

ASSOCIATION OF NATIVE SOIL ZINC WITH IRON AND
ALUMINUM OXIDES AND REACTION PRODUCTS OF ZINC
BANDED IN SOIL

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Mahmoud Kalbasi-Ashtari

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MAHMOUD KALBASI-ASHTARI

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ABSTRACT

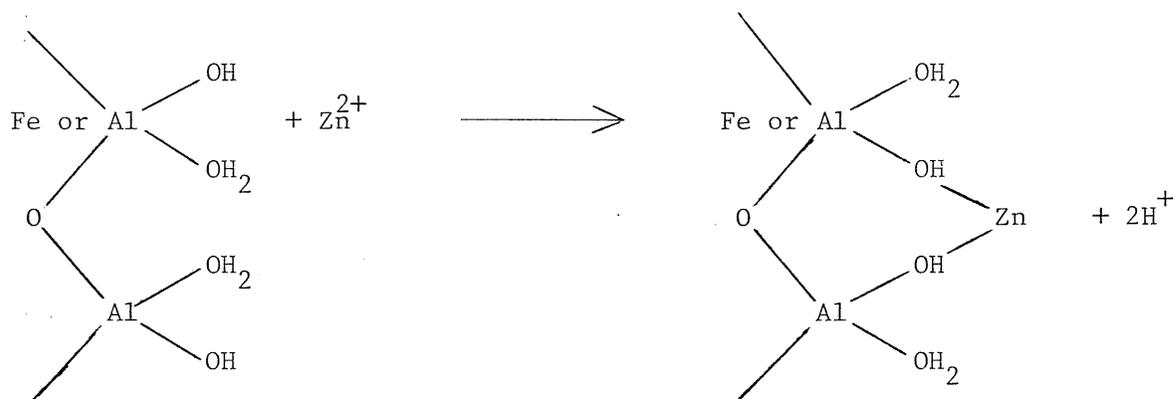
Zinc concentrations in soil solutions of four soils acidified to various pH values were compared with the concentration of Zn from sphalerite (ZnS), hemimorphite ($\text{Zn}_4(\text{OH})_2\text{SiO}_7 \cdot \text{H}_2\text{O}$) and willomite (Zn_2SiO_2). Concentration of Zn in solution from these minerals was much greater than concentration of Zn in soil solutions indicating that these minerals were too soluble to exist in soils as solid phases. Acidification of the soils resulted in the release of Fe as well as Zn and there was a close association between amounts of Fe and Zn released upon acidification indicating that Zn may be associated with Fe oxides or other oxides in soil.

Statistical correlation analysis of various components in eight soils taken from different locations in Manitoba indicated that total soil Zn concentration in these soils was highly correlated with total Fe concentration, total Al concentration and with clay content. ($r = 0.86, 0.95$ and 0.91 , respectively). Zinc was also significantly correlated with Fe and Al concentration when the clay size fraction was very low or absent.

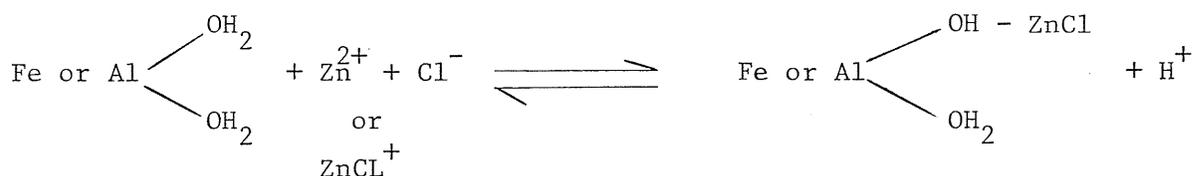
The soils used in the acidification experiment were successively extracted by an oxalate solution. Large quantities of Zn (45 to 71% of total Zn content) were extracted along with the amorphous and organic complexed Fe and Al from the soils indicating, once again, that Zn was in some manner associated with oxides of Fe and Al in the soils. The quantities of Zn, Fe and Al extracted from the soils by the oxalate solution were much greater than exchangeable Zn, Fe and Al, respectively.

The retention of Zn by Al_2O_3 and Fe_2O_3 from aqueous solutions was studied. Adsorption of Zn by hydrated Al_2O_3 and Fe_2O_3 was highly pH dependent and increased markedly with increasing pH. Fe_2O_3 had a higher Zn adsorption capacity, at equivalent pH values than Al_2O_3 . Hydrogen

ions were released upon adsorption of Zn on the surface of Al_2O_3 and Fe_2O_3 . The molar ratio of H^+ released to Zn adsorbed increased with pH from 1.53 to 1.96. Surface aquo ($-\text{OH}_2$) and hydroxo ($-\text{OH}$) groups were believed to be involved in Zn adsorption. Zinc adsorbed by Al_2O_3 and Fe_2O_3 was categorized into specific and nonspecific adsorption depending upon reversibility (exchangeability with Ba^{2+}) and two mechanisms of adsorption, one with and one without Cl adsorption were postulated. The specific adsorption involved adsorption of Zn^{2+} and release of two H^+ for each mole of Zn adsorbed and accounted for 60 to 90% of total Zn adsorption. A bonding mechanism for specifically adsorbed Zn was postulated and was as follows:



The nonspecific adsorption of Zn involved adsorption of ZnCl^+ or Zn^{2+} plus Cl^- and the release of one H^+ for each mole of Zn adsorbed and accounted for 40 to 10% of total Zn adsorption. The bonding mechanism for nonspecifically adsorbed zinc was thought to be a monodentate type of bonding and could be represented as follows:



The ratio of specific to nonspecific adsorption increased with increase of pH.

The reaction products or solid phases formed when soils were reacted with various Zn compounds were also studied. $ZnSO_4$, ZnEDTA, ZnS and $ZnSO_4$ plus $NH_4H_2PO_4$ were banded in soils and the solid-phase Zn compounds identified using x-ray diffraction analysis. Solubility of Zn in soil adjacent to the fertilizer band was determined by measuring the Zn concentration in soil-water extracts. The reaction product in a noncalcareous soil treated with $ZnSO_4$ was $Zn(OH)_2$ which was metastable and persisted for only a few weeks. $ZnSO_4$ was usually precipitated as $ZnCO_3$ and $Zn_5(CO_3)_2(OH)_6$ in the calcareous soils. No crystalline reaction products were detected in soils treated with ZnEDTA. ZnS was usually identified in soils treated with ZnS. In addition, $Zn_5(CO_3)_2(OH)_6$ and $Ca[Zn(OH)_3]_2 \cdot 2H_2O$ were found in a calcareous soil treated with ZnS and incubated for 32 weeks. Reaction products formed when $ZnSO_4$ plus $NH_4H_2PO_4$ were added in a band were $Zn_3(PO_4)_2 \cdot 4H_2O$ in the noncalcareous Newdale soil and $Zn_3(PO_4)_2 \cdot 4H_2O$, NH_4ZnPO_4 and $ZnCO_3$ in the calcareous Lakeland soil.

Concentrations of Zn in soils treated with Zn were greater than in untreated soils. Zinc concentration in soils was greatest with ZnEDTA and lowest with ZnS. Zinc concentration in calcareous soils was less than in noncalcareous soils treated with $ZnSO_4$. ZnEDTA was highly soluble in all soils. Zinc concentration decreased with time of incubation in soils treated with $ZnSO_4$ or ZnEDTA but Zn concentration increased with time in soils treated with ZnS. Zinc concentration in soils treated with phosphate plus $ZnSO_4$ was less than for soils treated only with $ZnSO_4$. The concentration of Zn in all soils treated with Zn was greater than in untreated soils indicating $ZnSO_4$, ZnS, and ZnEDTA would be good Zn fertilizers when banded in soils.

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I. INTRODUCTION

Zinc as an essential micronutrient has become increasingly important in agricultural production during the past decade. Widespread occurrence of Zn deficiency and frequent ineffectiveness of Zn fertilization have drawn the attention of soil chemists to the chemistry of Zn in soil. A knowledge of the Zn solid phase(s) occurring in soils is fundamental to understanding the chemical behavior of Zn in soil. Identifying these Zn phases has been difficult, primarily because the total Zn in soils is often quite low.

The high Zn fixing capacity of soils is often mentioned in the literature although the constituent(s) and the mechanisms involved in fixation of Zn in soils are not fully understood. Clay minerals, carbonates, sesquioxides and organic matter have been suggested as possible constituents involved in the fixation and/or precipitation of added Zn.

Investigations concerning the relationship between Zn and soil solid phase have traditionally been limited to calcareous soils and soils with natural pH values above 7. However, the well-established fact (Jenne 1968) that the liming of acid soils to pH's above 6.0 frequently induces Zn deficiency has caused concern for the agronomic management of acid soils. The foregoing fact, coupled with the fact that micronutrient deficiencies (except MnO) are not as frequent in naturally alkaline soils as in highly weathered old soils that have been limed has raised the question of the identity of the constituents in soils which fix or sorb micronutrients. Jenne (1968) proposed that hydrous oxides of Fe and Mn controlled the concentration of trace metals in soil solution and fresh water.

The fate of added Zn in both calcareous and noncalcareous soils is not fully understood. When very large amounts of Zn are applied to soil

or when microregions in soil are saturated with Zn, such as for band or point source applications, formation of new Zn solid phases are very likely. Identification of these new phases and study of their stability and solubility in the soil system, are of extreme importance in improving the methods, time and rate of Zn fertilizer application, as well as the kind of Zn compound which should be used as a fertilizer.

