have remained unsatisfactorily explained. Kalbasi et al. (1978b) proposed that Zn was adsorbed on surfaces of Fe and Al oxides through two mechanisms. The first mechanism likely involved adsorption of Zn^{2+} and Cl^- or the $ZnCl^+$ complex ion along with the release of one H^+ ion for each $ZnCl^+$ ion adsorbed. The

exact mechanism and location of ZnCl^+ adsorption on the surface was not clear. This adsorption was significant only at lower pH values, and they concluded that only aquo groups may have been involved. Adsorption of the ZnCl^+ complex ion was nonspecific for Zn, in that it could be replaced by divalent cations such as Ba^{2+} , Ca^{2+} , and Mg^{2+} . Considering the experimental evidence, they suggested the following mechanism of adsorption of the ZnCl^+ complex ion on the surface of Al_2O_3 and Fe_2O_3 :



The second mechanism likely involved adsorption of divalent zinc ions (Zn^{2+}) with the release of two H^+ ions for each Zn^{2+} ion adsorbed. In this mechanism, Zn^{2+} was adsorbed at pH values (6 to 7) below the isoelectric point of both Al_2O_3 and Fe_2O_3 . Therefore, they suggested, as was postulated by Quirk and Posner (1975), that hydroxo or aquo groups were more likely the source of H^+ ions because they were more abundant at pH values lower than the isoelectric point. In contrast to ZnCl^+ , adsorption of Zn^{2+} was

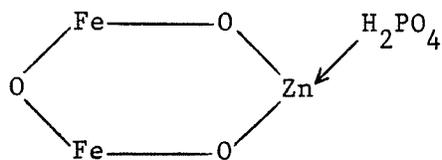
specific for Zn in that Ba^{2+} , Ca^{2+} , and Mg^{2+} could not replace it from the mineral surface. They further concluded that adsorption probably took place despite an unfavorable electrical potential caused by the large chemical affinity and therefore the Zn^{2+} ion was held by strong chemical bonding. The following mechanism, as was suggested by Quirk and Posner (1975), for specific adsorption of Zn^{2+} on the goethite surface was postulated by Kalbasi et al. (1978b):



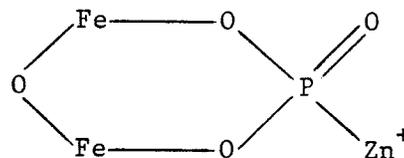
Kalbasi et al. (1978b) also reported that such adsorption could be viewed as a growth of an extension of the surface, since an octahedral bridge and ring structure was most likely formed as shown above. This type of bonding would be consistent with the lack of reversibility of such adsorption. They also found adsorption of Zn^{2+} ion was more significant at high pH than adsorption of the ZnCl^+ complex ion.

(c) Zinc Adsorption by Fe and Al Oxides in the Absence and Presence of Phosphate:

It is well established that adding large amounts of phosphate fertilizers to soils high in sesquioxides reduces zinc uptake by plants. Saeed and Fox (1979) found that phosphorus fertilization increased Zn adsorption by soils that contained colloids predominantly of the variable charge type. They concluded that phosphate additions to soils such as these increased zinc adsorption by increasing the negative charge on iron and aluminum oxide systems. Bolland et al. (1977) found that Zn adsorption by goethite in the absence of phosphate but in the presence of 0.1 M NaCl occurred at pH values below the isoelectric point of the goethite. They also found that the presence of phosphate or zinc on the goethite surface increased slightly the adsorption of zinc and phosphate, respectively. Their results suggested that Zn may adsorb on sites that do not adsorb phosphate and vice versa or that the zinc and phosphate form a complex on the surface of the goethite so that the phosphate adsorbs on adsorbed zinc and zinc adsorbs on adsorbed phosphate as follows:

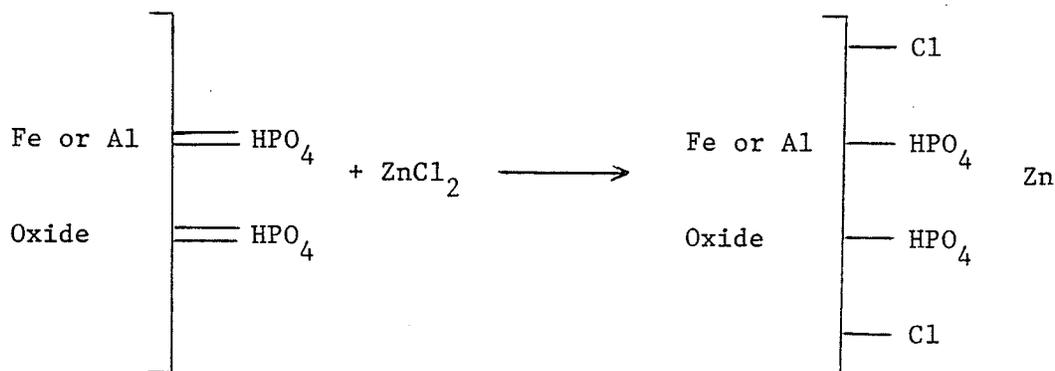


(a)



(b)

In a study conducted by Stanton and Burger (1967), they found that Zn absorption by Japanese millet decreased when grown in a system that contained Fe oxide but only when P was added. The effect of P was negligible in the absence of Fe oxide. They suggested that various hydrous oxides of Fe and Al can sorb Zn through the medium of adsorbed polyvalent phosphate ions as follows:



(d) Effect of Temperature on Zn Sorption by Fe and Al Oxides:

Very little information on the effects of temperature on amount of Zn sorbed by sesquioxides was found in the literature. Bowden et al. (1974) found that maximum Zn adsorption by goethite from 0.1 M NaCl solution occurred at 25 C. Temperature affects most adsorption-desorption processes and thus may play a significant role in sorption and desorption of Zn by sesquioxides. This in turn would affect the concentration of plant available Zn in the soil solution.

Plant Availability of Zn Sorbed by Fe and Al Oxides

Virtually no information was found in the literature on the availability to plants of zinc adsorbed on surfaces of any of the sesquioxides in soils. The only research concerning the determination of plant availability of zinc in a system containing Fe oxide is that of Stanton and Burger (1967). They employed two techniques in their studies. In one experiment, excised Japanese millet roots were exposed to aqueous systems containing Zn, P, and Fe oxide (or soil) in various combinations, and the absorption of Zn determined. In a second experiment the roots of intact Japanese millet plants were immersed in similar systems and the increase of Zn concentration in the aerial part of the plants determined. The results showed that the addition of phosphate, in absence of hydrous Fe oxide, had little effect on the absorption of Zn by the excised roots. Similarly, hydrous Fe oxide reduced Zn absorption only slightly in the absence of phosphate. But, when hydrous Fe oxide and phosphate were present together, no Zn was absorbed. Stanton and Burger (1967) concluded that in the absence of phosphate ions the availability of sorbed Zn apparently decreased as the crystallinity of the sesquioxide increased; although the amorphous hydrous sesquioxides had a strong affinity for Zn they did not fix it in a plant unavailable form, whereas goethite did. In contrast, the Zn was fixed strongly against plant uptake by the amorphous and crystalline sesquioxide varieties, if linked through the medium of polyvalent phosphate ions. These results may explain, in part,

why high rates of P in soils induce Zn deficiency in plants.

The review of literature shows that sesquioxides react with many metals such as zinc and the adsorption-desorption reactions involved may control the amounts of zinc in soil solution. Despite the many investigations showing that sesquioxides adsorb metals, very little information on the plant availability of these adsorbed metals was found in the literature.

III. MATERIALS AND ANALYTICAL METHODS

The investigations reported in this manuscript include several individual studies where different experimental methods were used. The experimental procedures used for these investigations are not described in a general methods section, but, for purpose of clarity, are discussed along with the results obtained, under the appropriate subsection. The analytical procedures employed in characterizing the soil, analyzing plant tissues, and the common experimental methods used for the growth chamber experiments are outlined below.

(A) Soil Analysis

The following procedures were used to characterize the soil used in the incubation and plant growth studies.

1. Soil pH:

Soil and distilled water (1:10 w/w) were equilibrated by shaking for 24 hours. The pH of the supernatant above the soil was measured using a glass electrode in conjunction with a calomel half-cell on a Beckman pH meter.

2. Electro-conductivity:

Conductivity of the same suspension used for the pH determination was read directly in mmhos/cm using a Radiometer conductivity meter.

3. Organic Carbon:

Organic carbon was determined as described by Walkley and Black

(1934). Excess potassium dichromate ($K_2Cr_2O_7$) was used to oxidize the organic carbon and the unreacted dichromate back-titrated with ferrous sulfate ($FeSO_4$) using barium diphenylamine sulphonate as an indicator.

4. Inorganic Carbonate Content:

One gram of air-dried soil sample was digested with 40 ml of 10% HCl for ten minutes. The carbon dioxide evolved was sucked through a drying and adsorption train and adsorbed by ascarite in a Nesbitt tube. The amount of CO_2 evolved was determined by weighing the tube before and after trapping the gas and the carbonate content of the soil calculated.

5. Mechanical Analysis:

The pipette method was used for particle size analysis. Ten-gram samples of air-dried soil were used. Organic matter was destroyed by the addition of 30% hydrogen peroxide. Ten ml of Calgon solution was added and the samples stirred mechanically for 30 minutes. The sand fraction was obtained by sieving the suspension through a 300 mesh sieve. The eluate was collected in a 1000 ml cylinder and made up to volume with distilled water. Aliquots were taken at a depth of 10 cm for an estimation of silt plus clay and clay fractions after allowing for the appropriate settling times. The percent sand, silt, and clay were then calculated.

6. Cation Exchange Capacity:

Soil cation exchange capacity (C.E.C.) was determined by the ammonium saturation method outlined by Chapman (1965). Exchange

sites of a 10 g soil sample were saturated with ammonium by shaking for one hour in 100 ml of 1.0 N $\text{CH}_3\text{COONH}_4$ solution containing 250 ppm lithium adjusted to pH 7 with dilute HCl. The suspension was filtered under suction and washed with $\text{CH}_3\text{COONH}_4$ until 250 ml was collected. The soil was washed with 250 ml of 95 percent ethanol. The adsorbed ammonium was displaced by leaching the soil with 250 ml of acidified 1.0 N NaCl. The filtrate was collected and transferred to an 800 ml Kjeldahl flask. Twenty-five ml of 1.0 N NaOH was added and the NH_3 distilled into 50 ml of 2% boric acid solution using a Kjeldahl distillation apparatus. The adsorbed NH_3 was titrated with standardized 0.1 N H_2SO_4 and the cation exchange capacity of the soil calculated.

7. Ammonium Acetate Extractable Ca and Mg:

Ten grams of air-dried soil was equilibrated with 100 ml of 1.0 N $\text{CH}_3\text{COONH}_4$ solution (pH = 7) by shaking for one hour. The suspension was transferred to a Büchner funnel and the soil leached with ammonium acetate solution to a volume of 250 ml. The Ca and Mg contents of the filtrate were determined by EDTA titration (Tucker and Kurtz 1961).

8. DTPA Extractable Zn, Cu, Fe, and Mn:

Plant available Zn, Cu, Fe, and Mn were determined using the procedure developed and described by Lindsay and Norvell (1978). The extractant consists of 0.005 M DTPA (diethylenetriamine-pentaacetic acid), 0.1 M TEA (triethanolamine), and 0.01 M CaCl_2 . The pH of extracting solution was adjusted to $\text{pH } 7.30 \pm 0.05$ using

1.0 N HCl. Triplicate ten gram samples of air-dried soil were placed into 125 ml conical flasks, and 20 ml of the DTPA extracting solution were added. Each flask was covered with stretchable Parafilm. The mixture was shaken, at room temperature (22 ± 1), for two hours using a mechanical horizontal shaker and then filtered through Whatman no. 42 filter paper. The filtrates were analyzed for Zn, Cu, Fe, and Mn using a Perkin-Elmer, Model 560 Atomic Absorption spectrophotometer.

9. Determination of Water Content at Field Capacity:

Triplicate air-dried soil samples were placed in acrylic cylinders measuring 4.5 cm in diameter and 20.5 cm in height. The bottom part of each cylinder was covered with Parafilm. Water was then slowly added to each cylinder until the wetting front had moved one third of the length of the soil column. After equilibrating for 48 hours, samples were taken from the wetted portion, dried at 105 C for 24 hours and the moisture content calculated on oven-dry basis. This moisture content was taken as the field capacity.

(B) Plant Analysis

Determination of Total Concentrations of Zn, Cu, Fe, and Mn:

Oven-dried plant samples were finely ground using a Wiley mill. One-gram samples were placed in digestion tubes. Six ml of concentrated nitric acid (HNO_3) were added to each sample. After two hours predigestion, three ml of 70% perchloric acid (HClO_4) were added to each sample and the samples were then digested by boiling

for approximately two hours until the solution completely cleared. The samples were allowed to cool for about two hours and then transferred into 25 ml volumetric flasks with 15 - 20 ml deionized water and made up to volume. Zn, Cu, Fe, and Mn in the diluted digest were determined using a Perkin-Elmer, Model 560 Atomic Absorption Spectrophotometer.

(C) Common Experimental Methods for the Growth Chamber Experiments

Soil:

The soil used in this study was collected from an Almasippi soil near St. Claude, Manitoba (NE $\frac{1}{4}$ 10-9-8W). The Almasippi soils in this area were suspected to be low in available Zn and/or Cu for maximum yield of crops. The soil was taken from the surface layer (0-15 cm depth) and stored under low temperature conditions to minimize the microbial activities. Later, it was air-dried, crushed, and mixed thoroughly. Some chemical and physical characteristics of the soil used is shown in Table 1.

Experimental Procedure:

The investigations involved two separate plant growth experiments using soybean (Glycine max L.) as a test crop. The soil samples were air-dried, crushed by hand to pass through a 2 mm sieve, and thoroughly mixed. Five kg soil were used for each pot in the first experiment and three kg soil were used for each pot in the

Table 1. Some characteristics of the soil used

- Soil Name	Almasippi
- Textural Class	Fine sand
Clay (%)	6
Sand (%)	90
Silt (%)	4
- pH	7.3
- Electro-conductivity (mmhos/cm)	0.4
- Organic Carbon (%)	0.84
- Inorganic CO ₃ (%)	None detected
- C.E.C. (cmole/kg)	9.1
- Exchangeable Ca (cmole/kg)	8.4
- Exchangeable Mg (cmole/kg)	0.9
- DTPA extractable Zn (ppm)	0.6
- DTPA extractable Cu (ppm)	0.2
- DTPA extractable Fe (ppm)	12
- DTPA extractable Mn (ppm)	9
- F.C. moisture content (%)	26.4

second experiment. Prior to seeding, the soil for each pot was thinly spread on a sheet of polyethylene and treated with the appropriate amounts of N, P, K, and S fertilizers in solution form. The N, K, and S fertilizer solutions were sprayed on the soil, but the P fertilizer solution was added by pipette. The entire soil mass was then thoroughly mixed and put in a plastic pot which was previously washed and cleaned to exclude any possible contamination of micronutrient elements.

The rates of nutrients added were calculated on an air-dried soil basis. All fertilizer salts were dissolved in deionized water. Nitrogen was added as NH_4NO_3 at a rate of 100 ppm N prior to seeding and every two weeks from planting date to harvest. Potassium and sulfur were added as K_2SO_4 at a rate of 100 ppm K and 40 ppm S. Phosphorus was added as $\text{NH}_4\text{H}_2\text{PO}_4$ at a rate of 50 ppm P. Zn and Cu treatments were varied and are outlined in detail for each experiment in the appropriate section.

Six soybean seeds, cultivar Maple Amber, were planted 1.5 cm below the soil surface in each pot and after 16 days the number of plants were thinned to four plants/pot in the first experiment and two plants/pot in the second experiment. Seeds were not inoculated in either experiment. The moisture content was then brought to 70% of field capacity and kept at this level until all seeds had emerged. After emergence the moisture content was brought to field capacity daily using deionized water.

The growth chamber temperature was maintained at 22 C for a

light period of 16 hours and at 16 C for an 8-hour dark period. The relative humidity was 35% and 80% for the light and dark periods, respectively. Both experiments were randomized complete block designs with four replicates in the first experiment, and three replicates in the second experiment. The position of the pots within the growth chamber was changed periodically to overcome any variation in environmental conditions. In both experiments, the plants were allowed to grow for about eight weeks. The aerial portion of the plants was harvested an inch above the soil surface, washed with deionized water, dried at 70 C for 24 hours and weighed. The dry matter yields were then determined. The plant materials were ground using a Wiley mill prior to tissue analysis.

Procedure for Cleaning Pots and Glassware:

Pots and glassware were cleaned using a three step procedure outlined below:

- (a) First, the pots and glassware were thoroughly soaked and washed with detergent and water to remove foreign particles, then rinsed with tap water, followed by 3-4 rinses with distilled water.
- (b) The pots and all glassware were then washed with 0.1 M Na_2EDTA to exclude any possible contamination of Zn, Cu, Fe, and Mn, and then rinsed thoroughly with deionized water about 3-4 times.

- (c) Finally, the pots and glassware were soaked in 1.0 N HCl for about 5 minutes and then rinsed 4-5 times with deionized water.

IV. PRESENTATION OF EXPERIMENTAL METHODS AND RESULTS

A. Zinc Sorption by Hydrous Iron Oxide.

(a) Effect of Equilibrium pH on Amounts of Zn Sorbed by Fe Oxide:

It is well established that a strong association exists between Zn and the hydrous oxides of Fe and Al in many soils. This association may be the reason for both the unavailability of native Zn forms and fixation of applied Zn into unavailable forms. However, from an agricultural standpoint, the need to understand the factor(s) influencing adsorption-desorption reaction(s) of Zn by Fe and Al oxides is of considerable importance in order to know whether or not Zn adsorbed on these oxides is reversible.

A strong dependence of Zn sorption, by Fe, Al and Mn hydrated oxides, on pH of the equilibrium solution has been reported. Many studies are in agreement that sorption of Zn by Fe oxides occurred at pH values below the isoelectric point of these oxides and increased with increases in pH, but, the effect of a wide range of suspension's pH on amounts of Zn sorbed has not been reported or was not found in the literature. Therefore, a sorption study was conducted to determine if a wide range of suspension's pH significantly affected amounts of Zn sorbed by iron oxide.

Samples of pure reagent grade Fe_2O_3 , obtained from Fisher Scientific Co. were used. The oxide was identified as crystalline $\alpha\text{-Fe}_2\text{O}_3$ (hematite). Duplicate sets of 0.1 g samples of

$\alpha\text{-Fe}_2\text{O}_3$ were placed in polypropylene centrifuge tubes. Increasing volumes of 0.1 M NaOH (0, 0.2, 0.4, 0.6, 0.8 and 1.0 ml) were added to the tubes and the final volumes adjusted to 25 ml with deionized water. The suspensions were then equilibrated by shaking for 24 hours on a mechanical horizontal shaker at room temperature (22 ± 1 C). After equilibration, the suspensions were centrifuged for 15 minutes at 12000 RPM and the supernatants filtered using Whatman number one filter paper. The pH's of filtrates were measured immediately after filtration (these pH values were designated initial pH values). Twenty-five ml of ZnCl_2 solution (80 ppm Zn, pH 5.8 ± 0.05) was then added to the oxide sediments in the same tubes, and the new suspensions equilibrated by shaking for 24 hours. Preliminary experiments showed that periods of equilibrium greater than 24 hours did not result in any detectable difference in the amounts of Zn sorbed. The suspensions were centrifuged after equilibration, filtered, and pH's of filtrates measured (these pH values were designated final pH values). Zinc ion concentrations of the filtrates were determined using a Perkin-Elmer, Model 560 Atomic Absorption Spectrophotometer. Amounts of Zn sorbed was calculated from the difference between Zn concentration after equilibration and the initial concentration of Zn added (80 ppm). Eighty ppm was chosen since preliminary experiments showed that no Zn precipitated as $\text{Zn}(\text{OH})_2$ from an 80 ppm Zn solution unless the pH was greater than 7.5.

A second experiment was conducted, using the procedure outlined

above, to study the effect of pH with respect to the pH of the ZnCl_2 solution added on the amounts of Zn sorbed by iron oxide. One-tenth g samples of $\alpha\text{-Fe}_2\text{O}_3$ (hematite) were placed in centrifuge tubes and different volumes of 0.1 M HCl or 0.1 M NaOH added to the tubes. Each treatment was duplicated and the final volume of each tube was adjusted to 25 ml with deionized water. The suspensions were then shaken for 24 hours, the samples centrifuged, the supernatants filtered, and the initial pH's measured. Twenty-five ml of ZnCl_2 solution (80 ppm Zn) was then added to each tube. The pH's of the ZnCl_2 solutions were previously adjusted to pH 6 or 7. The suspensions were equilibrated by shaking, centrifuged, filtered, and the final pH's measured. The filtrates were saved for measurement of Zn concentration using an Atomic Absorption Spectrophotometer. The amounts of Zn sorbed were calculated by subtracting the concentration of zinc in the filtrates from the initial concentration of Zn added (80 ppm).

It is well established in the literature that the adsorption of Zn on surfaces of iron and aluminum oxides results in a decrease in the pH of the equilibrium solution, indicating that protons are released from the oxide surface accompanying such adsorption. Therefore, a third experiment was conducted to obtain information on whether or not increasing the pH of the equilibrium solution, after the initial sorption reaction(s) has taken place, has an effect on the amounts of Zn adsorbed on surfaces of the iron oxide. The experimental procedure used was similar to that employed in the

previous two experiments. Duplicate samples of 0.1 g α -Fe₂O₃ (hematite) were placed in centrifuge tubes, different volumes of 0.1 M HCl and 0.1 M NaOH added, and the final volumes adjusted to 25 ml with deionized water. The suspensions were equilibrated, centrifuged, filtered, and the pH of filtrates measured (initial pH's). Twenty-five ml of ZnCl₂ solution (adjusted to pH 7, 80 ppm Zn) was added to each tube and the suspensions equilibrated. At equilibrium, one-half of the samples were treated with 0.1 ml of 0.1 M NaOH, and one-half of the samples were treated with 0.2 ml of 0.1 M NaOH. The suspensions were again shaken for 24 hours to attain equilibrium, the tubes centrifuged and the supernatants filtered. The pH's of filtrates were measured (final pH's) and the Zn concentration determined by Atomic Absorption Spectrophotometry. The amounts of Zn sorbed were calculated from the difference between amounts of Zn added and amount of Zn remaining in solution after equilibration.

It is of importance in sorption studies to know all possible ionic species and complex ion forms of the metal ion under study. In this zinc sorption study, the possible ionic species of zinc in equilibrium systems were: divalent zinc ions (Zn²⁺), monovalent zinc complex ions (ZnOH⁺ and ZnCl⁺), and neutral molecules of Zn(OH)₂ ion pairs.

Sorption of zinc by the hydrated α -Fe₂O₃ (hematite) was conducted at initial suspension pH values ranging from about 4.5 to 10 (Tables 2, 3, and 4), the pH values varied from 4.39 to 6.82 after

the sorption reaction(s) took place. Sorption occurred at pH values as low as 4 to 5. These pH values are less than the pH at the isoelectric point of the hematite which is approximately 8 (Parks 1965). Thus, zinc was adsorbed onto a positive surface despite a strong electrostatic repulsion between the positively charged surface and the positively charged ionic species of zinc (Zn^{2+} , ZnCl^+ , ZnOH^+) which exist in the diffuse double layer and the ambient solution, i.e. the adsorption took place despite an unfavorable electrical potential suggesting that Zn was probably held by strong chemical bonding onto the hematite surfaces. However, the amounts of zinc sorbed at initial pH's below the isoelectric point were quite low. Since the neutral molecules of $\text{Zn}(\text{OH})_2$ exist in insignificant concentration at low pH values, and since in acid and neutral solutions the ionic ratio of $\text{Zn}^{2+}/\text{ZnOH}^+$ is so large that it tends to preclude any significant sorption of ZnOH^+ , the divalent zinc ions (Zn^{2+}) and the monovalent complex ions of ZnCl^+ were most likely the dominant forms of zinc ionic species adsorbed on surfaces of the hematite at the low pH values and below the isoelectric point. However, ZnCl^+ , ZnOH^+ , and $\text{Zn}(\text{OH})_2$ may be adsorbed in preference to divalent Zn ions because the solvation energy resisting adsorption is smaller for these species than for Zn^{2+} ions, and the electrostatic repulsion between the positive hematite surface and them is less (James and Healy 1972). The low adsorption at low initial pH values may also be due to reduction in the surface area of the oxide that resulted from dissolving a proportion

of the solid particles of the hematite under acid conditions.

Sorption increased markedly with increases in pH between initial pH's of 5 to 7, probably due to a reduction of net positive charge and development of new neutral and negative adsorption sites on the hematite surfaces. Also, at higher pH values, hydrogen from surface aquo ($-\text{OH}_2$) groups would be more easily replaced, and the concentrations of Zn^{2+} , ZnOH^+ , and $\text{Zn}(\text{OH})_2$ ionic species would be higher. Therefore, the affinity of the surface for the different ionic species of zinc which exist in the equilibrium solution will be so high as to cause an abrupt increase in Zn sorption. Although the maximum sorption (Table 2) occurred at an initial pH of about 7, the maximum sorption could not be accurately estimated because the maximum sorption would be expected at high pH values. Precipitation of zinc as $\text{Zn}(\text{OH})_2$ at high pH's, however, precluded the use of higher pH values than that used in this study.

After the abrupt increase in zinc sorption, sorption markedly decreased at an initial pH of about 8 (Table 2). The depletion in Zn sorption at high pH values may due to the decrease of Zn concentration in the equilibrium solution which probably resulted from precipitation of $\text{Zn}(\text{OH})_2$. The results also show that pH values of the equilibrium suspensions dropped after the sorption reaction(s) took place. The final pH values varied from 4.96 to 5.76 indicating that H^+ ions were desorbed from the oxide surfaces during zinc adsorption. This significant fact is consistent with

Table 2. Sorption of Zn by iron oxide suspended in aqueous solutions of varying pH.