The research reported here was undertaken to explore:

- (a) - the existence of some postulated Zn minerals in soil.
- (b) - the role of hydrous oxides of Fe and Al in controlling Zn solubility.
- (c) - the mechanism(s) of Zn sorption by Fe and Al hydrous oxides.
- (d) - identifying the reaction products and determining the solubility of Zn banded in some soils.

II. REVIEW OF LITERATURE

Zinc Minerals in Soils

Zinc is one of the micronutrients most commonly deficient in soils from the standpoint of crop production. A knowledge of the Zn phase(s) occurring in soils is fundamental to the understanding of Zn deficiency and its correction. Identifying these Zn phases has proven to be a difficult problem, primarily because the total Zn in the soil is so low (generally in the range of 10-300 ppm).

Generally Zn is not a major constituent in any mineral in igneous rocks, nor does it occur to any great extent in quartz and feldspars. However Zn^{2+} with an ionic radius of 0.83 Å substitutes to some extent for Mg^{2+} (0.78 Å) and Fe^{2+} (0.83 Å) in silicate minerals (Goldschmidt 1954). Krauskopf (1972) reviewed the geochemistry of Zn and pointed out that Zn occurs most frequently in the lithosphere as the mineral ZnS (sphalerite).

The greatest concentration of Zn in sedimentary rocks is found in shales as is typical for most of the heavy metals. Wedepohl (1953) reported that one third to one half of the total Zn in the black shales of northern Germany is present as sphalerite with the remainder occurring in clay minerals. In sedimentary rocks a portion of the Zn is absorbed as Zn^{2+} on fine-grained material and the remainder is in the structure of clay minerals, probably substituting for Mg^{2+} (White, 1957, Elgabaly, 1950). Zinc is also an essential constituent in the clay mineral "Sauconite" but the pure mineral is rare.

Both Krauskopf and Lindsay (1972) are of the opinion that sphalerite (ZnS) is unstable under normal oxidizing conditions. Nevertheless, Kittrick (1976) examined the solubility of ZnS in the presence of H_2S

and found that concentrations of H_2S actually found in the atmosphere are high enough to engender control of Zn^{2+} in the soil solution of aerated soils by ZnS . However, these results contradict findings of McGregor (1972) who reported that applied ZnS maintained a higher concentration of Zn^{2+} in soil solution than found for untreated soils indicating that ZnS did not govern the concentration of Zn^{2+} in soil solution of these soils.

Weathering of Zn minerals releases Zn^{2+} into solution. Unlike Cu^{2+} , the simple ion remains dominant at pH values of about 9 or less. Zinc ions released may then be removed from the soil solution in several ways. Ions may combine with anions in the soil solution forming a new solid phase such as Zn carbonate or Zn hydroxide. Alternatively Zn ions may be adsorbed on different soil minerals and subsequently fixed irreversibly.

Most of the simple compounds such as ZnO (Zincite), or $ZnCO_3$, resulting from reactions of Zn^{2+} with common anions in soil are too soluble to persist in soils. Not only are common Zn compounds relatively soluble, but the complex ions that might form between Zn and the commonly occurring inorganic anions are too soluble to account for the low solubility of Zn in soil (Chester, 1965). In basic solution, $Zn(OH)_2$ may precipitate if the concentration of Zn^{2+} is high. But, such high Zn^{2+} concentrations seldom occur. The minimum solubility of $Zn(OH)_2$ occurs at pH 9.5. It dissolves at higher pH values to form zincate ions, $Zn(OH)_4^{2-}$. The precipitated hydroxide is unstable, decomposing under both natural and laboratory conditions to zincite, ZnO . This compound is rare as a mineral, however, because usually enough carbonate or silicate is present to precipitate Zn as $ZnCO_3$ (smithsonite), $Zn_4(OH)_2Si_2O_7 \cdot H_2O$ (hemimorphite) or, at higher temperatures, Zn_2SiO_4 (Willomite)

(Harker & Hutta, 1956; Roy & Mumpton, 1956; Takahashi, 1960). Solubility data for hemimorphite and willomite are not available, but Norvell and Lindsay (1970) found that for precipitation of the simple silicate, ZnSiO_3 , pH and Zn concentration have to be almost as high as for precipitation of Zn(OH)_2 . Volk (1970) equilibrated ZnEDTA with a Wisner silty clay soil at various pH values and carbon dioxide concentrations. He concluded that postulated compounds such as ZnCO_3 , Zn(OH)_2 and ZnSiO_3 are too soluble to account for the low levels of Zn in the soil solution.

All the above mentioned Zn compounds are too soluble to account for the small concentrations of Zn found in most soil solutions. Adsorption and fixation by clay minerals, sesquioxides, carbonates and organic matter are much more likely mechanisms controlling Zn concentration in soil solution. Jenne (1968) proposed that Zn, along with several other heavy metal ions may be occluded and coprecipitated with hydrous oxides of iron and manganese, and that these oxides constitute the principle matrix in which the less abundant heavy metals are held. Nair and Cottenie (1971) presented convincing statistical proof to show that amorphous Fe_2O_3 , possibly by way of surface coating of finer particles, may retain a large proportion of the trace elements investigated. White (1957) found evidence to indicate that much of the Zn in the soils of the Eastern United States is tied up with hydrous ferric oxides. He stated that 30 to 60 percent of the total Zn is associated with Fe oxides, 20 to 45 percent is held in the lattice position of the clay minerals, and 1.0 to 7 percent is base-exchanged in the clay minerals. However, the nature of the associations is not known. Furthermore, the extractant he used, could have also extracted Al and Mn oxides.

Zinc enriched horizons in the soil profile are also often enriched with clay. According to Michell (1955), the clay fraction is often richer

in some micronutrients than the associated sands. Stanton and Burger (1966b) found the distribution of total Zn, in some soil profiles of South Africa, to follow closely the distribution of soil colloids, both values increasing markedly with depth. Average Zn concentrations in the clay, silt, fine sand and coarse sand were 75.0, 51.5, 6.2 and 3.4 ppm, respectively. The total Zn content of the clay and silt fraction did not vary greatly with depth, but Zn concentration in the sand fraction increased markedly with depth. They felt that this increase resulted from an increase with depth of ferruginous concretions in the sand fraction. Stanton and Burger (1967a) also reported these concretions to be considerably richer in Zn than the surrounding soil from which they were taken. These results suggest that the enrichment is associated, in some way, with cementing materials such as oxides of Fe and possible Al and Mn.

Another possible control mechanism for zinc, in the soil system, is the interaction of Zn with silica associated with clay minerals. Tiller (1967) related Zn adsorption by montmorillonite to increasing levels of silica in solution. He concluded that this reaction which occurred over a wide range of pH values and Zn concentrations was probably restricted to an adsorbed layer rather than a separate ZnSiO_3 phase. The absence of ZnSiO_3 as a separate phase was demonstrated by Norvell and Lindsay (1969, 1970) when they calculated this compound to be too soluble to exist in natural soil systems.

Zinc probably exists, in soils, primarily as the simple ion adsorbed or fixed on fine-grained constituents. There is little doubt about the association of Zn with clay minerals, sesquioxides, carbonates and organic matter. However, the nature of these associations are not fully understood. It also seems that the degree with which Zn is tied up with

the different minerals in the soil varies from soil to soil.

Adsorption and Fixation of Zn in Soils

The Zn ion possesses an 18-electron outer shell, a small ionic radius, and a relatively large charge density. These properties produce a cation with strong polarizing ability. Consideration of the polarization phenomena in the chemistry of soil Zn helps explain the strong adsorption of Zn to clay and other soil minerals and also its tendency to form numerous complexes.

Zinc can be held at cation exchange sites and adsorbed to soil surfaces. Separation of Zn reactions into those of precipitation, fixation or adsorption is most difficult. One of the major problems in studying adsorption reactions is the failure to consider which of the various hydrolysis and complex species of Zn in solution are adsorbed (Lindsay, 1972).

a. Adsorption and Fixation by Clay Minerals

Soil colloids play an important role in the fixation of Zn by soil. Murty and Mehta (1974) reported that Zn fixation measured 72 hours after Zn addition was greatest in clay soils (71%) followed by a sandy clay loam (67%) and finally a loamy sand (38%).

Cation exchange studies with soil colloids and salts of polyvalent metals often result in retention of the metal ion in excess of the cation exchange capacity as measured with NH_4^+ . Elgabaly & Jenny (1943), and DeMembrun & Jackson (1956a) reported that Cu and Zn were retained by soil colloids in quantities greater than possible if the metals were adsorbed exclusively as divalent ions. The explanations offered for the excess retention postulated either the formation of complex metal ions such as ZnOH^+ , ZnCl^+ , $\text{Zn}(\text{CH}_3\text{Coo})_2$ or precipitation

of zinc hydroxide. However, the possibility of hydroxide precipitation was not critically examined, and adsorption of complex metal ions was only inferred. Chu (1968) in x-ray studies, however, found that bentonite did not expand appreciably when it was saturated with Zn using a variety of Zn salt solutions. This suggested that there was neither ZnCl^+ nor ZnAc^+ ion adsorption by bentonite. However, vermiculite expanded somewhat which was attributed to the adsorption of ZnOH^+ ions. Differential thermal analysis confirmed that there was no appreciable ZnAc^+ ion adsorption on bentonite and vermiculite. Also, chloride concentration data confirmed that there was no ZnCl^+ ion adsorption on bentonite and vermiculite.

Elgabaly and Jenny (1943) reported that some adsorbed Zn becomes nonextractable by entering the octahedral layer of montmorillonite. Later Elgabaly (1950) suggested that Zn^{2+} might be fixed in holes normally occupied by Al^{3+} in the octahedral layer decreasing the cation exchange capacity of the mineral. In minerals with Mg in octahedral positions Zn substituted for Mg with no change in the cation exchange capacity.