NaOH added (ml)	Initial pH of* suspension	Final pH of** suspension	Zn sorbed (mg/g)
Control	5.1	5.0	0.78
0.2	7.1	5.2	2.06
0.4	8.6	5.5	0.95
0.6	9.2	5.6	0.51
0.8	9.7	5.7	0.46
1.0	9.9	5.8	0.38

*pH of the equilibrium solution before sorption of Zn.

**pH of the equilibrium solution after sorption of Zn.

Table 3. Sorption of Zn by iron oxide suspended in aqueous solution
of varying pH as affected by the pH of the ZnCl₂ solution.

Amount of acid or base added	ZnCl ₂ (pH 6)			ZnCl ₂ (pH 7)		
	Initial pH of suspension	Final pH of suspension	Zn sorbed (mg/g)	Initial pH of suspension	Final pH of suspension	Zn sorbed (mg/g)
0.2 ml HCl	4.6	4.4	4.29	4.6	4.6	4.26
0.1 ml HCl	4.7	4.5	4.64	4.8	4.6	4.51
Control	6.0	4.7	4.74	6.1	5.4	4.63
0.2 ml NaOH	7.5	5.0	5.82	7.5	5.1	5.62
0.4 ml NaOH	8.8	5.0	5.85	8.8	5.5	5.60
0.6 ml NaOH	9.4	5.1	5.47	9.5	6.0	5.00
0.8 ml NaOH	9.9	6.3	5.50	9.9	6.3	5.40
1.0 ml NaOH	10.1	6.2	5.70	10.1	6.3	5.52

Table 4. Sorption of Zn by iron oxide suspended in aqueous solution of varying pH with respect to volume of 0.1 M NaOH added after equilibrium.

Amount of acid or base added	0.1 ml NaOH added			0.2 ml NaOH added		
	Initial pH of suspension	Final pH of suspension	Zn sorbed (mg/g)	Initial pH of suspension	Final pH of suspension	Zn sorbed (mg/g)
0.2 ml HCl	5.3	6.4	4.54	5.1	6.0	7.89
0.1 ml HCl	5.7	6.2	4.80	5.3	5.8	8.02
Control	6.0	6.4	4.63	5.9	5.7	8.12
0.2 ml NaOH	7.8	6.3	5.65	7.8	5.4	9.52
0.4 ml NaOH	8.9	5.9	5.81	8.9	6.4	8.65
0.6 ml NaOH	9.6	6.7	4.84	9.6	6.5	9.15
0.8 ml NaOH	9.8	6.8	5.14	9.8	5.5	9.59
1.0 ml NaOH	10.1	5.7	6.11	10.0	5.7	9.57

the findings of other investigators (Forbes 1973; Kalbasi et al. 1978b; McKenzie 1980).

Zn sorption by $\alpha\text{-Fe}_2\text{O}_3$ increased when the pH of the ZnCl_2 solution added was increased from a pH of about 5.8 (Table 2) to pH of about 6 or 7 (Table 3). The amounts of Zn sorbed with the ZnCl_2 adjusted to a pH of 6 or 7 was about 3 to 10 fold greater than amounts of Zn sorbed when the pH of the ZnCl_2 solution used was 5.8. No significant differences were observed between the amounts of Zn sorbed from ZnCl_2 solutions at pH 6 and 7 (Table 3).

The results in Table 4 show that the addition of 0.1 and 0.2 ml of 0.1 M NaOH to the suspensions after equilibrium in order to increase the pH of the systems after the initial sorption reaction(s) resulted in a very large increase in Zn sorption by the oxide. The amounts of Zn sorbed when 0.2 ml of 0.1 M NaOH was added after the initial sorption reaction was complete were almost twice that sorbed when 0.1 ml of 0.1 M NaOH was added (Table 4), and that sorbed without the addition of NaOH during equilibration (Table 3). The results generally indicate that the pH of the equilibrium solution was a very important parameter affecting amount of Zn sorbed. The results in Table 4 also indicate that $\alpha\text{-Fe}_2\text{O}_3$ (hematite) has a very high capacity for Zn sorption provided the pH of the equilibrium solution is maintained at levels which favour sorption.

The data reported in Tables 3 and 4 show an increase in Zn sorption above initial pH values of about 4 to 8 with sorption

remaining relatively constant to a pH of about 10. The pH values after sorption of zinc varied from 4.39 to 6.82. It was expected that the sorption of zinc would decrease at high initial pH values because of precipitation of $\text{Zn}(\text{OH})_2$, but this interesting phenomenon suggests that Zn was probably chemically precipitated as $\text{Zn}(\text{OH})_2$ on the oxide's surfaces or in the diffuse double layer as well as being adsorbed. Precipitation of $\text{Zn}(\text{OH})_2$ which probably occurred at the higher pH values, caused problems in interpretation of the data since sorption would no longer be the only mechanism removing zinc from solution. Healy et al (1968) suggested that at pH values below the pH values of abrupt sorption increase, the OH^- ion concentration at the oxide-solution interface may be higher than in the bulk solution and, therefore, nucleation of a hydroxy precipitate might occur at pH values lower than would be expected for solutions. According to this suggestion it can be concluded that prior to strong sorption, the oxide's surface is positively charged and thereby the diffuse double layer will necessarily show a high adsorption of negatively charged ionic species (OH^- and Cl^-) and less adsorption of positively charged ionic species (Zn^{2+} , ZnCl^+ , ZnOH^+). As the pH increased, the surface charge will reverse sign from positive to negative and the hydroxide concentration will rapidly increase in the diffuse double layer and bulk solution. At this point the inner layer of the solution (close to the oxide's surface) will be heavily populated with positively charged ionic species. The combination of the high OH^- ion concentration, in the

inner and outer solutions, and high Zn^{2+} ion concentration may result in hydroxy precipitation of the inner layer Zn^{2+} ions. The precipitated $Zn(OH)_2$ on the oxide's surface was probably adsorbed as well.

The decrease in pH of the equilibrium solution after the sorption reaction(s) took place (Tables 2, 3, and 4) indicate that the adsorption of Zn on surfaces of the iron oxide was accompanied by the release of H^+ ions. This agreed with the findings of Forbes (1973) for Cu, Kalbasi et al (1978b) for Zn, and McKenzie (1980) for different metal ions. They confirmed that the adsorption process was always accompanied by the release of protons and the molar ratio of H^+ released to metal ion adsorbed increased with equilibrium pH and amount of the metal ion adsorbed. This ratio was between one and two per metal ion adsorbed. It was postulated that surface aquo ($-OH_2$) and hydroxo ($-OH$) groups were the sources of protons released during the adsorption process.

Generally, it can be concluded from the results of this study that the pH of the equilibrium system was a very important factor influencing the adsorption of Zn on surfaces of the iron oxide. This interesting fact may partly explain the low availability of Zn in soils high in pH and high in sesquioxides content.

(b) Effect of Temperature on Zn Sorption by Fe Oxides:

Information on the effect of temperature on surface adsorption reaction(s) of zinc with any variety of sesquioxides have not been reported or were not found in the literature. Results of preliminary experiments showed that the amount of Zn adsorbed on iron oxide (hematite) was probably dependent on the ambient temperature during the equilibration period, therefore the following two experiments were conducted to investigate the effect of temperature on Zn sorption by α -Fe₂O₃ (hematite).

In the first experiment, triplicate sets of 0.1 g samples of α -Fe₂O₃ were placed in polypropylene centrifuge tubes, and 25 ml of ZnCl₂ solution (80 ppm Zn) added. The pH of the ZnCl₂ solution was previously adjusted to pH 7 using 0.1 M NaOH. The tubes were covered with stretchable Parafilm and the suspensions equilibrated at various temperatures by shaking for 24 hours on a horizontal mechanical shaker that was placed in a large thermostatically controlled incubation room. The temperature of the incubation room was controlled at 17, 20, 25, or 30 C during the equilibration period. After equilibrium, the supernatants were centrifuged, filtered using Whatman number one filter paper, and the concentrations of Zn in filtrates determined by Atomic Absorption Spectrophotometry. Amounts of Zn sorbed were calculated by subtracting the amounts of Zn in the filtrates from that initially added.

The same procedure as outlined above was employed in the second

experiment, but after equilibrating the iron oxide with the ZnCl_2 solution, 0.2 ml of 0.1 M NaOH was added to each tube in order to increase the pH of the system. The suspensions were then equilibrated again by shaking at the various temperatures, and the supernatants immediately centrifuged and filtered after shaking. Zn concentrations in filtrates were determined by Atomic Absorption Spectrophotometry and the amounts of Zn sorbed calculated. The results of these two experiments are shown in Table 5.

Sorption of Zn by $\alpha\text{-Fe}_2\text{O}_3$ (hematite) increased slightly as the ambient temperature increased from 17 to 25 C, but decreased at 30 C particularly when NaOH was not added to the system (Table 5). Although maximum sorption of Zn occurred at about 25 C which is consistent with the findings of Bowden et al (1974), interpretation of these results was difficult as there are no significant differences between the amounts of Zn sorbed at the various temperatures. It can thus be concluded that temperature between 17 and 30 C played an insignificant role in the sorption of Zn by $\alpha\text{-Fe}_2\text{O}_3$ (hematite) from aqueous solutions. It is possible that a significant effect of temperature on amounts of Zn sorbed would have been obtained if a wider range of temperatures had been employed.

The most important feature in these results is the tremendous increase in amounts of Zn sorbed at all temperatures when 0.2 ml of 0.1 M NaOH was added to the equilibrium solutions after the initial sorption took place. Addition of NaOH resulted in about a

Table 5. Sorption of Zn by α -Fe₂O₃ from aqueous Zn solution at various temperatures.

Temperature	Zn sorbed (mg/g)	
	Fe ₂ O ₃ + ZnCl ₂	Fe ₂ O ₃ + ZnCl ₂ + NaOH
C		
17	2.56	15.58
20	2.65	15.80
25	2.85	16.10
30	1.61	15.83

five fold increase in the amounts of Zn sorbed by α -Fe₂O₃ (Table 5), indicating once again that sorption of Zn was strongly dependent on the pH of the equilibrium solution.

B. Desorption of Zinc from Hydrous Iron Oxide Surfaces.

The factors affecting the desorption of specifically and nonspecifically adsorbed zinc from the surfaces of iron oxides or any variety of sesquioxides, have not been studied or were not found in the literature. The amounts of Zn desorbed and the mechanism(s) of desorption would be relevant to the chemical availability and plant uptake of zinc from these sources in soils.

The following studies were conducted in order to obtain information on the reversibility of zinc adsorbed on surfaces of α -Fe₂O₃ (hematite), the amounts of zinc desorbed, and the effect of temperature on desorption.

(a) Reversibility at Room Temperature of Zn Sorbed by Fe Oxide:

Triplicate 0.1 g samples of α -Fe₂O₃ (hematite) were placed in four sets of polypropylene centrifuge tubes and 25 ml of ZnCl₂ solution (80 ppm Zn) added to each tube. The pH's of ZnCl₂ solutions were previously adjusted to pH 6 or 7 using 0.1 M NaOH. The tubes were covered with Parafilm and shaken for 24 hours at room temperature (22 ± 1 C), the suspensions centrifuged, and the supernatant solutions decanted and filtered. Zinc concentrations in the filtrates were determined by Atomic Absorption Spectrophotometry in order to calculate the total amounts of Zn sorbed by the α -Fe₂O₃. The samples were then successively extracted using deionized water and 1.0 M MgCl₂ solution to determine the

reversibility of sorbed Zn. Eight successive extractions were conducted using 25 ml portions of each extractant. MgCl_2 solution was chosen as an extractant since the Mg^{2+} ion has an ionic radius ($\approx 0.78 \text{ \AA}$) very similar to that of Zn^{2+} ion ($\approx 0.74 \text{ \AA}$). Preliminary experiments showed that the amounts of zinc extracted by H_2O and MgCl_2 solution did not significantly differ with time of extraction (after 24 hours). Thus, the suspensions were equilibrated for this period of time. After equilibrium, the suspensions were centrifuged and the supernatants filtered through Whatman number one filter paper. The filtrates were saved to measure concentrations of zinc by Atomic Absorption Spectrophotometry, and the amounts of the Zn extracted were calculated.

A second experiment was conducted using the procedures outlined above with the following exceptions; the ZnCl_2 solution was adjusted to pH 7 prior to addition, and 0.2 ml of 0.1 M NaOH was added to the suspensions after the initial equilibration period, followed by 24 hours of shaking. The NaOH was added to increase the amounts of Zn sorbed. Amounts of Zn sorbed were calculated by subtracting the amounts left in solutions from that initially added. The sorbed zinc was then extracted as described in the previous experiment except that nine successive extractions were conducted and a DTPA buffered solution (pH ≈ 7.3), deionized water, and 1.0 M MgCl_2 solution were used as extractants. The DTPA extracting solution was prepared as described by Lindsay and Norvell (1978), and consisted

of 0.005 M DTPA (diethylenetriaminepentaacetic acid), 0.1 M TEA (triethanolamine), and 0.01 M CaCl_2 .

The results shown in Tables 6 and 7, and Figure 1 indicate that a large portion of the total zinc sorbed by the iron oxide was exchangeable and was released upon extraction. Amounts of zinc extracted was highest for the first extraction, decreased markedly from the first to about third extraction and then remained relatively constant with numbers of extractions. The portion of total sorbed zinc extracted was about 85 percent for DTPA, 33 to 60 percent for MgCl_2 , and 6 to 50 percent for deionized water, indicating that the ability of the extracting solutions used in this study to extract sorbed zinc decreased in the order: DTPA, MgCl_2 , H_2O . This sequence may be due to the strong chelating power of the DTPA solution, and the ability of Mg^{2+} ions to exchange with the exchangeable zinc present on the iron oxide surfaces.

An interesting fact is that the experimental conditions under which the zinc was adsorbed onto the iron oxide had a pronounced effect on the total amount of Zn sorbed. The amount of Zn sorbed increased as the pH of the equilibrium solution increased (Tables 6 and 7).

Desorption of Zn was generally assumed to be the reverse of adsorption reaction(s), and the amount of Zn desorbed was expected to be a function of the total amount of Zn adsorbed onto the iron oxide surfaces. But, in fact, careful examinations of the results shown in Tables 6 and 7 indicate that the release of sorbed Zn,

Table 6. Amounts of Zn extracted by H₂O and MgCl₂ from Zn sorbed by α-Fe₂O₃ at two pH's .

Number of Extractions	Zn Sorbed at pH 6 (mg/g)	Zn Extracted				Zn Sorbed at pH 7 (mg/g)	Zn Extracted			
		H ₂ O		MgCl ₂			H ₂ O		MgCl ₂	
		(mg/g)	(%)*	(mg/g)	(%)		(mg/g)	(%)	(mg/g)	(%)
(1)	6.67	1.24	18.60	2.08	31.20	11.89	1.75	14.72	2.11	17.75
(2)		0.53	7.94	0.69	10.34		1.29	10.85	2.18	18.33
(3)		0.21	3.15	0.32	4.80		0.51	4.30	0.76	6.40
(4)		0.27	4.05	0.27	4.04		0.71	5.97	0.69	5.80
(5)		0.25	3.75	0.20	2.99		0.50	4.20	0.54	4.54
(6)		0.14	2.09	0.12	1.80		0.47	3.95	0.32	2.69
(7)		0.12	1.80	0.09	1.35		0.35	2.94	0.29	2.44
(8)		0.08	1.20	0.08	1.20		0.27	2.27	0.18	1.51
Total		2.84	42.58	3.85	57.72		5.85	49.20	7.07	59.46

* % of total sorbed Zn.

Table 7. Amounts of Zn extracted by H₂O, MgCl₂, and DTPA from Zn sorbed by α-Fe₂O₃.

No. of Extrac.	Zn Sorbed (mg/g)	Zn Extracted					
		H ₂ O		MgCl ₂		DTPA	
		(mg/g)	(%)*	(mg/g)	(%)	(mg/g)	(%)
(1)	16.33	0.37	2.30	2.16	13.23	11.43	70.00
(2)		0.14	0.85	1.09	6.67	1.32	8.08
(3)		0.14	0.85	0.66	4.04	0.37	2.27
(4)		0.12	0.73	0.46	2.82	0.25	1.53
(5)		0.09	0.55	0.34	2.08	0.19	1.16
(6)		0.07	0.43	0.27	1.65	0.13	0.80
(7)		0.04	0.24	0.21	1.29	0.11	0.67
(8)		0.03	0.18	0.19	1.16	0.08	0.49
(9)		0.03	0.18	0.15	0.92	0.07	0.43
Total		1.03	6.31	5.53	33.86	13.95	85.43

* % of total sorbed Zn

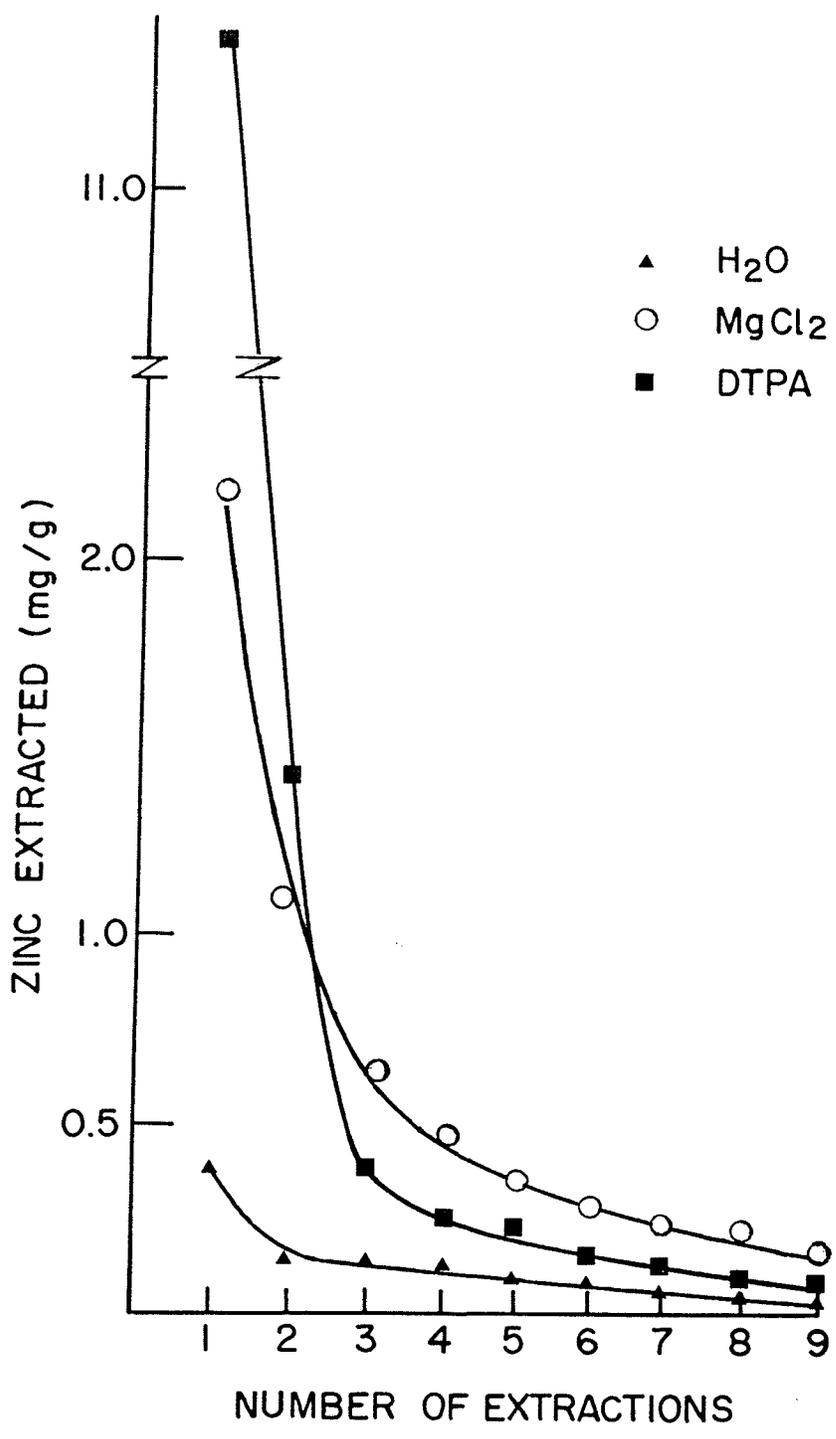


Figure 1. Extractability of zinc sorbed by hematite ($\alpha\text{-Fe}_2\text{O}_3$) .

i.e., desorption, was not the reverse of adsorption. The amounts of zinc extracted by H_2O and $MgCl_2$ from large amounts of sorbed Zn were greater than that from low amounts of sorbed zinc (Table 6), but the portion extracted decreased with the amount which was previously sorbed. This may suggest that the circumstances under which the $Zn-Fe_2O_3$ was prepared have, at least to some extent, effects on the mechanism(s) of desorption and in turn on the total amounts of zinc desorbed from the hematite ($\alpha -Fe_2O_3$) surfaces.

Most of the total extractable zinc was extracted in the first two successive extractions, and then decreased markedly with extraction (Tables 6 and 7, and Figure 1), i.e., the extent of reversibility decreased as zinc was extracted. This indicates that there were possibly two fractions of adsorbed zinc on $\alpha -Fe_2O_3$ surfaces, one of which was easily removed by H_2O and $MgCl_2$; termed "readily desorbed" fraction. The second fraction, was difficult to extract, termed "less readily desorbed" fraction. Apparently, the less readily desorbed fraction was strongly bound to specific high energy bonding sites existing on the oxide's surfaces by chemical and/or physical bonds.

The amount of Zn extracted by DTPA was about 2.5 fold greater than the amounts extracted by 1.0 M $MgCl_2$ and about 14 fold greater than that extracted by deionized water (Table 7). Although DTPA extracted 85 percent of the total sorbed Zn in the nine successive extractions, there was a portion of the sorbed zinc that was not released suggesting the presence of a fraction of Zn that was

hardly reversible or irreversible. This fraction may be strongly held on surfaces of the hematite by chemical bonds or occluded and/or fixed in the oxide lattice.

According to the results of this study it can generally be concluded that the adsorbed Zn on hematite (α -Fe₂O₃) surfaces can be divided into two main classes, and adsorption can be attributed to essentially two sets of energetically different and distinct adsorption sites as follows:

(i) One set of specific sites of low bonding energy corresponding to the readily desorbed fraction. This fraction of the adsorbed zinc was easily released into solution phase because of its low bonding energy. Monodentate, electrostatic, binding of Zn species such as ZnCl⁺ and ZnOH⁺ are probably the major components of the readily desorbed fraction.

(ii) Another set of specific sites of high bonding energy; zinc adsorbed on these sites was less readily desorbed. Zinc was probably adsorbed as the divalent ion (Zn²⁺) and strongly bonded to these sites. Bidentate, covalent bonding was the most likely mechanism of retention. This fraction may be easily released when the pH of the system is lowered since preliminary experiments using 1.0 M MgCl₂ extracting solutions with pH values 5, 6 and 7, respectively, showed that the lower the pH of the salt solution, the greater was the amount of Zn desorbed. This phenomenon strongly indicates that desorption of Zn from surfaces of the iron oxide is highly pH dependent.

It is also possible that some Zn^{2+} (of ionic radius $\approx 0.74\text{\AA}$) may isomorphously substitute for the similarly sized lattice Fe^{3+} (of ionic radius $\approx 0.67\text{\AA}$), resulting in Zn^{2+} becoming fixed or occluded in the oxide lattice. This may occur at relatively low pH values, when the zinc would be mostly present as the divalent zinc ion (Zn^{2+}) and of the size comparable to lattice Fe^{3+} . This mechanism of retention may partly explain why the extent of reversibility of sorbed Zn decreased with successive extractions. This occluded and/or fixed portion of Zn would be expected to be easily released into solution phase if acid solutions were used as extractants.

(b) Reversibility of Zn Sorbed by Fe Oxide as a Function of Temperature:

It was mentioned earlier that information on the effect of temperature on adsorption-desorption reactions of Zn on surfaces of sesquioxides were not found in the literature. The study reported previously, in this manuscript, on the effect of the ambient temperature during equilibrium on sorption of Zn by hematite ($\alpha\text{-Fe}_2\text{O}_3$) showed that temperatures of 17 to 30 C had no significant effect on Zn sorption by the iron oxide. However, temperature may play a significant role on desorption of Zn from iron oxide surfaces and thus affect the concentration of plant available zinc in soil solution. Therefore, the following study was conducted to obtain information on the effect of temperature on the reversibility of

adsorbed Zn from α -Fe₂O₃ surfaces.

Zn-Fe₂O₃ was prepared by shaking a 50 g sample of hematite (α -Fe₂O₃) with 12.5 L of ZnCl₂ solution (80 ppm Zn, pH 7) for 24 hours at 25 ± 1 C. After equilibrium, 100 ml of 0.1 M NaOH was added and the suspension shaken for another 24 hours. The suspension was filtered through a Büchner funnel using Whatman number one filter paper. The Zn-Fe₂O₃ sediment was collected on the filter paper, air dried at room temperature (22 ± 1 C), and analyzed to determine the amount of adsorbed Zn on the iron oxide by dissolving 0.1 g samples of Zn-Fe₂O₃ in 25 ml of 1.0 N HCl. Zn concentration in the acid solution was measured by Atomic Absorption Spectrophotometry and the amount of sorbed Zn was calculated.