Bingham et al (1964) attributed adsorption of Cu and Zn by H-montmorillonite in excess of the NH_4^+ -exchange capacity, under alkaline conditions, to the precipitation of $\text{Cu}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$. Under conditions in which the pH of the equilibrium solution was too acid for the formation of $\text{Zn}(\text{OH})_2$ or $\text{Cu}(\text{OH})_2$, the amount of Cu and Zn retained by H-montmorillonite was similar for the Cl^- , NO_3^- , and SO_4^{2-} salts and equal to the cation exchange capacity as measured with NH_4^+ . However, in an acetate system, Cu and Zn retention was usually greater than the CEC even under acid conditions. Zinc adsorption in excess of the NH_4^+ -exchange capacity was also observed by Misra and Tiwari (1966) when the

pH was high and free carbonates were present. But, acid leaching of the soils caused them to lose the property of excess retention of Cu and Zn. In addition to hydrolysis or precipitation of the hydroxides, they suggested that hydroxy carbonates could also precipitate. For calcareous soils, Udo et al (1970) found that the ion concentration products of $Zn(OH)_2$ in solution were within the range of solubility of the hydroxide, when the amount of Zn adsorbed corresponded to the Langmuir adsorption maxima. However, the system remained under-saturated with respect to either $Zn(OH)_2$ or $ZnCO_3$ at the adsorption maxima, when the soil pH was less than 7.5.

DeMembrum and Jackson (1956a) observed that Ca-montmorillonite and Ca-peat could accumulate Zn or Cu from very dilute, neutral solutions either in the presence or absence of Ca ions. They concluded that montmorillonite and peat had specific adsorption sites for Zn and/or Cu. In another paper (1956b), they reported that cations that form weak bases were sorbed in excess of cations that form strong bases in quantities of about 10% for montmorillonite and 40% for peat. Copper or Zn saturation decreased the intensity of the 2.8μ infrared adsorption band of the hydroxyl ions in montmorillonite, vermiculite and kaolinite, indicating a reaction or bonding with the octahedral OH in layer silicates. This bond could be visualized as a $Zn-O-Al$ or $Zn-\overset{H}{O}-Al$ in positions where access by the Cu or Zn ions is possible because of silica net openings, crystal defects or at edges. These data, together with the observation by Hodgson (1963) that a large part of heavy metals adsorbed could be replaced by acid or even less destructive means, suggest that most of the specific adsorption is not by substitution into the octahedral layer, but adsorption by exposed -OH groups. Findings of Durg (1974) also support the above

hypothesis. He found that the amounts of Zn^{2+} adsorbed by illite, montmorillonite and kaolinite were not those expected from the cation-exchange capacity (CEC). The amount of Zn^{2+} adsorbed occurred in the following order: illite, montmorillonite, kaolinite; whereas the CEC of montmorillonite was about four times greater than that of illite. Almost all of the CEC of illite and kaolinite is situated on the edges of the clay layers, but for montmorillonite 80% of the capacity is located between basal layers. The similarity in amount of Zn^{2+} adsorption for illite and montmorillonite suggested that Zn^{2+} cations were mainly adsorbed on the edges of clay layers. Reddy and Perkins (1974), however, found that Zn fixation between basal layers could be enhanced in 2:1 type clays upon alternate wetting and drying. One half as much Zn was fixed by bentonite and illite, under moist incubation, as under alternate wetting and drying. X-ray analysis indicated that Zn was entrapped in the intermicellar spaces of the 2:1 lattice type clays.

Adsorption isotherms have been used for many years to investigate the nature of various types of adsorption phenomena. They provide useful models for physical adsorption, and in addition, some of the equations are well suited to chemadsorption. The Langmuir adsorption isotherm was derived for the adsorption of gases on solids (Langmuir, 1918) and has since been used to describe the relationship between the adsorption of ions by a solid and the concentration of the ions in solution. The Langmuir adsorption equation has often been applied to soil P (Kuo and Lotse 1974, and Syers et al 1973). The latter authors found that with P there were two linear portions of the Langmuir plot presumably corresponding to two types of adsorption sites. Few attempts have been made to apply the equation to soil micronutrients. Adsorption isotherms for Zn in soil have been studied by Jurinak and Bauer (1956),

Warncke and Barber (1973) and Udo et al (1970). The only authors who discussed the Langmuir coefficients for Zn were Udo et al (1970). They found that Zn^{2+} adsorption at low concentration in calcareous soils was described by the Langmuir adsorption equation. The calculated Langmuir adsorption maxima were related to the carbonate and organic matter contents of the soils. When the added Zn^{2+} exceeded the adsorption maximum, $Zn(OH)_2$ precipitated.

Recently Shuman (1975) studied the adsorption of Zn on four soils of varying texture. He found that Zn adsorption conformed to the Langmuir isotherm and that there were two linear portions on the curve. The adsorption sites for the lower linear portion had very high bonding energy coefficients and low adsorptive capacities compared with the adsorption sites of the upper linear portion corresponding to higher Zn concentrations. Soils high in clay or organic matter had higher adsorptive capacities and a higher bonding energy for Zn than sandy soils low in organic matter. Low pH reduced Zn adsorption more for sandy soils than for those high in colloidal material.

Sharpless et al (1969) concluded that pH and cation exchange capacity were the most important factors controlling the extent and strength of Zn retention by soil colloids. They observed that addition of a concentrated solution of $ZnSO_4$ to soil resulted in rapid adsorption of Zn, about 75% of the total being accounted for by cation exchange during the first minute.

The dependence of Zn adsorption on pH is thought to be due to the competition effect of the H^+ ion and to the change of cation exchange capacity with pH. Chu (1968) demonstrated the pH dependence of Zn adsorption by kaolinite, bentonite and vermiculite. He found that Zn adsorption increased slightly with increasing pH for bentonite and

kaolinite, but increased sharply with increasing pH for vermiculite. He attributed the marked increase in the Zn adsorption of vermiculite to the competition effect of Mg and Al at low pH's. The pH dependence of Zn adsorption was also reported by Mangaroo et al (1965) who found that soils formed under slightly acid or neutral conditions adsorbed larger quantities of Zn than soils formed under very acid conditions. The stability constant for the soil-Zn systems were also higher for the near neutral soils.

Another factor which influences Zn adsorption by clay minerals is the silica or silicic acid concentration in the soil solution. Tiller (1968) showed that addition of silicic acid facilitated the reaction of heavy metal cations with clay and, conversely, that the presence of clays facilitated the reaction between those cations and silicic acid. Tiller (1967) related Zn adsorption by montmorillonite to increasing levels of silica in solution. Evidence suggested that over a wide range of pH levels and Zn concentrations there was an interaction between Zn and soluble silica that probably was restricted to an adsorbed layer rather than a separate Zn silicate phase. The presence of clay mineral increased the formation of a $Zn-Si(OH)_4$ complex, presumably because of the higher concentration of reactants at the clay surface. Zinc adsorption by bentonite and kaolinite has also been reported to increase by addition of silicic acid (Newton, 1971). He suggested the normal distribution of silicic acid from soil constituents under field conditions might be involved in Zn fixation in soils.

b. Adsorption and Fixation of Zn by Sesquioxides

The role of the hydrous oxides of Fe, Al and Mn 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) believed that pH, concentration of the metal of interest, concentration of competing metals, concentration of other ions capable of forming inorganic complexes, and organic chelates to be the principle factors affecting the adsorption and desorption of the heavy metals by sesquioxides of Fe and Mn. Hodgson (1963) reported that secondary iron oxide and siliceous minerals which form during weathering must surely present reactive surfaces for the adsorption of micronutrients. Ions adsorbed in this way would largely be occluded as the precipitate continues to develop.

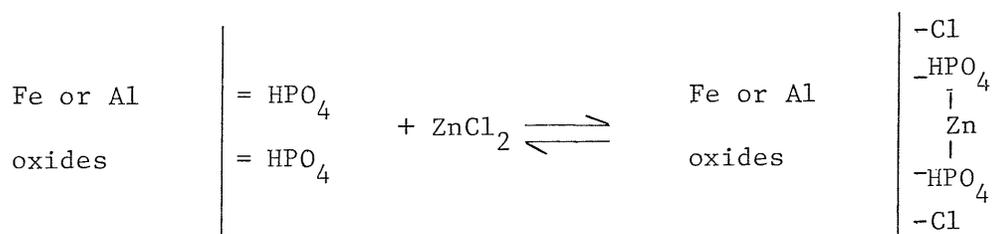
The retention of Zn on Al and Fe-hydroxides was studied by Chu (1968). The results revealed a pronounced anion influence as well as a pH effect on Zn adsorption. The amounts of Zn adsorbed by the hydroxides increased with increasing pH. More Zn was adsorbed by the hydroxides from sulfate solution than from chloride and acetate solution due to the valence effect and difference in the peptizing power of the anions. The adsorption isotherms at a constant pH obeyed the Freundlich equation.

Adsorption of Zn by manganese oxide (MnO_2) was studied by Zasoski (1974). The adsorption was found to depend upon both the pH of the suspension and the amount of sorbed Zn (surface coverage). The Zn^{2+} adsorption, in this study was described well by a multisite Langmuir expression, while a single-site Langmuir expression was found to fit the Ca^{2+} sorption data. The fitted Langmuir expression suggested that there were two or more binding sites for Zn, and that the sorption energy decreased with increased surface coverage.

Adsorption and fixation of Zn by hydrous oxides of the polyvalent

metals most likely occurs. However, the nature and extent of its occurrence in soils is not fully understood. The only research concerning the mechanism of Zn reaction with Fe and Al-oxides is that of Stanton and Burger (1970) whose results are given below:

1. The presence of Fe and Al cations in solution markedly lowered the pH at which precipitation of Zn occurred, while Mn had no effect.
2. Various oxides of Fe and Al in the solid phase sorbed Zn in an analogous manner. The sorbing capacity was a function of pH and the amount of phosphate ions adsorbed by the oxides.
3. In the absence of phosphate ions, adsorption commenced at a higher pH and increased with pH. The sorption reaction is probably associated with surface OH-groups, and is specific for Zn in that Ca^{2+} , Mg^{2+} , NH_4^+ and K^+ ions did not interfere.
4. The ratio of Zn sorbed to phosphate sorbed at a given pH was reasonably constant for different Fe and Al oxides. It was concluded that the phosphated hydrous oxide of Fe and Al sorb Zn through the medium of polyvalent phosphate ions as follows:



Stanton and Burger (1967b) tested the availability of Zn adsorbed by Fe and Al-oxides by adding these oxides to culture solution. They found that Zn bound to hydrated Fe and Al-oxides in soils by polyvalent phosphate ions was unavailable to plants. In the absence of phosphate ions, only more strongly crystalline hydrated Fe oxides, such as goethite, fix Zn so that it cannot be taken up by plants. These results

explain, at least in some instances, the often reported Zn and P interaction (P induced Zn deficiency). According to Penas (1973) high concentration of P in the nutrient solutions reduced the Zn uptake of corn plants regardless of the concentration of iron, Zn, or bicarbonate in the nutrient solutions. Also, Zn uptake was depressed by iron when the level of phosphate was low.

Zinc Interaction with Organic Matter

High levels of organic matter in the surface horizon of soil are probably, at least partially, responsible for the greater availability of Zn in that horizon. Numerous studies have demonstrated a high correlation between organic matter and chemically extractable or plant available Zn (Follett and Lindsay, 1970).

Zinc is essential to all forms of life-born plants and animals. Naturally all forms of organic matter and bio-residues contain Zn that will be released during decomposition and made available to plants and organisms in the soil.

Zinc deficiencies are frequently found in areas where the surface soil has been removed. Nevertheless application of organic waste is effective both in correcting Zn deficiencies and in causing deficiencies (Lindsay, 1972). Apparently organic matter can interact with Zn in two ways. First, insoluble Zn can be mineralized and made available to plants. Secondly, Zn can be bound into organic constituents that are immobile in soils. Such Zn is not readily released to plants and therefore can be considered fixed. DeRemer and Smith (1964) showed that incorporation of sugar beet residues can cause Zn deficiency during the early stages of decomposition.

The presence of soluble Zn-organic complexes in soils was demonstrated by Hodgson et al (1966). They concluded that on the average

about 60% of the soluble Zn in soils is complexed. The degree of complexing of Zn was correlated with soluble organic matter ($r = 0.88$).

Stevenson and Ardakani (1972) reviewed the reactions of organic matter with micronutrients. They concluded that insoluble metal combinations are most likely bound to the humic fraction, particularly humic acids, while soluble metal complexes are mainly associated with individual biochemical molecules, for example organic acids and amino acids. Metal complexes with fulvic acids have high water solubilities.

Randhawa and Broadbent (1965a,b) studied the adsorption of Zn by humic acids. The Zn fraction which was less stably bound was believed to be associated with phenolic OH and weakly acidic-COOH groups. The more stable fraction of Zn was bound by strongly acidic-COOH groups. In their study, strongly bound Zn represented less than 1% of the total Zn retained, but was considered to be of great significance because of its preferential adsorption.

Complex reactions of Zn with organic matter extracted from sewage sludge was studied by Tan *et al.* (1971). They reported that the low molecular weight fraction of fulvic compounds was twice as effective in complexing Zn as the high molecular weight compounds. The complexing power and stability constant of fulvic compounds increased with increasing pH. A shift in infrared characteristics of OH band from 3500 cm^{-1} to 3200 cm^{-1} and a sharp increase in carboxyl stretching at 1650 and 1400 cm^{-1} , indicated the formation of coordinate covalent bonds between OH groups and Zn and electrovalent linkage between COO^- and Zn, respectively.

Much remains to be learned about the interaction of Zn with organic matter in soils. Nevertheless, it is obvious that both soluble and insoluble Zn-organic matter complexes are formed and play an important

role in soils.

Reaction Products of Zn Fertilizers in Soils

Zinc fertilization has become increasingly important in agricultural production during the past decade. Frequently, the addition of Zn fertilizers to soils is rather ineffective because the element becomes fixed in plant unavailable forms.

The role of clay minerals, hydrous oxides of Fe and Al, carbonates and organic matter in fixing native soil Zn was discussed. The degree and strength with which Zn is tied up was shown to be mainly dependent on soil-pH, type of soil mineral, kind and concentration of anion in the soil solution and Zn concentration [DeMumbrum and Jackson (1956a), Udo et al (1970), Reddy & Perkins (1974), Stanton and Burger (1970)].

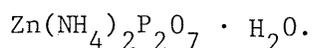
The fate of added Zn in both calcareous and non-calcareous soils is not fully understood. Zinc adsorption in calcareous soils, from $ZnSO_4$, was found to conform to the Langmuir adsorption isotherm (Udo et al, 1970). However, when the concentration of added Zn exceeded the adsorption maximum, the solubility of Zn in the soil solution corresponded to the solubility of Zn hydroxide or Zn carbonate indicating the possible formation of solid phases such as $ZnCO_3$ and $Zn(OH)_2$ when very large amounts of Zn are applied to soil. In accordance with the above findings, Shuman (1975) and Reddy & Perkins (1974) reported that oversaturation of the cation exchange capacity (CEC) with $ZnSO_4$ could have been caused by the formation of $Zn(OH)_2$ due to the relatively high pH. Bingham et al (1964) also explained the retention of the Zn in excess of the cation exchange capacity in terms of precipitation of $Zn(OH)_2$ in the clay systems. Zinc adsorption in excess of the NH_4^+ -exchange capacity was also observed by Misra and Tiwari (1966) when

the pH was high and free carbonates were present. In addition to hydrolysis or precipitation of the hydroxide, they suggested that hydroxy carbonates could also precipitate.

Clarke and Graham (1968) and more recently Melton et al (1973) studied Zn diffusivity in soil and suggested the possible precipitation of the applied Zn as $Zn(OH)_2$, $ZnCO_3$ and calcium zincate $[CaZn(OH)_4]$. Hoover (1966) also suggested the possible formation of $Zn(OH)_2$ or $ZnCO_3$ in soils treated with 500 ppm Zn. He added that the clay mineralogy of the soil did not affect the Zn reaction as much as the soil pH. Whether or not the soil was calcareous or noncalcareous was the most important factor influencing the solubility of applied Zn.

Dhillon et al (1975) observed that $Zn(OH)_2$ and $ZnCO_3$ were the immediate reaction products in an incubation study on various physico-chemical parameters governing solubility of Zn in alkali soils. Upon further aging, however, those compounds were converted into more sparingly soluble compounds. In addition, they hypothesized that $ZnNH_4PO_4$ and $Zn_3(PO_4)_2$ should be immediate reaction products when alkaline soils are fertilized simultaneously with Zn and P. Jones et al (1936) also suggested the possible formation of $Zn_3(PO_4)_2$ in the fertilizer band, when orthophosphate and Zn fertilizers are applied simultaneously.

Hossner and Blanchar (1969) prepared ammonium phosphate mixtures containing varying proportions of total P as pyrophosphate at different pH values. They blended those mixtures with $ZnSO_4$ (2-8% Zn) and reacted them with the soil solution. Residues were recovered and analyzed. Two Zn ammonium orthophosphates, $ZnNH_4H_3(PO_4)_2 \cdot H_2O$ and $ZnNH_4PO_4$, were identified by x-ray analysis. Zinc ammonium pyrophosphates identified were $Zn(NH_4)_2H_4(P_2O_7)_2 \cdot 2H_2O$, $Zn_3(NH_4)_2(P_2O_7)_2 \cdot 2H_2O$ and



The amphoteric nature of Zn may influence the chemical activity in alkaline soils. If a transformation from a positively charged Zn ion to a negatively charged zincate ion were realized under slightly alkaline conditions, the behaviour of Zn in an alkaline soil system would be quite different from that previously discussed. Jurinak and Thorne (1955) investigated the possible formation of zincate ions in K, Na and Ca-bentonite systems. In both the Na and K systems, Zn solubility reached a minimum in the pH range of 5.5 to 6.7. That was perhaps due to the precipitation of $\text{Zn}(\text{OH})_2$. As the pH was increased, the solubility of Zn also increased suggesting the formation of soluble alkali zincates. In the Ca system, however, Zn solubility reached a minimum at a pH of 7.6 with no increase in soluble Zn as the pH of the system was increased. The formation of insoluble Ca zincate was postulated.

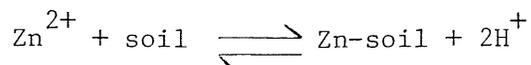
Solubility of Zn in Soils

A - Concentration of Zn in soil solution.

Zinc is only sparingly soluble in soils. Solid phase minerals and adsorption reactions prevent a high concentration of Zn from persisting. Hodgson et al (1966) measured total soluble Zn in several New York and Colorado soils. They reported an average of about 75 ppb of Zn in several acidic New York soils and 2 ppb in 20 alkaline Colorado soils. Those results suggested one possible explanation for Zn deficiencies being more common on alkaline than on acidic soils.