Triplicate 0.1 g samples of the prepared Zn-Fe₂O₃ were placed in three sets of polypropylene centrifuge tubes. Twenty-five ml of deionized water, 1.0 M MgCl₂, or DTPA solution was added to each tube in the first, second, and third set, respectively. The tubes were covered with stretchable Parafilm and shaken for 24 hours on a horizontal mechanical shaker which was placed in a large thermostatically controlled incubation room. The temperature of the incubation room was controlled at 17, 20, 25, or 30 C, during the equilibration period. The suspensions were centrifuged, the supernatants filtered using Whatman number one filter paper, and the concentrations of Zn in the filtrates determined by Atomic Absorption Spectrophotometry.

Desorption of Zn from the α -Fe₂O₃ surfaces increased markedly with increasing ambient temperature over the range 17 to 30 C (Table 8). The results generally indicate that desorption of Zn from surfaces of the hematite was an endothermic type of reaction. This fact may suggest that heat is required to break the zinc species- to-iron oxide surface bond, and/or to enhance the release of zinc species that are strongly held to the high energy sites on the oxide surfaces. Also, it may be required to enhance the release of the occluded and/or fixed zinc fraction from the mineral lattice. The results also show that the extractable zinc decreased in the order DTPA, MgCl₂, deionized H₂O at a given temperature (Table 8).

It is commonly reported in the literature that Zn deficiency symptoms in field crops often occur during cool and wet periods of the growing season, and disappear when soil temperature increases (Lindsay, 1972). Several explanations are usually given to account for these observed zinc deficiency patterns: (1) the root system of the plants is not well established in cool soils and thus uptake of zinc is reduced due to restriction of the feeding zone; (2) a large fraction of the plant available Zn in soil comes from the decomposition of organic residues, and lower temperatures in cool soils reduce the microbiological activity and the mineralization rate of soil organic matter, and in turn insufficient available zinc is released. Explanations relevant to the effect of temperature, per se, on the chemical availability of zinc in soils were not given to date. The present results demonstrate that temperature, per se,

Table 8. Amounts of Zn extracted at various temperatures by H₂O, MgCl₂, and DTPA from Zn sorbed by α-Fe₂O₃.

Temperature	Zn Sorbed	Zn Extracted					
		H ₂ O		MgCl ₂		DTPA	
C	(mg/g)	(mg/g)	(%)*	(mg/g)	(%)	(mg/g)	(%)
17	16.30	0.27	1.65	1.43	8.76	8.02	49.11
20		0.29	1.78	1.45	8.88	8.59	52.60
25		0.30	1.84	1.88	11.51	8.96	54.87
30		0.41	2.50	1.92	11.76	9.52	58.30

* % of total sorbed Zn.

affects the desorption of zinc from iron oxides surfaces and probably from similar complexes present in soils as adsorbents for Zn such as clay minerals, other sesquioxides, CaCO_3 , and humic substances. These results indicate that the higher the temperature the greater is the amount of zinc released into the solution phase. Thus, when a soil warms up more Zn^{2+} would be released into soil solution which could be readily used by plants. This information may explain, to some extent, the disappearance of Zn deficiency symptoms when soil temperature increases except on severely Zn deficient soils.

Successive extractions of the Zn adsorbed on surfaces of iron oxides over a wider range of temperatures would have provided more points on the desorption isotherm giving a better description of the effect of temperature on the reversibility of zinc sorbed by sesquioxides. These types of studies would provide an insight into the nature of the adsorption-desorption reactions in soils which control the concentration of the plant available Zn in soil solution. Unfortunately, time did not permit a thorough investigation of the effects of temperature on the desorption of zinc from iron oxides.

C. Chemical Availability in Soil of Zinc Combined with Iron Oxide.

Studies reported by other investigators, and the results reported in this manuscript showed that different zinc ionic species are adsorbed and perhaps occluded and/or co-precipitated with hydrous oxides of iron, aluminum, and manganese in soils. These chemical processes most likely control the concentration of zinc in the soil solution and, in turn, affect plant uptake. Therefore, it is of extreme importance to determine the reversibility of adsorbed Zn in soils to provide information on the nature of soil chemical conditions under which the efficiency of Zn fertilizers can be maximized.

Studies on the desorption of Zn from iron oxide surfaces, reported in the previous subsection showed that a large portion of the adsorbed Zn on α -Fe₂O₃ surfaces was released into the solution phase, i.e., that adsorbed Zn was highly exchangeable. This interesting fact led the author to examine the chemical extractability of Zn associated with iron oxide (hematite) when added to soil.

The surface sample of an Almasippi sandy soil was used in this study (Table 1). The experiment consisted of three treatments; a control, ZnCl₂ and Zn-Fe₂O₃ each added at a rate of 5 ppm Zn (soil basis). Zn associated with iron oxide (Zn-Fe₂O₃) was prepared as described on page 60 in the previous subsection.

One hundred g samples of air-dried finely sieved soil were thinly spread on pieces of polyethylene. ZnCl₂ equivalent to 5 ppm

Zn on air-dried soil basis was thoroughly mixed with a small portion of the soil sample, and then the treated sample was thoroughly mixed with all the soil. The treated soil was placed in a glass beaker which was previously washed and cleaned as described in the materials and analytical methods section to exclude any possible contamination of micronutrient elements. Zn-Fe₂O₃ was mixed with the soil sample in the same manner as the ZnCl₂. The zinc compounds were mixed throughout the soil instead of banding since previous studies showed that inorganic Zn fertilizers were more plant available when mixed throughout the soil as compared to banded treatments. Each treatment was replicated twice. The samples were wetted to field capacity using deionized water and maintained at that moisture content during incubation. The beakers were covered with clean watch glasses and incubated at room temperature (22 ± 1 C).

After incubation for 1, 2, 4, and 6 weeks the samples were spread on pieces of polyethylene and air dried for 48 hours at room temperature. Three extractants; deionized water, 1.0 M MgCl₂, and DTPA buffered solution were used to estimate the chemical availability of Zn for treated soil samples and for the soil without added Zn. Duplicate 10 g subsamples were placed in 250 ml conical flasks, and 100 ml of deionized water, 100 ml of 1.0 M MgCl₂, or 20 ml of DTPA solution added. Each flask was covered with Parafilm and the deionized water and MgCl₂ suspensions were then shaken for 24 hours on a horizontal shaker at room temperature. The soil-DTPA

mixture was shaken for 2 hours since a 2 hour shaking period was enough to reach equilibrium (Lindsay and Norvell 1978). After shaking the suspensions were filtered through Whatman no. 42 filter paper and the filtrates were analyzed for Zn using a Perkin-Elmer, Model 560 Atomic Absorption Spectrophotometer. Concentrations of Zn extracted with water and $MgCl_2$ solution were very low and below the detection limits of the Atomic Absorption Spectrophotometer. The results of the DTPA extractable Zn are shown in Table 9 and Figure 2. The extractable native soil Zn value was subtracted from the Zn value for each treatment receiving Zn in order to arrive at a value reflecting the availability of only the added Zn.

The Almasippi soil selected for study was found to contain a low level of plant available Zn (Tables 1 and 9). It was found to contain less DTPA-extractable Zn than the 0.8 ppm critical level suggested by Lindsay and Norvell (1978) indicating that this soil is probably deficient in labile Zn and probably would not supply adequate levels of Zn to plants. The results of this study show that the concentration of the plant available Zn (DTPA-extractable Zn) in soil solution, whether the source of that labile Zn was $ZnCl_2$ or $Zn-Fe_2O_3$, was on an average, equal to or greater than the critical level of 0.8 ppm, indicating that $ZnCl_2$ and $Zn-Fe_2O_3$ would be good inorganic sources of Zn on the Almasippi soil.

The proportion of Zn added as $ZnCl_2$ which was extracted by DTPA increased slightly from one to two weeks of incubation (Table 9 and Figure 2), but remained constant with time after two weeks of

Table 9. Amounts of DTPA-extractable Zn from an Almasippi soil treated with ZnCl_2 and $\text{Zn-Fe}_2\text{O}_3$ and incubated for different periods.

Incubation Time (week)	DTPA-Extractable Zn (ppm)		
	Control	ZnCl_2	$\text{Zn-Fe}_2\text{O}_3$
1	0.44	1.03 (0.59)*	1.29 (0.85)
2	0.42	1.16 (0.74)	1.45 (1.03)
4	0.44	1.23 (0.79)	1.28 (0.84)
6	0.44	1.27 (0.83)	1.34 (0.90)

* Values in brackets indicate the amounts of DTPA-extractable Zn after subtracting amounts of native soil Zn.

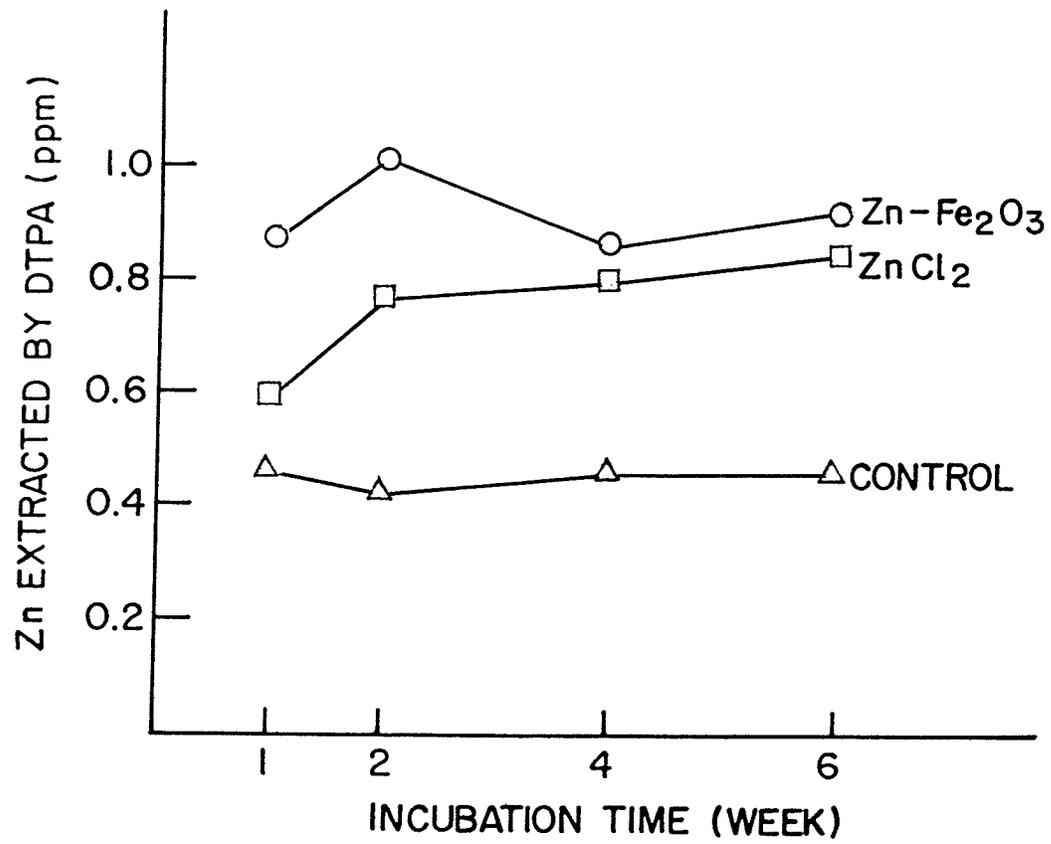


Figure 2. Effect of incubation time on availability of zinc in a sandy soil treated with ZnCl₂ and Zn-Fe₂O₃.

incubation. It is doubtful if the increase in extractability between one and two weeks of incubation was significant and most likely due to experimental error. The amounts of Zn extracted by DTPA when applied as Zn-Fe₂O₃ was variable but generally remained constant with time of incubation. A significant feature of the data obtained was that Zn added as Zn-Fe₂O₃ was more readily extracted by DTPA than Zn added as ZnCl₂. This suggests that Zn-Fe₂O₃ may be a better source of labile Zn and plant available Zn than ZnCl₂. The higher extractability of Zn from Zn-Fe₂O₃ as compared to that when ZnCl₂ was applied may be due to zinc ions from the ZnCl₂ being adsorbed, co-precipitated, occluded and/or fixed through reactions different than that of Zn with Fe₂O₃. The Zn from ZnCl₂ may have reacted with clay minerals, organic matter, etc. in a manner in which the Zn was less available than when Zn reacts only with Fe₂O₃.

It can be concluded from the present study and the desorption study, which was reported in the previous subsection, that adsorption-desorption reactions of zinc on surfaces of iron oxide in soils play a significant and a very important role in controlling the concentration of the plant available zinc in the soil solution. It is well known that the simplest process governing the concentration of ionic species of a specific ion in solution is the "solubility product principle". In many situations in soil, pure phases of zinc are not formed as the concentrations of zinc ions are not high enough to reach the solubility product of many zinc compounds. Therefore, under these circumstances, adsorption

equilibria govern the concentration of different ionic species of zinc in soil solution. It can also be concluded that the Zn associated with iron oxide probably would be a good source of the plant available zinc in neutral and calcareous soils. The readily desorbed zinc from the surfaces of iron oxides would be expected to be readily available to plants.

D. Availability to Plants of Zinc Associated with Iron Oxide.

The availability of a nutrient element in the soil is determined by the various factors that affect absorption of the nutrient by plants. Although soil analysis can give a good indication of the available level of a nutrient in soil the amount of the nutrient available to a plant depends not only upon the soil test itself but also upon the specific conditions under which a given crop is grown. Thus, the plant is the only agent that can more precisely determine the availability of a nutrient in a soil. Since many studies have shown that hydrated Fe and Al oxides play a significant role in controlling the amount of plant available zinc in soil by sorption, and since a high degree of reversibility and high chemical availability of sorbed Zn in soil was found in the desorption and soil incubation studies. (presented previously), it was deemed necessary to test the possibility of plants being able to extract and utilize zinc sorbed by sesquioxides. Very little or no information was found in the literature on the plant availability of Zn sorbed by any variety of sesquioxides.

Growth Chamber Experiment (1):

Two different inorganic sources of zinc were used in this experiment; reagent-grade $ZnCl_2$, obtained from Fisher Scientific Co., and $Zn-Fe_2O_3$ which was prepared as described on page 60. Zinc was added at the rate of 5 ppm Zn on the basis of 5 kg air dried soil. Zinc treatments were applied after treating each

soil in each pot with the appropriate amounts of N, P, K, and S fertilizer solutions as was described in the materials and analytical methods section. The experiment consisted of five treatments: (1) control; (2) ZnCl_2 mixed throughout the soil- (20 ml of ZnCl_2 solution was uniformly pipetted and thoroughly mixed with the 5 kg of soil for each pot); (3) ZnCl_2 banded into the soil- (20 ml of ZnCl_2 solution was pipetted as uniformly as possible in a band 2.5 cm below the seed level or 4 cm below the soil surface); (4) $\text{Zn-Fe}_2\text{O}_3$ mixed throughout the soil. The prepared $\text{Zn-Fe}_2\text{O}_3$ was initially thoroughly mixed with a small portion of soil, and then the treated portion was thoroughly mixed with the entire soil mass and placed in the pot; (5) $\text{Zn-Fe}_2\text{O}_3$ banded into the soil in which the $\text{Zn-Fe}_2\text{O}_3$ was uniformly banded 2.5 cm below the seed level or 4 cm below the soil surface.

Although the soil analysis showed that the Almasippi sandy soil contained 0.2 ppm DTPA-extractable Cu, equal to the critical level suggested by Lindsay and Norvell (1978), Cu fertilizer was not applied in this experiment in order to study response to the supplemental zinc in absence of any other micronutrient fertilizers.

Yield of soybeans was increased by the addition of zinc only when applied in the chemically combined form with the iron oxide (Table 10). The increase in dry matter yield was about 40% when the $\text{Zn-Fe}_2\text{O}_3$ was mixed throughout the total soil volume and about 25% when it was placed in a band below the seed. These interesting data

Table 10. Dry matter yield and micronutrient cation content of soybeans as influenced by Zn source and method of application of zinc fertilizer.

Zn Treatment	Method of application	Dry matter yield (g/pot)	Concentration in plant tissue (ppm)			
			Zn	Cu	Fe	Mn
(1) Control		32.2 a*	4 a	0.4 a	48 ab	64 b
(2) ZnCl ₂	mixed	32.7 a	4 a	0.5 a	46 a	59 ab
(3) ZnCl ₂	banded	29.5 a	4 a	0.5 a	45 a	57 a
(4) Zn-Fe ₂ O ₃	mixed	44.9 b	7 b	1.0 b	53 b	55 a
(5) Zn-Fe ₂ O ₃	banded	40.1 c	12 c	1.0 b	60 c	63 b

* Means within the column followed by the same letter are not significantly different at the 5% level according to Duncan's New Multiple Range Test.

indicate that Zn sorbed by hematite (α - Fe_2O_3) was highly available to plants in this soil and Zn- Fe_2O_3 was a good inorganic source of zinc for plants. The high plant availability of Zn sorbed by the iron oxide is strongly supported by the results obtained for the desorption and incubation studies. These studies showed that the Zn adsorbed on surfaces of hematite was highly reversible. The dry matter yield obtained with the Zn- Fe_2O_3 mixed throughout the soil was significantly higher than that of the banded treatment suggesting that mixing of Zn- Fe_2O_3 throughout the total soil volume was a much more effective method of supplying zinc to the plants.

The ZnCl_2 treatments, whether mixed or banded, did not increase the dry matter yield of plants and yields with ZnCl_2 were significantly lower than those with Zn- Fe_2O_3 . Inorganic Zn fertilizer applied in a band has been found by other investigators to be ineffective in increasing yields even on Zn deficient soils (Shaw et al 1954; Mortvedt et al 1969; Hedayat 1977). The lack of a yield increase has been attributed to little or no plant uptake of Zn from the fertilizer band. It is generally accepted that root contact with the Zn in the zinc fertilizer band is very low and thus utilization of Zn by plants is very small or negligible. In contrast, it has been found that mixing inorganic Zn fertilizer throughout the soil as uniformly as possible i.e. increasing the root contact between the Zn fertilizer and the plant roots, increases plant utilization of the Zn fertilizer and zinc added in

this manner will usually enhance yield of plants of Zn deficient soils (Shaw et al 1954; Mortvedt et al 1969; Hedayat 1977). The findings noted above for the $ZnCl_2$ banded into the soil is consistent with that of other workers. In contrast, the lack of a yield increase with $ZnCl_2$ mixed throughout the soil is inconsistent with the findings of other workers. It is possible that in this study the $ZnCl_2$ (applied with a pipette followed by mixing of the soil) was not thoroughly mixed with the total soil volume and therefore Zn uptake and utilization was severely reduced due to lack of sufficient root contact with the Zn fertilizer.

Generally, the soybean plants did not have a healthy appearance throughout the eight-week growth period. Zinc and copper deficiency symptoms were observed on both the control and treated plants particularly during the early stages of growth. These deficiencies were verified by the results obtained from the plant tissues analysis which indicated that both Zn and Cu levels were not sufficient. Copper concentration in the plants for all treatments was very low indicating a severe deficiency of Cu in the plants (Table 10). Zinc concentration in plants of the control and $ZnCl_2$ treatments was very low and below the critical level of Zn reported in the literature (Viets et al 1954; Small et al 1973; Jones 1972; Ohki 1977; Hedayat 1977). The plants were severely stunted with severely shortened internodes. The stunting was accompanied with interveinal chlorosis which was scattered on the young developing and recently matured leaves. These deficiency symptoms were expressed shortly

after emergence. With time, the older leaves developed severe interveinal chlorosis accompanied with wrinkled leaf surfaces, and later abscised. Plants treated with $\text{Zn-Fe}_2\text{O}_3$ had moderate deficiency symptoms; stunting was not observed, and the young developing leaves showed a slight interveinal chlorosis but the chlorosis disappeared in the later growth stages. These deficiency symptoms were probably due to a Cu deficiency rather than a Zn deficiency as indicated by results of plant tissues analysis.

Zinc concentration in the plants treated with $\text{Zn-Fe}_2\text{O}_3$ was significantly higher than that of the control and ZnCl_2 treated plants indicating again that zinc associated with the hematite was much more available to plants in this soil than ZnCl_2 . Although a significantly higher yield was obtained when the $\text{Zn-Fe}_2\text{O}_3$ was mixed throughout the soil as compared to the yield with the $\text{Zn-Fe}_2\text{O}_3$ banded into the soil, the concentration of zinc in the plants was higher when the $\text{Zn-Fe}_2\text{O}_3$ was banded into the soil (Table 10). Interpretation of these results is very difficult since zinc was not the only growth-limiting nutrient. Part of the difference in Zn concentrations may be a result of a dilution effect; where the relative rate of dry matter accumulation increased more rapidly in plants treated with the $\text{Zn-Fe}_2\text{O}_3$ mixed throughout the soil.

Iron and manganese concentrations in both the control and treated plants were reasonably adequate suggesting that the Almasippi sandy soil contained enough labile Fe and Mn for soybean growth. The variations in the concentrations of these two nutrients

between the treated and control plants were probably due to experimental error as well as the effect of zinc treatments per se.

The results of this experiment showed that zinc chemically combined with hematite ($\alpha\text{-Fe}_2\text{O}_3$) was highly available to plants and perhaps would be much more effective than ZnCl_2 as a source of Zn for plant absorption and utilization; i.e. $\text{Zn-Fe}_2\text{O}_3$ may be a better zinc fertilizer than ZnCl_2 or other inorganic zinc salts. This information is considered to be very important particularly since information of this nature was not found in the literature. The results of the desorption and soil incubation studies which were presented in the previous two subsections tend to confirm the above observation.

Growth Chamber Experiment (2):

In the first growth chamber experiment soybeans responded only to added zinc in the form of $\text{Zn-Fe}_2\text{O}_3$. The highest dry matter yield was obtained when $\text{Zn-Fe}_2\text{O}_3$ was mixed throughout the soil, but the highest zinc uptake by plants occurred when $\text{Zn-Fe}_2\text{O}_3$ was banded below the seed. The second growth chamber experiment was a continuation of the first experiment to investigate:

- (a) The effect of zinc source (ZnCl_2 , $\text{Zn-Fe}_2\text{O}_3$ and Zn-EDTA), method of application and rate of added zinc on dry matter yield and zinc content of soybean plants.
- (b) The plant availability of zinc from ZnCl_2 mixed with iron oxide (hematite) in a fertilizer band.

The experiment consisted of fourteen treatments. The experimental procedures followed were as outlined for the first growth chamber experiment except that in addition to N, P, K and S; copper was added to all treatments at a rate of 5 ppm Cu, and 3 Kg of air dried soil was added to each pot. The appropriate amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in deionized water and uniformly sprayed onto the soil spread thinly on a sheet of polyethylene. The entire soil mass was then thoroughly mixed. ZnCl_2 was dissolved in deionized water and applied in a manner similar to that for the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The $\alpha\text{-Fe}_2\text{O}_3$, $\text{Zn-Fe}_2\text{O}_3$ and Zn-EDTA , either mixed or banded, were added in solid form as described for the application of $\text{Zn-Fe}_2\text{O}_3$ in the first growth chamber experiment. In treatments 11 through 14, ZnCl_2 at rate of 5 ppm Zn (based on 3 Kg air-dried soil)

was mixed in dry powder form as uniformly as possible with 1.0, 0.5, 0.25 or 0.1 g of hematite (α - Fe_2O_3) on a sheet of polyethylene using a stainless steel spatula and then banded 2.5 cm below the seed or 4 cm below the soil surface. Iron oxide, without any zinc, was also added to test if hematite alone had any effect on plant growth. The amount of α - Fe_2O_3 added to this treatment equaled to the amount of iron oxide added when 10 ppm Zn was added as Zn- Fe_2O_3 .

Soybean plants in all treatments, except the control and α - Fe_2O_3 treated plants, had a healthy appearance and normal vegetative growth during the entire growth period indicating that the macro and micro-nutrients supplied by the soil, supplemented by the amounts added through fertilization were reasonably adequate. The control plants and plants treated only with α - Fe_2O_3 showed severe Zn deficiency symptoms shortly after emergence. The plants were stunted, and interveinal chlorosis occurred on the young developing leaves. The plant tissue analysis also showed that the Zn concentration in the aerial portions of these plants was very low and below the critical level reported in the literature (Viets et al 1954; Small et al 1973; Jones 1972; Ohki 1977; Hedayat 1977) indicating that these plants were Zn deficient. The dry matter yields of plants treated with iron oxide were lower than that of the control plants, the differences however were not significant (Table 11).

Yield of soybeans was greatly increased when zinc as ZnCl_2 , Zn- Fe_2O_3 or Zn-EDTA were added, regardless of rate and method of

Table 11. Dry matter yield and micronutrient cation content of soybeans as influenced by Zn source, rate, and method of application of zinc fertilizer.