Norvell and Lindsay (1969, 1972) allowed ZnEDTA (zinc ethylenediaminetetraacetate) and ZnDTPA (zinc diethylenetriaminepentaacetate) to react with soils of different pHs and were able to calculate the free

Zn^{2+} concentration for the following relationship.



Log K, the equilibrium for the above relationship was -6.0. The solubility relationship of Zn^{2+} in soils was then expressed as:

$$(Zn^{2+}) = 10^6 (H^+)^2$$

This equation emphasizes a significant pH relationship of Zn^{2+} solubility in soils.

B - Stability of Synthetic Zn Chelates in Soils

Synthetic chelating agents can be used to prevent the precipitation of Zn^{2+} and other metal ions from solution. Naturally the question arises as to whether synthetic chelates are stable in soils, or is Zn^{2+} displaced from the metal chelates by other cations. Lindsay et al (1967) made the initial attempts in developing theoretical models for the equilibrium relationships between metal ions and chelating agents in soils. The predicted stability diagrams for ZnEDTA and ZnDTPA in soils were developed later by Lindsay and Norvell (1969). At low pH's, Fe^{3+} displaces Zn^{2+} from these chelates whereas at high pH's, Ca^{2+} displaces Zn. Zinc EDTA has a maximum stability at pH 6.5 where approximately 70% of the EDTA ligand is chelated with Zn^{2+} . ZnDTPA, on the other hand, has a maximum stability at pH 7.3.

The loss of EDTA ligands from soil solutions results primarily from its adsorption by particles. The rate of adsorption or fixation is usually rapid initially and decreases sharply with time. According to Norvell and Lindsay (1969), the rate of Zn loss from the reaction of ZnEDTA with soil solution having pH's near neutral was very rapid initially. Further loss occurred, however, quite slowly and in most cases the percentage of ZnEDTA became nearly constant with time.

C - Effectiveness of Zn Carriers in Soils

Reports in the literature concerning the solubility of Zn applied to the soil in different forms are limited. The few reports found in the literature concerning the plant availability of Zn applied in different forms are summarized below. Most researchers reported that Zn applied to the soil as a chelate was more readily utilized by plants than Zn applied as an inorganic salt. Boawn et al (1957) found in Pot experiments that bean (Phaseolus vulgaris L.) plants took up 3.5 times more Zn from ZnEDTA than from $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, when 2 ppm Zn was applied to an alkaline silt loam soil. Brown and Krantz (1966), however, found that Zn uptake by corn from ZnSO_4 and from ZnEDTA was comparable when the sources were mixed with the soil, but when the Zn sources were banded under the seed, ZnEDTA was utilized more readily than ZnSO_4 .

Judy (1968) observed that Zn uptake and bean (Phaseolus vulgaris L.) yields were highest with Zn applied as ZnEDTA. He also found that more water-soluble and exchangeable Zn was extracted from incubated soil treated with ZnEDTA than from ZnSO_4 -treated soil.

Most of the slightly soluble Zn compounds may be used as a source of Zn fertilizers. However, their effectiveness is governed mainly by the pH, texture and carbonate content of the soil. Holden and Brown (1965) reported that hemimorphite ($2\text{ZnO} \cdot \text{H}_2\text{O} \cdot \text{SiO}_2$) dissolved at a satisfactory rate in a neutral Florida sand, but not in a Western calcareous loam. Willomite ($2\text{ZnO} \cdot \text{SiO}_2$) supplied only very low levels of Zn, and sphalerite (ZnS) had no effect on the crop. ZnEDTA was two times as effective as ZnSO_4 in increasing the Zn content of the crop in a neutral soil and up to six times as effective in a calcareous soil. In contrast to the above findings, McGregor (1972) found ZnS

to be the best Zn fertilizer when a variety of soluble and slightly soluble inorganic zinc salts were added to calcareous and noncalcareous base-saturated soils. He also reported Na_2ZnEDTA to be the best source particularly for calcareous soils.

The results from field experiments agree well with those from pot experiments. Boawn (1973) reported that one unit of Zn applied as the chelate, in the field, was equivalent to approximately 2 to 2.5 units applied in the sulfate form. The effectiveness ratio appeared to be slightly greater, at least 2.5, when Zn was banded prior to planting. Anderson (1964) reported the effectiveness of Zn sources in calcareous soils to be, in decreasing order, DTPA, EDTA, EDDHA, ZnSO_4 and Rayplex.

III. MATERIALS AND METHODS

The investigations reported in this manuscript include several individual studies where different experimental procedures were used. The experimental methods used for each of 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 the investigations and in characterizing the soils are outlined below. A brief description of the soils studied is also included.

Soils

Four surface soils selected for their varying texture, carbonate content and organic matter were used throughout most of these investigations (Tables 1 and 14). A subgroup designation of the soils studied is given below:

<u>Soil Name</u>	<u>Subgroup</u>
Stockton	Orthic Black
Newdale	Orthic Black
Lakeland	Gleyed Carbonated Rego Black
Plum Ridge	Gleyed Carbonated Rego Black

Analytical Procedures

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. Inorganic carbonate content.

A one gram soil sample was digested in 10% HCl for ten minutes. The carbon dioxide evolved was sucked through a drying and adsorption train

Table 1. Some characteristics of soils studied.

Soil	pH (1:10) (soil:H ₂ O)	Texture			Inorganic CO ₃ (%)	Organic C (%)	Total Content		
		Sand (%)	Silt (%)	Clay (%)			Fe (%)	Al (%)	Zn ppm
Stockton	7.2	78.3	10.7	10.0	0.3	2.0	1.27	1.75	58
Newdale	8.2	41.2	30.8	28.0	0.4	3.5	2.42	3.70	80
Lakeland	8.3	9.6	64.0	26.4	15.6	2.6	1.72	2.30	52
Plum Ridge	8.2	75.2	11.9	12.9	7.5	1.5	0.90	1.05	47

and adsorbed on Ascarite in a Nesbitt tube. The weight of carbon dioxide adsorbed on the Ascarite was determined and the carbonate content of the soil calculated.

3. Soil Organic Matter.

Soil organic matter was determined as described by Walkley and Black (1934). Excess potassium dichromate was used to oxidize the organic matter and the unreacted dichromate back-titrated with ferrous sulfate using barium diphenylamine sulphonate as an indicator.

4. Ammonium Acetate Extractable Ca and Mg.

One hundred ml of 1 N $\text{CH}_3\text{COONH}_4$ solution (pH = 7) was equilibrated with 10 g of soil by shaking for one hour. The suspension was transferred to a Buchner 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).

5. Soil Cation Exchange Capacity.

Soil cation exchange capacity (CEC) was determined by the ammonium saturation method outlined by Chapman (1965). Exchange sites of a 10.0 g soil sample were saturated with ammonium by shaking for one hour in 100 ml of 1 N $\text{CH}_3\text{COONH}_4$ solution containing 250 ppm lithium and adjusted to pH 7.0 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 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 2.0 percent boric acid solution using a Kjeldahl distillation apparatus. The absorbed NH_3 was titrated with standardized 0.1 N H_2SO_4 and the cation exchange capacity of the soil calculated.

6. Mechanical Analysis.

The pipette method for particle size analysis was used. Duplicate 10.0 g samples were used. Organic matter was destroyed by the addition of 30 percent 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.

7. Soluble Carbonate Content of Soil.

Air dried soil was ground to pass a one mm sieve. Duplicate five gram samples were shaken with 50 ml of distilled water in centrifuge tubes open to the atmosphere for 24 hours. The suspensions were filtered using Whatman filter paper number 42. A twenty ml aliquot of filtrate was titrated with standardized 0.01 N H_2SO_4 for CO_3^{2-} and HCO_3^- using phenolphthalein and methyl orange as indicators. The concentration of CO_3^{2-} and HCO_3^- were calculated.

8. Total Concentration of Zn, Fe, Al and Mn in Soil.

Air dried soil was ground to pass a one mm sieve. Duplicate one gram samples of soil were placed into micro Kjeldahl flasks. Fifteen ml of 70% HClO_4 and 10 ml of concentrated HNO_3 were added and the soil digested by boiling until the solutions turned completely clear. The digest was allowed to cool and diluted with approximately 25 ml of deionized water. The digest was allowed to sit one hour, filtered into a 50 ml volumetric flask, and brought to volume with deionized water.

Zinc, Fe, Al and Mn concentrations were measured in the filtrates and the Zn, Fe, Al and Mn content of the soil calculated.

The concentration of Zn, Fe, Al and Mn in all the soil extracts, were determined using a Perkin Elmer, Model 303 Atomic Absorption Spectrometer. The standard solutions for Zn, Fe, Al and Mn were prepared with the same solutions used for extraction of the soil. Deionized water was used in all preparations.

9. Determination of Cl^- Ion Concentration in Solution.

Duplicate 10 ml aliquots of solution was titrated with standardized 0.05 N AgNO_3 using an automatic titrometer model Radiometer Titrator II. The end point of titration was +70 mv. Blank determinations were conducted using distilled water.

10. pH of Fe_2O_3 and Al_2O_3 Suspensions.

The pH of the Fe_2O_3 and Al_2O_3 suspensions was determined electrometrically by the use of the glass and calomel electrodes on an Orion Research Ionalyzer model 801 digital pH meter. The suspensions were shaken vigorously before the combination electrode was placed into the suspensions. The pH was read when it no longer changed.

X-ray Techniques

1. Identification of Al_2O_3 and Fe_2O_3 .

The sample was finely ground (<300 mesh) and placed in a special sample container mounted on a Philips P.W. 1050 diffractometer equipped with a wide range goniometer. The diffractometer was positioned on a Philips P.W. 1010 x-ray generator attached to a Philips P.W. 1051 electronic circuit panel detector (recorder). The x-ray tube was operated at 36 KV and 8 ma and equipped with a cobalt target and an iron filter. Exposure time was about 60 minutes. Using the

position and height of the peaks on the chart, d- spacings and relative intensities of the diffraction lines were calculated. The calculated d-spacings for Al_2O_3 and Fe_2O_3 were compared with the known values in the A.S.T.M. x-ray powder data file and the crystalline structure of Al_2O_3 and Fe_2O_3 identified.

2. Identification of Zn Reaction Products in Soil.

The sample was finely ground (<300 mesh) and placed into a glass capillary tube (0.3 mm diameter) obtained from Caine Scientific Sale Company, Chicago, Illinois. The tube was then centred in a Philips cylindrical power diffraction camera. The camera was then loaded with Kodak no-screen medical x-ray film and positioned on a Philips P.W. 1010 x-ray generator. The x-ray generator was operated at 36 kv and 8 mamps and equipped with a cobalt target and an iron filter. The sample tube was rotated mechanically during exposure. Exposure time was 22 hours for all samples. After exposure, the film was removed from the camera, immersed in Kodak rapid x-ray developer for five minutes, rinsed with water, and placed into Kodak x-ray fixer for twenty minutes. The film was again rinsed, then dried. The distance between the diffraction lines were measured on a Philips film illuminator and measuring device. Calculated d-spacings for the samples were compared to known values listed in the A.S.T.M. x-ray powder data file and the crystalline Zn species present in the samples identified.

IV. PRESENTATION OF EXPERIMENTAL METHODS AND RESULTS.

A. Zinc Mineral(s) in Soils

a. Solubility of Zn in Soils and Minerals

Zinc is one of the most commonly deficient essential micronutrients in soils. A knowledge of the Zn phase(s) occurring in soils is fundamental to understanding Zn deficiency and its correction. Identifying these Zn phases has been difficult, primarily because total Zn in soil is often very low.

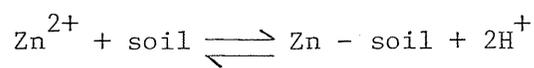
Sphalerite (ZnS), one of the most sparingly soluble Zn compounds, and the more complex Zn-silicate compounds hemimorphite ($\text{Zn}_4(\text{OH})_2\text{SiO}_7 \cdot \text{H}_2\text{O}$), and willomite (Zn_2SiO_2) have been postulated as the native forms of Zn in soils (Krauskopf, 1972 and Kittrick, 1976). To examine this hypothesis, solubility of Zn from these compounds was compared with solubility of Zn in soils.

Solubility diagrams (concentration of Zn vs pH of a saturated system) for these three Zn compounds was constructed from data for aqueous non-buffered systems. Reagent grade sphalerite (ZnS) and samples of hemimorphite ($\text{Zn}_4(\text{OH})_2\text{SiO}_7 \cdot \text{H}_2\text{O}$) and willomite (Zn_2SiO_2), obtained from the Department of Geology, University of Manitoba, were ground to pass a 60 mesh sieve. Duplicate 10 g samples of each mineral were placed in centrifuge tubes. Twenty ml of distilled H_2O and increasing amounts of HCl were gradually added to the tubes to obtain pH values ranging from seven to one. The suspensions were shaken for 24 hours with the tubes open to the atmosphere. During shaking, regular inspections were made to ensure that all the suspensions remained saturated with respect to the solid mineral, i.e. both solid and liquid phases existed in the system. Small amounts of the minerals were added

wherever the solutions seemed to be undersaturated with respect to the solid mineral. pH of the suspension above the sediment was measured after 24 hours of shaking. The suspensions were filtered using whatman filter paper No. 5. Zinc concentration of the filtrate was measured. Zinc concentration of the solution was then plotted versus final equilibrium pH of the solutions (Figure 1).

Air dried samples of Lakeland, Newdale, Stockton and Plum Ridge soils (Table 1) were ground to pass a 60 mesh sieve. Sets of duplicate samples of each soil were acidified to pH values ranging from eight to one by adding increasing amounts of concentrated HCl to 10 g of soil. The final volumes were adjusted to 100 ml and the suspensions were shaken for 24 hours in centrifuge tubes open to the atmosphere. Preliminary experiments indicated that equilibrium was reached after 24 hours of shaking, i.e. no significant pH change occurred after 24 hours of equilibration. Final pH was measured in the supernatant above the sediment. The suspensions were then filtered using whatman No. 42 filter paper. Zinc, Mn and Fe concentrations of the filtrates were measured. Metal concentrations in the filtrates were plotted versus final equilibrium pH values (Figures 2, 3 and 4).

Norvell and Lindsay (1969, 1972) reacted Zn EDTA and Zn DTPA with soil at various pH values; the following equation, representing the reaction of Zn with soil, had a pK value of 6.0.



The amount of Zn^{2+} in soil solution as a function of soil pH was expressed as:

$$(\text{Zn}^{2+}) = 10^{6(\text{H}^+)^2}$$

Comparison of this relationship with solubility diagrams obtained for hemimorphite, willomite and sphalerite (Figure 1) indicated the following:

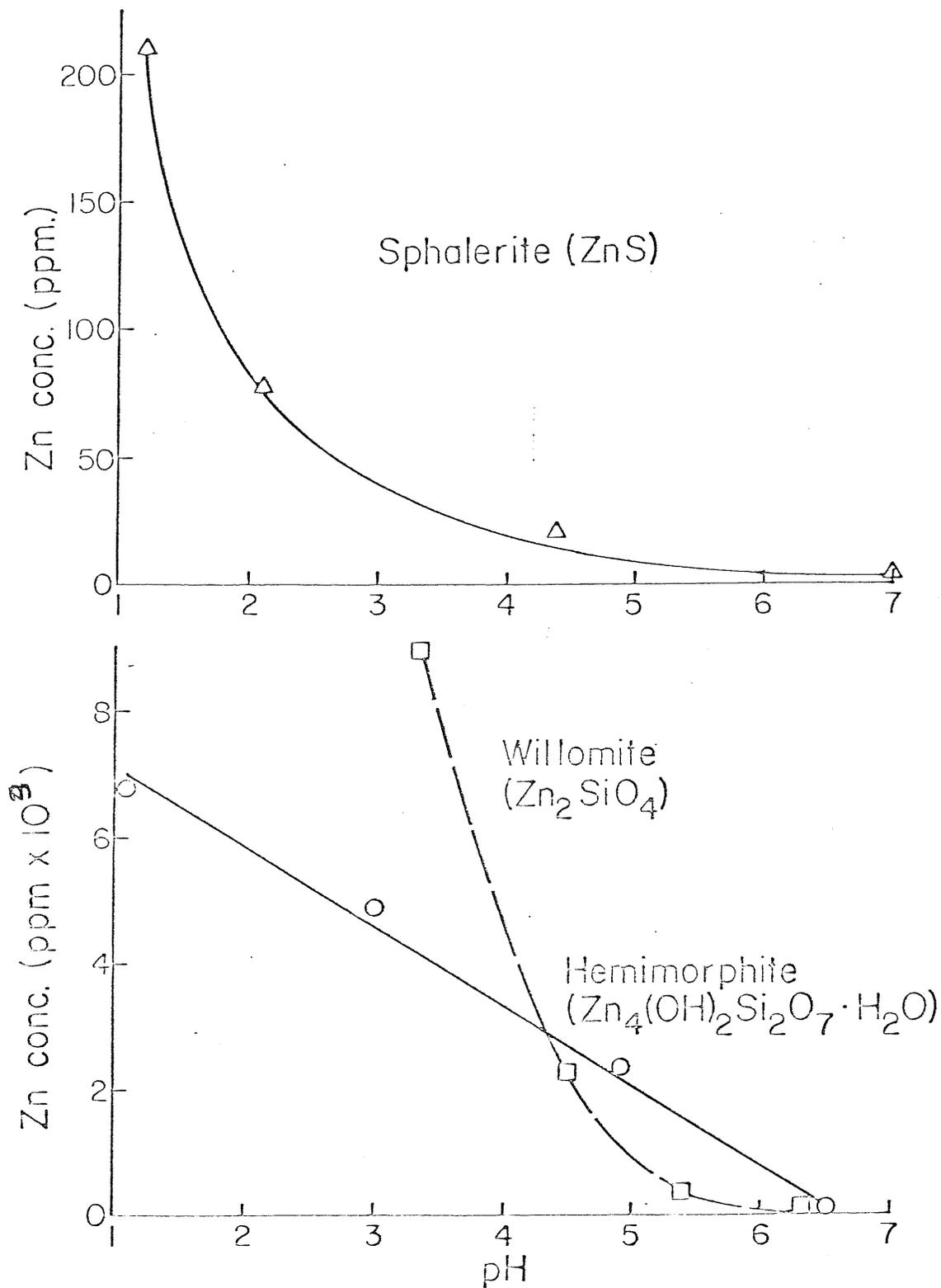


Fig. 1. Concentration of Zn in saturated solution of sphalerite, willomite and hemimorphite as a function of pH.