Zn Treatment	Method of application	Dry matter yield (g/pot)	Concentration in plant tissue (ppm)			
			Zn	Cu	Fe	Mn
(1) Control		20.4 a*	8 a	5 ab	42 a	68 ef
(2) α -Fe ₂ O ₃	mixed	20.2 a	8 a	6 bc	48 a	62 ef
(3) α -Fe ₂ O ₃	banded	17.5 a	9 a	6 bc	52 a	69 f
(4) ZnCl ₂ (5 ppm Zn)	mixed	36.5 c	21 c	5 ab	53 a	49 abc
(5) ZnCl ₂ (10 ppm Zn)	mixed	40.8 cd	28 d	5 ab	47 a	51 abcd
(6) Zn-Fe ₂ O ₃ (10 ppm Zn)	mixed	36.8 c	20 c	6 bc	45 a	60 def
(7) Zn-Fe ₂ O ₃ (5 ppm Zn)	mixed	30.2 b	14 b	6 bc	43 a	59 cdef
(8) Zn-Fe ₂ O ₃ (5 ppm Zn)	banded	30.0 b	11 ab	6 bc	42 a	58 bcde

Table 11 - (Continued)

Zn Treatment	Method of application	Dry matter yield (g/pot)	Concentration in plant tissue (ppm)			
			Zn	Cu	Fe	Mn
(9) Zn-EDTA (5 ppm Zn)	mixed	39.6 cd	50 f	8 e	48 a	44 a
(10) Zn-EDTA (5 ppm Zn)	banded	38.3 cd	49 f	8 e	48 a	48 ab
(11) ZnCl ₂ (5 ppm Zn) + 1.0 g Fe ₂ O ₃	banded	33.3 bc	37 e	6 bc	47 a	66 ef
(12) ZnCl ₂ (5 ppm Zn) + 0.5 g Fe ₂ O ₃	banded	39.9 cd	36 e	7 ce	53 a	64 ef
(13) ZnCl ₂ (5 ppm Zn) + 0.25 g Fe ₂ O ₃	banded	40.6 cd	38 e	7 ce	49 a	64 ef
(14) ZnCl ₂ (5 ppm Zn) + 0.1 g Fe ₂ O ₃	banded	41.9 d	35 e	7 ce	48 a	63 ef

* Means within the column followed by the same letter are not significantly different at the 5% level according to Duncan's New Multiple Range Test.

application of Zn fertilizer. Application of zinc as ZnCl_2 and Zn-EDTA at a rate of 5 ppm of Zn (treatments 4, 9 and 10), regardless of the method of application, resulted in a very large and significant increase in dry matter yield and Zn concentration in the aerial portions of the plants compared to those of the $\text{Zn-Fe}_2\text{O}_3$ treated plants (treatments 7 and 8). Thus, in this experiment Zn-EDTA and ZnCl_2 were more effective in increasing soybean dry matter yield and zinc uptake by plants than the chemically combined zinc with the iron oxide. The results also show that Zn-EDTA was better than ZnCl_2 in enhancing the zinc content of plants. Therefore, it can be concluded that the effectiveness of the three different sources of zinc in increasing yield and Zn content of soybeans was in the order: $\text{Zn-EDTA} > \text{ZnCl}_2 > \text{Zn-Fe}_2\text{O}_3$. The high yield and Zn uptake with Zn-EDTA was probably due to the role of the EDTA-chelate in increasing the solubility and availability of Zn as well as the movement of zinc ions in the soil by diffusion and/or mass flow. The good response of soybean to the addition of zinc as ZnCl_2 (treatments 4 and 5) in this experiment and the greater response with ZnCl_2 than with $\text{Zn-Fe}_2\text{O}_3$ (treatments 6, 7 and 8) was probably due to the method of application of ZnCl_2 in this experiment. The ZnCl_2 solution in this experiment was uniformly sprayed onto the soil. Hence, zinc was well distributed throughout the entire volume of soil and therefore a large portion of the plant roots were in contact with the zinc fertilizer which resulted in a significant increase in zinc uptake and yield.

Increasing the rate of zinc added as ZnCl_2 and $\text{Zn-Fe}_2\text{O}_3$ from 5 to 10 ppm (treatments 4 to 7) resulted in a large increase in dry matter yield and zinc concentration in the aerial portions of the plants. The effectiveness of $\text{Zn-Fe}_2\text{O}_3$ added at rate of 10 ppm Zn in increasing yield and zinc content of plants was about equal to that of ZnCl_2 added at rate of 5 ppm Zn.

Concentration of zinc in the aerial portions of the plants when 5 ppm Zn as $\text{Zn-Fe}_2\text{O}_3$ was thoroughly mixed with the total soil volume was slightly higher than when placed in a band. Dry matter yield was also higher when the $\text{Zn-Fe}_2\text{O}_3$ was mixed with the soil than when banded but the differences were not statistically significant. The results also show that yield and zinc concentration in the plants treated with the Zn-EDTA mixed with the soil were slightly higher than when banded. These differences, however, were not statistically significant. These findings are generally in agreement with those of several investigators. Shaw et al 1954, Mortvedt et al 1969 and Hedayat 1977, concluded that mixing the zinc as uniformly as possible with the total soil volume was the most effective method of zinc application in increasing dry matter yield and Zn uptake by plants.

The data of this experiment verify the observation and conclusions drawn from the first growth chamber experiment. It was again shown that zinc chemically combined with iron oxide (hematite) was highly available to plants and probably could be used commercially as a zinc fertilizer. More investigations, however,

need to be conducted on the efficiency of $\text{Zn-Fe}_2\text{O}_3$ before final conclusions on the use of $\text{Zn-Fe}_2\text{O}_3$ as a fertilizer can be made.

The most important and interesting observation obtained from this experiment is the tremendous increase in the yield and zinc uptake by soybeans when the ZnCl_2 was mechanically mixed with the iron oxide and placed in a band below the seed. Soybean dry matter yield increased markedly with decreases in the amounts of iron oxide added (treatments 11 to 14). Soybean yields when the ZnCl_2 was mixed with 0.5 or 0.25 g of hematite (treatments 12 and 13) were slightly higher than those treated with only ZnCl_2 (treatment 4), Zn-EDTA (treatments 9 and 10) or $\text{Zn-Fe}_2\text{O}_3$ when applied at rate of 10 ppm Zn (treatment 6), and were significantly higher than yields with $\text{Zn-Fe}_2\text{O}_3$ (treatments 7 and 8). The yield with 0.1 g of iron oxide mixed with the ZnCl_2 was slightly higher than the yield with ZnCl_2 (10 ppm Zn) and Zn-EDTA , and significantly higher than the yields obtained with ZnCl_2 (treatment 4) or $\text{Zn-Fe}_2\text{O}_3$ (treatments 6, 7 and 8).

Zinc concentration in the aerial portions of the plants was also tremendously increased by application of the ZnCl_2 + hematite mechanical mixes. The amount of hematite added did not significantly change Zn concentrations in the plants. The results also show that zinc concentration in these plants was significantly higher than zinc concentration in all other treated plants except those of the Zn-EDTA treatments (Table 11). It was shown in the first growth chamber experiment that ZnCl_2 banded in the soil was an ineffective

method of enhancing yields and Zn uptake by soybeans. Results obtained by other investigators (Shaw et al 1954; Mortvedt et al 1969; Hedayat 1977) also indicated that banding of inorganic zinc fertilizers into the soil was ineffective in enhancing yield and zinc uptake. In this growth chamber experiment, application of various amounts of hematite mixed with $ZnCl_2$ resulted in high yields and high Zn uptake. The yield increased with decreases in amount of the iron oxide mixed with the $ZnCl_2$. Unfortunately, due to limitations of growth chamber space and since $ZnCl_2$ without iron oxide banded in soil had generally been ineffective in increasing yield, a treatment with only $ZnCl_2$ banded into the soil was not included in this experiment. Thus, the lack of a definitive control for these treatments (only $ZnCl_2$ banded) precluded a complete evaluation of these treatments. Despite these limitations, it would appear from the data obtained with the $ZnCl_2$ + hematite mechanical mixes in this study as compared to results obtained when only $ZnCl_2$ was banded in the first growth chamber experiment and also from results of other investigators that the hematite enhanced Zn uptake from the fertilizer band.

Concentrations of copper, iron and manganese in the aerial portions of the control and treated plants were relatively high (Table 11) indicating that these micronutrient cations supplied by the soil and through fertilization were adequate for soybean growth. Iron concentrations in plants did not significantly vary with treatment whereas copper and manganese concentrations did significantly

vary with treatment. Copper concentration in ZnCl_2 treated plants (treatments 4 and 5) was equal to Cu concentration in control plants, but significantly lower than that in Zn-EDTA and ZnCl_2 + hematite treated plants. Manganese concentration in ZnCl_2 treated plants was significantly lower than that in control and iron oxide treated plants, and plants treated with ZnCl_2 mixed with the hematite. The reduction in Cu and Mn concentrations in plants treated with ZnCl_2 was probably due to competition of Zn^{2+} , Cu^{2+} and Mn^{2+} ions for the same absorption sites on root surfaces and/or for a common carrier mechanism (Moore 1972). The results also showed that Mn concentration in plants treated with Zn-EDTA was significantly lower than that for all other treatments. This may have been due to the replacement of Zn by Mn on the EDTA-chelate (Lindsay 1980). The formation of Mn-EDTA in the soil probably reduced the solubility and availability of manganese.

It is interesting to note that the plant content of Cu and Fe was higher for plants treated with the ZnCl_2 + hematite than for control plants. The increases in Cu concentration were statistically significant when low rates of iron oxide were added, but the increases in Fe concentration were not significant. It seems, therefore, that application of ZnCl_2 mechanically mixed with the hematite in a fertilizer band offered the advantage of a well-balanced Zn, Cu, Fe and Mn supply to the soybean plants. However, more investigations are required to confirm these findings.

The results of this plant growth study demonstrate two interesting new facts; firstly, the chemically combined zinc with

the iron oxide (hematite) was highly available for plant uptake and secondly, the presence of the hematite mechanically mixed with the zinc chloride in a fertilizer band resulted in high soybean yields and high zinc concentration in the plants. In order to explain these results two hypotheses are proposed:

(1) Restricted movement of ions is one of the great differences between a nutrient solution and a natural soil system. In culture solutions the nutrient ions are free to move (diffusible) and therefore are immediately available for absorption by roots, whereas in soils they are adsorbed on colloidal particles, occluded and/or fixed in crystals and thus exist under conditions of constraint. However, when ions are present in the adsorbed state, their ease of release from the adsorption medium becomes a major factor affecting their availability. The concentrations of zinc adsorbed on the iron oxide used in both growth chamber experiments were in the range relevant to plant growth. Thus the amount of $\text{Zn-Fe}_2\text{O}_3$ which contained a zinc concentration of about 5-10 ppm was found to supply, in general, sufficient zinc to prevent zinc deficiency in soybeans. The "readily desorbed" zinc (extractable by H_2O and MgCl_2) was expected to be readily available to plants by diffusion and/or mass flow, but the amount of "readily desorbed" zinc on surfaces of the iron oxide would not be enough to supply adequate quantities of zinc to the plant. Therefore, the sufficient concentrations of Zn in the aerial portions of the plants indicate that both the "readily desorbed" and "less readily desorbed" zinc

fractions were taken up by plants.

Release of the "less readily desorbed" zinc from the oxide's surfaces and its availability to plants can be explained by an ionic exchange process and/or some special mechanisms associated with root-soil interface. This could have been due to:

(a) A liberation of adsorbed zinc may occur as a result of ionic exchange between ions on the root surfaces and the zinc on the iron oxide. It is postulated that the negatively charged surfaces of plants have ionic exchange properties, and the roots excrete inorganic ions to balance the surface charge when unequal absorption of cations and anions exist. When more cations are absorbed than anions, H^+ ions are released by the roots to balance the charge, and OH^- or HCO_3^- are released to balance the charge when more anions are absorbed than cations. According to this phenomenon, the released H^+ ions by roots most likely replaced the zinc ions on surfaces of the iron oxide enabling them to enter the plant. For every Zn^{2+} ion that is released from the oxide's surface, two H^+ ions should be found on the oxide's surface in an exchangeable form or involved in the aquo ($-OH_2$) and the hydroxo ($-OH$) groups which are components of the surface structure of the iron oxide.

(b) The ability of plant roots to absorb zinc from the strongly held fraction could also be explained by the lower pH in the immediate vicinity of plant roots than that in the bulk of the soil. Although little is known about the actual pH near and at the root surfaces in a soil, it is believed that it is on the acid side

of the pH scale. Williams et al (1950) found that the pH in the immediate vicinity of soybean roots was within the range 2.85 - 3.60. The H^+ ions and the organic and amino acids exuded by plant roots are responsible for the low pH near and at the root surfaces. However, lowering of pH at the root-soil interface probably enhanced release of the readily and the less readily desorbed zinc and perhaps the occluded fraction from surfaces of the iron oxide. Thus, the sorbed zinc became much more available for plant uptake. This hypothesis could be true since lowering of pH of the extracting solution was found to readily release the strongly held fraction of zinc from the hematite's surfaces as was reported previously in this manuscript.

(2) The mechanism for enhancement of zinc content of the aerial portions of soybeans and the tremendous increase in yield when the iron oxide was mechanically mixed with $ZnCl_2$ in a band below the seed is mostly unknown, but there are two possible explanations for the results obtained:

(a) Since the Almasippi sandy soil has a low buffering capacity, the effect of root exudates in lowering the pH of the root zone particularly at soil-root interfaces would be pronounced. Alterations in the pH of the fertilizer band probably would also exist due to the release of H^+ ions from the oxide's surfaces as a result of adsorption of zinc ions and/or other ions present in the soil solution. Lowering the pH of the immediate vicinity of plant

roots and the fertilizer band would increase the chemical availability of zinc in the band and at the soil-root interfaces, and possibly reduce adsorption and/or fixation reaction(s) between zinc ionic species and the other soil constituents. Even if zinc was adsorbed on surfaces of the oxide, it would be held in a plant available form as indicated by these studies. The high chemical availability of zinc in the soil would result in more Zn absorbed from the fertilizer band by roots and, in turn, high zinc content and increases in dry matter yield.