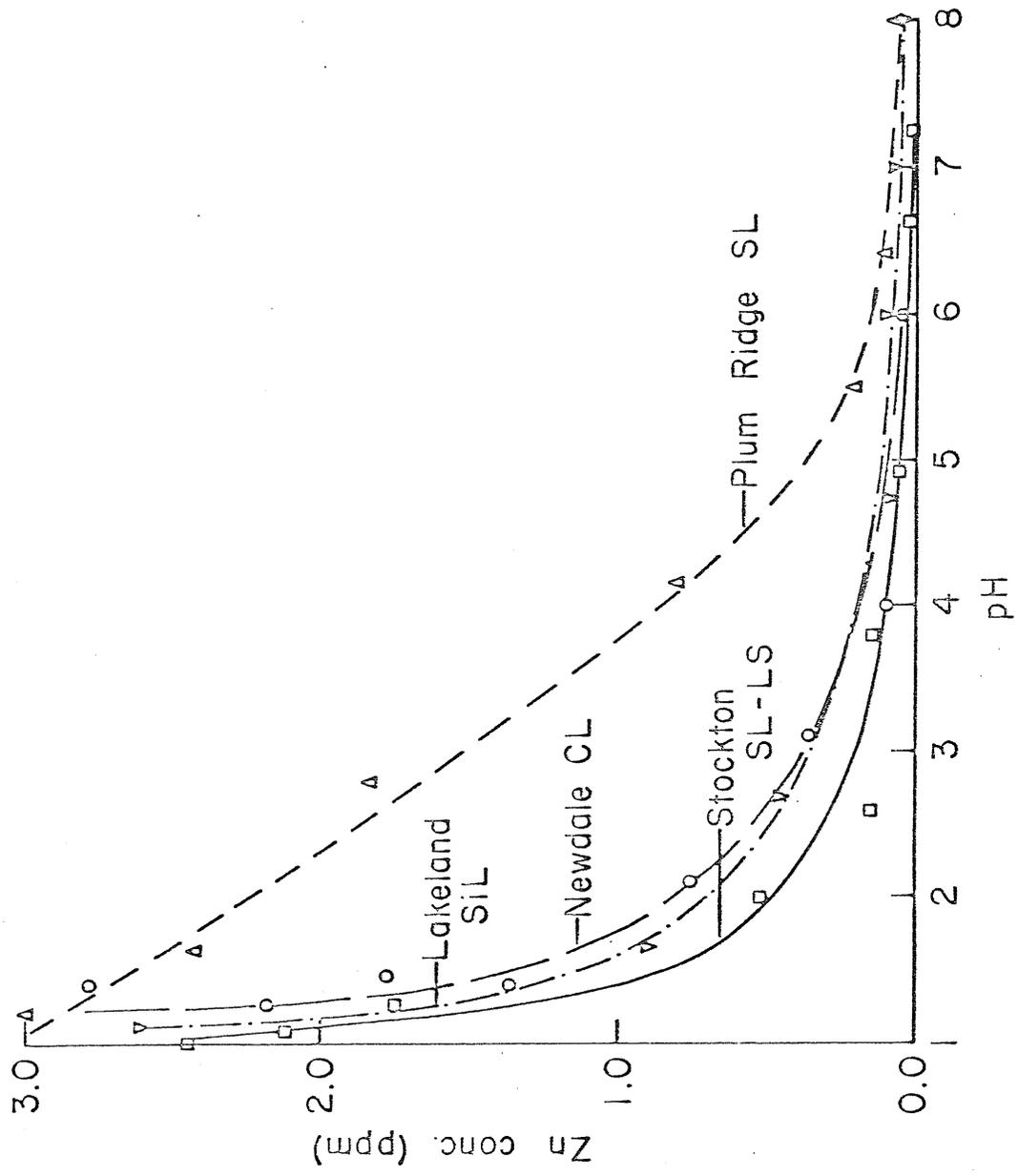


Fig. 2. Zinc concentration in soil solution as affected by pH.

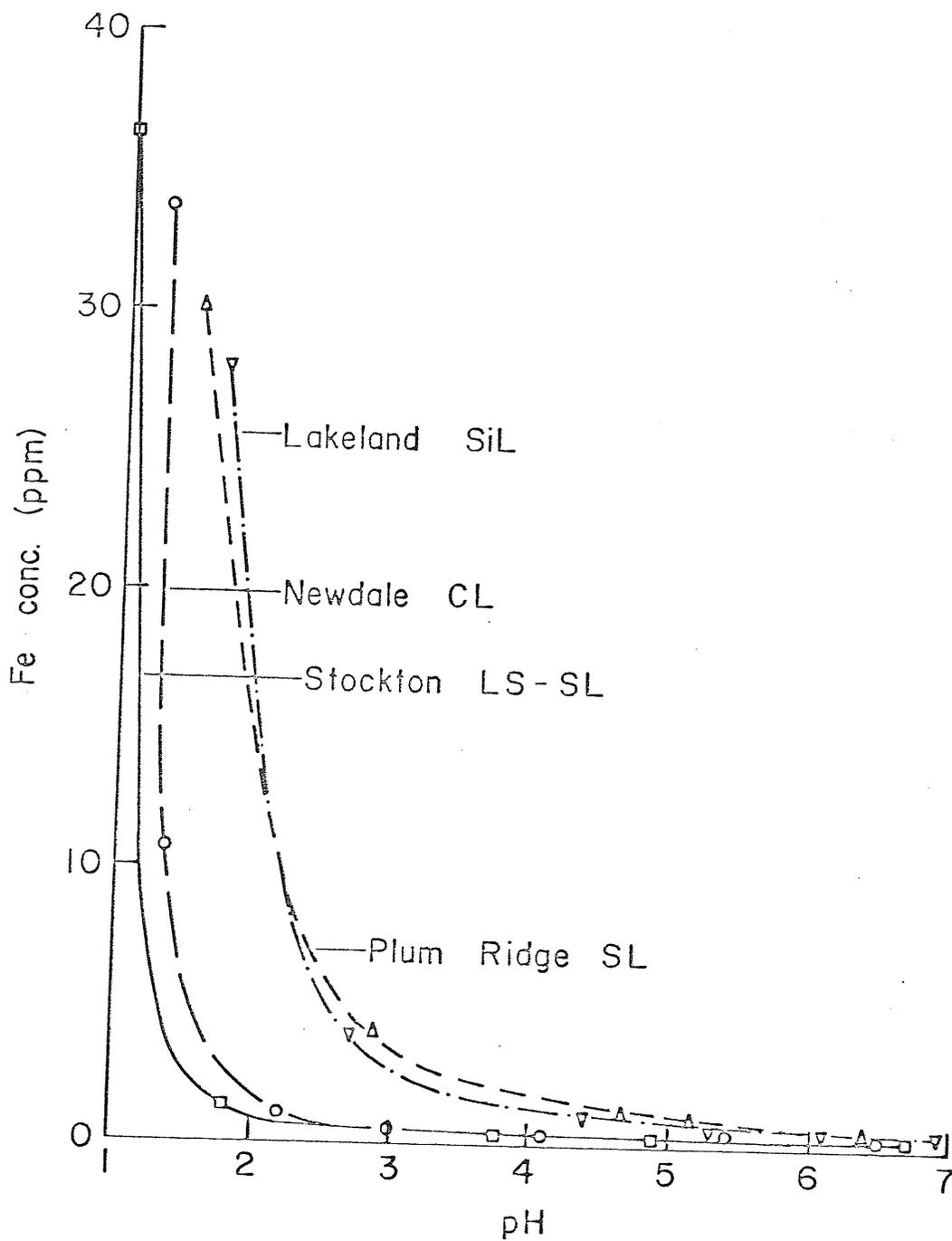


Fig. 3. Iron concentration in soil solution as affected by pH.

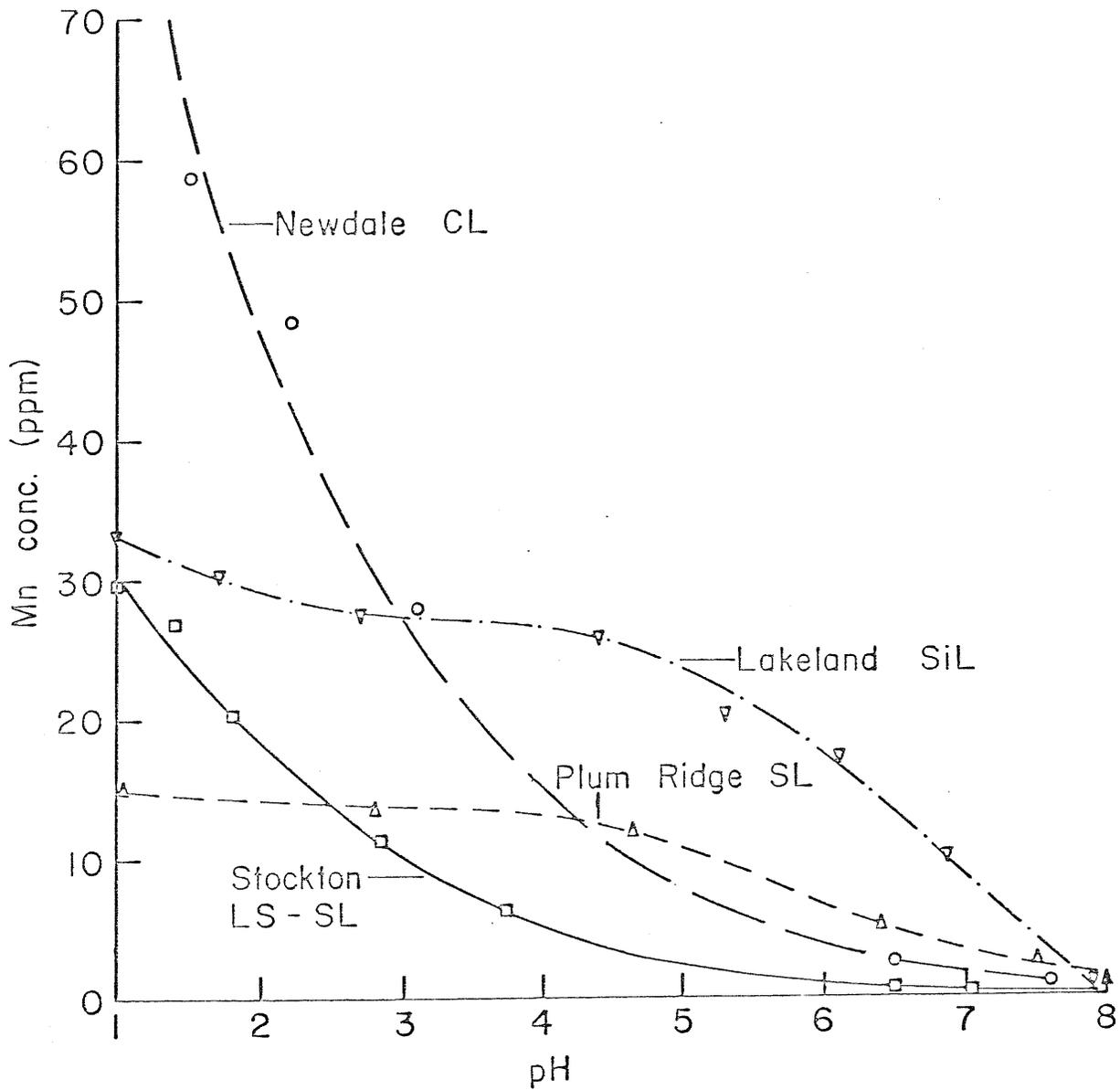


Fig. 4. Manganese concentration in soil solution as affected by pH.