(b) The other possible reason for enhancement of zinc uptake could be due to an effect on root growth and proliferation in the fertilizer band caused by the presence of the iron oxide mixed with the $ZnCl_2$ in the band. The fertilizer zinc absorbed by the roots is a function of both the absorption capacity per unit root surface area and the root surface area in contact with the fertilizer zinc, i.e., the amount of ion absorbed by the plant is a function of the amount supplied to the roots and the amount of roots present per unit volume of soil. Since the Zn^{2+} ion is regarded as a relatively immobile nutrient in soil, the absorption of Zn is highly dependent on root soil contact. Increased contact between root surface and the fertilized soil could occur either through an increased growth of roots in a given volume of fertilized soil or an increase in the volume of soil fertilized. If the addition of iron oxide to the $ZnCl_2$ in a fertilizer band increased either of these factors, an increased absorption of fertilizer zinc would be expected. Since it

is well known that banding zinc chloride in a soil does not result in any significant increase in Zn absorption by plant roots, it is suspected that the increased Zn uptake, and the high dry matter yield of soybeans, was probably due to a combination of root growth and proliferation in the fertilizer band. It is postulated that 1 to 2 moles of H^+ are released for each Zn^{2+} ion adsorbed on surfaces of the iron oxide. The released hydrogen ions most probably enhanced root proliferation and growth through its effect on cell elongation. This increased root growth as well as the high chemical availability of Zn in the band and at the soil-root interfaces resulted in an increase in Zn absorption from the fertilizer band and a large increase in yield.

V. SUMMARY AND CONCLUSIONS

The hydrous metal oxides of iron and aluminum are found, at least to some extent, in all soils and have a very large influence on the chemical behavior of many elements. Because of the chemical nature of these oxides they have an ability and high capacity to specifically and nonspecifically adsorb different ions particularly those of the heavy metal elements such as Zn in soils, sediments and natural waters at certain pH levels. It has been postulated that they are the principal solid phase reactive components controlling the labile fraction and determining the chemical and plant availabilities of the heavy metal nutrient ions in soils.

A few previous studies showed that adsorption of Zn on surfaces of Fe and Al oxides was greatly affected by the pH of the equilibrium solution. In the research work presented in this manuscript the effect of a wide range of suspension pH's on Zn sorption by iron oxide (hematite) was investigated. Zinc sorption from aqueous solutions by the hydrated α -Fe₂O₃ increased markedly with increasing initial pH of the suspension from 5.14 to about 8 but sharply decreased at an initial pH of above 8, indicating that sorption of Zn was highly dependent upon the pH of the equilibrium system. The suspension pH's dropped after sorption reaction(s) took place and varied from 4.96 to 5.76 indicating that H⁺ ion(s) release from the oxide's surfaces accompanied Zn sorption. The highest amount of Zn sorbed by the hematite occurred at an initial pH about

7 but, the maximum Zn sorption could not be accurately estimated because precipitation of Zn as $\text{Zn}(\text{OH})_2$ was expected to take place at higher pH values.

The investigation also involved the effect of pH of the ZnCl_2 solution added and the effect of increasing the pH of the equilibrium system after the initial sorption reaction(s) took place on Zn sorption by iron oxide (hematite). These studies were conducted at initial pH values ranging from 4.55 to 10.12 achieved by the addition of different volumes of 0.1 M HCl or 0.1 M NaOH to the systems. Sorption of Zn increased significantly when the ZnCl_2 solution was adjusted to pH of 6 or 7 as added compared to that with the ZnCl_2 solution at a pH of 5.8. No significant differences were observed between the amounts of Zn sorbed from ZnCl_2 solutions of pH 6 and 7. Increasing the pH of the equilibrium suspensions by addition of 0.1 or 0.2 ml of 0.1 M NaOH after the initial sorption reaction(s) took place resulted in a very large increase in the amounts of Zn sorbed by the hematite. The amounts of Zn sorbed when 0.2 ml NaOH was added were almost twice that sorbed without the addition of NaOH during equilibration. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) showed a very high capacity for Zn sorption provided the pH of the equilibrium solution was maintained at levels which favoured sorption.

High zinc sorption from aqueous solutions occurred despite the high initial pH values which favoured precipitation of Zn as $\text{Zn}(\text{OH})_2$. This interesting phenomenon suggested that Zn was probably

chemically precipitated as $\text{Zn}(\text{OH})_2$ on the oxide's surfaces or in the diffuse double layer as well as being adsorbed.

An extremely interesting fact was the depression in pH values of the equilibrium solutions after the initial sorption reaction(s) took place. The final pH values varied from 4.39 to 6.82. This fact strongly indicated that protons were released from aquo ($-\text{OH}_2$) and/or hydroxo ($-\text{OH}$) groups present on surfaces of the iron oxide upon adsorption.

In an attempt to determine some of the factors which affected Zn sorption from aqueous solution by the hydrated iron oxides, a temperature study was conducted to obtain information on the effect of the ambient temperature during equilibration on Zn sorption by hematite. Temperature over the range 17 to 30 C did not significantly affect amounts of Zn sorbed by hematite. Addition of the NaOH to the equilibrium suspensions resulted in about five fold increase in the amounts of Zn sorbed compared to that when NaOH was not added indicating that sorption of Zn by the hematite was strongly dependent upon the pH of the equilibrium solution rather than the ambient temperature during equilibration.

The reversibility of zinc adsorbed on surfaces of hematite ($\alpha\text{-Fe}_2\text{O}_3$) was investigated. Sorbed Zn at pH 6 or 7 by this oxide was successively extracted eight times using 25 ml portion of each of deionized water and 1.0 M MgCl_2 solution at room temperature. In a second experiment, the sorbed Zn at pH 7 was successively extracted using deionized H_2O , 1.0 M MgCl_2 , and 0.005 M DTPA

buffered solution. Nine successive extractions were conducted at room temperature using 25 ml of each extractant. A large portion of the total Zn sorbed on surfaces of the hematite was highly exchangeable and was released upon extraction. The portion of total sorbed Zn extracted was about 85% for DTPA, 33 to 60% for MgCl_2 and 6 to 50% for deionized H_2O . Most of the total extractable Zn was extracted in the first two successive extractions and amounts extracted decreased markedly with extraction. The results generally provided evidence for postulation of the presence of three fractions of adsorbed Zn on $\alpha\text{-Fe}_2\text{O}_3$ surfaces, namely, "readily desorbed", "less readily desorbed" and "fixed and/or occluded" zinc. The readily desorbed fraction was easily extracted by deionized H_2O and MgCl_2 solution, but the less readily desorbed Zn was difficult to extract by these two extractants. The fixed and/or occluded fraction was hardly extractable by DTPA buffered solution.

Effect of the ambient temperature on desorption of Zn was also studied. Samples of the prepared Zn- Fe_2O_3 were equilibrated with 25 ml portions of each of deionized H_2O , 1.0 M MgCl_2 or 0.005 DTPA buffered solution at various temperatures. The temperature of the incubation room during equilibration was controlled at 17, 20, 25 or 30 C. Amounts of Zn extracted by each extractant were determined. Zinc desorption from the hematite surfaces increased markedly with increasing ambient temperature over the range 17 to 30 C indicating that desorption reaction(s) of Zn was an endothermic type of reaction. Extractable Zn decreased in the order: DTPA, MgCl_2 , deionized H_2O

at a given temperature. It was concluded that zinc deficiencies noted by other workers at low soil temperatures followed by the disappearance of Zn deficiency symptoms when soil temperature increases may be due to the effect of temperature, per se, on the amounts of zinc supplied to the soil solution from the hydrated Fe and Al oxides in soils.

A soil incubation study was conducted to estimate the extractability and chemical availability of Zn combined with the hematite when added to soil. The chemical availability of the Zn added was determined by measuring the Zn concentration in soil-DTPA extracts. Incubation time of 1 to 6 week had no significant effect on the extractability of Zn from the Almasippi soil whether the source of labile Zn was $ZnCl_2$ or $Zn-Fe_2O_3$. Concentrations of Zn in extracts of soil treated with $Zn-Fe_2O_3$ was higher than that of soil treated with $ZnCl_2$ suggesting that Zn associated with the iron oxide was more available in soil than Zn added as $ZnCl_2$. Zn from $ZnCl_2$ probably reacted with other soil constituents such as clay minerals, organic materials, etc. and was less easily extracted than the Zn combined with the iron oxide. It was concluded that the $Zn-Fe_2O_3$ would be a good inorganic source of plant available zinc in soil and the readily desorbed Zn from the surfaces of the oxide would be expected to be highly available and readily absorbed by plant roots.

A growth chamber experiment using soybean as a test crop was conducted in order to obtain information on whether or not the chemically combined Zn with the iron oxide (hematite) would be

available to plants. The yield of soybeans was significantly increased with the addition of 5 ppm Zn as $\text{Zn-Fe}_2\text{O}_3$, both when applied in a band below the seed and when thoroughly mixed with the soil. In contrast, yield was not increased when 5 ppm Zn as ZnCl_2 was added. The increase in dry matter yield was about 40% when $\text{Zn-Fe}_2\text{O}_3$ was mixed throughout the soil and about 25% when it was banded 2.5 cm below the seed indicating that mixing $\text{Zn-Fe}_2\text{O}_3$ as uniformly as possible with the total soil volume was much more effective than banding in increasing soybean yield. Zinc concentration in the aerial portions of the $\text{Zn-Fe}_2\text{O}_3$ treated plants was relatively low but higher than that of the control and ZnCl_2 treated plants indicating that Zn sorbed by the hematite ($\alpha\text{-Fe}_2\text{O}_3$) was highly available in soil and, in turn, for absorption by plants. It is concluded, therefore, that $\text{Zn-Fe}_2\text{O}_3$ would be a good inorganic source of plant available zinc in soil and probably more effective as a zinc fertilizer than inorganic salts such as ZnCl_2 .

A second growth chamber experiment was established to evaluate the effect of method and rate of Zn applied as $\text{Zn-Fe}_2\text{O}_3$, ZnCl_2 and Zn-EDTA on yield and zinc utilization of soybeans, and to estimate the availability and plant uptake of zinc from ZnCl_2 mixed with iron oxide (hematite) in a fertilizer band. Significant increases in yield and Zn content of soybean plants resulted from the addition of Zn as ZnCl_2 , $\text{Zn-Fe}_2\text{O}_3$ and Zn-EDTA. The effectiveness in increasing soybean yield and zinc content of the three different sources of Zn increased in the order $\text{Zn-Fe}_2\text{O}_3$, ZnCl_2 , Zn-EDTA.

Increasing the rate of Zn added as $\text{Zn-Fe}_2\text{O}_3$ and ZnCl_2 from 5 to 10 ppm resulted in large and significant increases in the yield and Zn concentration in the aerial portions of the plants. The effectiveness of $\text{Zn-Fe}_2\text{O}_3$ when added at a rate of 10 ppm Zn was about equal to that of ZnCl_2 added at rate of 5 ppm Zn. Zinc in plant tissues derived from the $\text{Zn-Fe}_2\text{O}_3$ was derived from both the "readily desorbed" and "less readily desorbed" fractions.

Concentration of zinc in plants and dry matter yield were markedly increased when Zn was mixed throughout the soil indicating that mixing the zinc as uniformly as possible with the total soil volume was the most effective method in increasing the yield and Zn concentration in soybean plants. Generally, the data obtained in the second experiment verified the results obtained in the first growth chamber experiment which showed that the Zn chemically combined with hematite was highly available to plants and would be a good inorganic zinc fertilizer.

The most interesting fact obtained in this plant growth study was the large and significant increase in yield and Zn content of soybean plants when ZnCl_2 at rate of 5 ppm Zn was mixed with different rates (from 0.1 to 1.0 g) of hematite and banded 2.5 cm below the seed. It was found by other investigators that application of only ZnCl_2 in a band was ineffective in increasing yields and Zn uptake by plants even on Zn deficient soils. In this study, uptake of Zn by soybean plants from the band was enhanced due to the presence of the iron oxide. Concentration of Zn in these

plants was significantly higher than that of control and all other treated plants except those treated with Zn-EDTA. The mechanism by which the hematite enhanced Zn uptake from the ZnCl_2 + hematite fertilizer bands is unknown. It was postulated that the combination of the hematite and the Zn fertilizer in the band stimulated root growth and/or root proliferation in the band. This increased root growth resulted in an increase in Zn absorption and yield of the plants.

Although many studies have been conducted to determine the response of various crops to application of one or more micronutrients, less attention has been given to determining the most effective and economical method of supplying these nutrients. Most plants utilize soil applied micronutrients inefficiently because of rapid fixation of some micronutrients by many soils which reduces their availability for plant uptake. In certain situations, seed treatment may provide adequate amounts to prevent deficiencies of some micronutrients, whereas foliar applications may correct existing deficiencies. However, soil application is usually the preferred method of application of many of inorganic and organic micronutrient fertilizers. Recently, chelated micronutrients have been extensively used because they are often more effective than inorganic salts when applied at the same rate and may be less reactive with other fertilizer and soil components, but their high cost can negate this advantage.

The results of the research presented in this manuscript provided new information which indicated that in particular circumstances zinc adsorbed on hematite or the application of hematite with inorganic zinc salts, and perhaps other micronutrients, may be very effective micro element fertilizers.

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