1. Zn concentration in solution from both hemimorphite and willomite were much greater than predicted by the above relationship obtained by Norvell and Lindsay (1969, 1972) and therefore most likely are not the native form(s) of Zn in soils.

2. Solubility behaviour of ZnS, although much closer to the solubility relationship obtained by Norvell and Lindsay (1969, 1972) also did not fit the relationship. At high pH, the solubility of Zn from ZnS was higher and at low pH lower than those obtained using the Norvell and Lindsay's (1969, 1972) relationship. Furthermore, solubility of ZnS is a function of H_2S partial pressure which may not be the same in soil solution as in the atmosphere. In addition, according to both Krauskopf and Lindsay (1972), ZnS is unstable under normal oxidizing conditions and is oxidized to less sparingly soluble compounds. The reaction product study conducted by the author also indicated that when ZnS was banded in soils and incubated for varying periods of time, Zn concentration in solution of all the soils increased. $Zn_5(CO_3)_2(OH)_6$ and $Ca[Zn(OH)_3]_2 \cdot 2H_2O$ were formed in the calcareous Plum Ridge soil, after 32 weeks of incubation, indicating oxidation of ZnS to less sparingly soluble Zn compounds.

The above comparison was made between the solubility behaviour of three Zn minerals (Figure 1) and solubility of Zn in soils treated with ZnEDTA and ZnDTPA obtained by Norvell and Lindsay (1969, 1972). This comparison, although useful in indicating that hemimorphite and willomite were much too soluble to account for the low solubility of Zn in soils, was of little aid in determining the nature of the native form(s) of Zn in soils. Norvell and Lindsay's (1969, 1972) relationship was derived for Zn treated soils and is probably not valid for the solubility of Zn in untreated soils. According to this relationship, Zn^{2+} concentration

in equilibrium with a soil solution having a pH of four should be about 650 ppm. Total Zn concentration in agricultural soils is generally below 100 ppm. A more meaningful comparison would be between concentration of Zn in solutions of untreated soils at varying pH's and solubility of Zn from the Zn minerals.

b. Zinc, Fe and Mn Concentrations of Soil Extracts as a Function of pH.

Concentration of Zn, Fe and Mn in all four soil solutions increased as pH decreased (Figures 2, 3 and 4). With the exception of the Plum Ridge soil, the Zn concentration-pH relationships (Figure 2) were exponential, i.e. the increase in Zn concentration with decreases in pH was initially very slow until a pH value of about 2.5. Zinc concentration increased sharply with decreasing pH beyond 2.5 (Figure 2). The higher Zn concentration in the Plum Ridge soil solution was probably due to the high exchangeable Zn in this soil as compared to the other three soils.

Comparison of Zn concentration in solutions of untreated soils (Figure 2) and zinc concentrations in saturated solutions of sphalerite, hemimorphite and willomite (Figure 1) clearly showed that all of these Zn minerals have a much greater solubility than that of zinc in soils and probably could not persist in soil to control Zn concentration. For example, concentration of Zn at a pH of four in all of the soil solutions was less than one ppm (Figure 2) whereas Zn concentration in equilibrium with the above mentioned minerals at a pH of four was about 20 ppm for sphalerite and greater than 3000 ppm for both willomite and hemimorphite (Figure 1).

All of the aforementioned Zn minerals were too soluble to account for the small concentrations of Zn found in most soil solutions. With

the exception of the Plum Ridge soil, curves for concentration of Zn and Fe vs pH were similar, particularly for the noncalcareous Newdale and Stockton soils. Except for Zn concentration in the Plum Ridge soil solution, curves for concentration of Zn and Fe in soil solutions vs pH were exponential with inflection points at a pH of approximately 2.5, indicating that Zn was released largely into the solution at about the same pH as Fe dissolved. Figures 2 and 3 also indicated that for every 10 ppm increase in Fe concentration in soil solution, Zn concentration increased about one ppm. This ratio was relatively constant especially for the noncalcareous Newdale and Stockton soils at low pH. Most of the known existing Fe compounds in soils such as hydrous oxides of Fe dissolve at pH's lower than the Zn compounds suggested as forms of native soil Zn. Therefore, it may be hypothesized that either a Zn compound not as yet identified or postulated existed in those soils which dissolved largely at about the same pH as hydrous oxides of Fe and had no essential association with Fe oxides or that Zn was in some way associated with hydrous oxides of Fe in Zn-Fe complexes with Zn:Fe ratios of about 1:10. Association of Zn with hydrous oxides of Fe and Al has been reported by Jenne (1968). He suggested that Zn along with several other heavy metal ions may be occluded and coprecipitated with hydrous oxides of Fe and Mn, and that these oxides constitute the principal matrix in which the less abundant heavy metals are held. Thus, the association of Zn with sesquioxides is the more likely mechanism.

Curves for concentrations of Mn in soil solution vs pH (Figure 4) showed different patterns than those for Zn and Fe. Zinc and Fe concentrations in the soil solutions were more or less exponentially related to pH in all soils. But, for Mn such relationships occurred

only in the noncalcareous soils and even in those soils the points of inflection were not as pronounced as for Zn and Fe. Manganese concentrations in the calcareous soil solutions were not exponentially related to pH. Instead, Mn concentration increased rapidly with decreasing pH particularly in Lakeland SiL and then remained constant after approximately pH 4.5 (Figure 4). There were very few similarities between concentration diagrams of Zn and Mn (Figures 2 and 4). That was particularly true for calcareous soils at high pH where Mn was much more soluble than either Fe or Zn. Curves for concentration of Mn in soil solution vs pH for the Newdale soil revealed some resemblance with curves for Zn. However, the Mn curves were smoother and did not have the sharp increase at the lower pH's (Figures 2 and 4). These results confirmed findings of Stanton and Burger (1970). They reported that the presence of Fe and Al cations in solution markedly lowered the pH at which precipitation of Zn occurred whereas Mn had no effect indicating that Zn coprecipitated with Fe and Al but not with Mn.

Evidence presented in this section indicated that Zn compounds such as sphalerite, hemimorphite and willomite were too soluble to account for the small concentrations of Zn found in the soil solutions. It was also shown that Zn was possibly occluded and coprecipitated with hydrous oxides of Fe. Manganese did not seem to have any significant control over Zn solubility. More experimental evidence, however, was required to prove those postulations. Furthermore, the role of Al seemed important and required further investigation.

c. Statistical Evaluation of the Inter-relationships Between Total Fe, Al, Mn, Zn and Clay Content of Some Manitoba Soils.

Hydrous oxides of Fe, Al and Mn are nearly ubiquitous in clay soils

and sediments. The reason for their occurrence is that during the formation of clays the various ions are seldom, if ever, present in the exact amount required for the secondary silicates (clay minerals) to be stable under the prevailing conditions. Silicon, Fe, Al and occasionally Mn are commonly present in excess and may be deposited in the form of sparingly-soluble oxides, either as discrete particles or as surface coatings on other mineral particles. By virtue of their frequent occurrence as coatings on the clay micelles, the oxides are far more important than their amounts in the soil would indicate.

Chemical enrichment of certain size fractions or horizons at the expense of others occur during soil development. The most common approach in most investigations of micro-element distribution patterns in soils has been to fractionate the micro-elements into distinct size classes. The chief drawback in this approach is the inevitable loss of micro-elements by solution and displacement. An alternative approach might be to determine independently of one another the micro-element composition and particle size distribution in all horizons of a number of soils and then by employing appropriate statistical procedures, arrive at the inherent relationships between the two. Such an approach would be free of the aforementioned limitations and would help determine the precise association of not only the individual elements with particular size fractions, but also relationships among the heavy metals themselves.

Eight soils in Manitoba, varying in Great Soil Groups, in texture and in amount of clay movement were chosen (Tables 2-9). Percent sand, silt, and clay as well as total content (concentration) of Fe, Al, Mn and Zn were measured in every horizon of each soil (Tables 2 to 9).

Table 2. Texture and concentration of Fe, Al, Mn and Zn of a Dystric Brunisol (Soil No. 1)

Horizon	Depth (cm)	Texture			Total					
		Sand (%)	Silt (%)	Clay (%)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Fe + Al (%)	
L-H	6-0									
Ae	0-4	96.0	2.5	1.5	.36	.35	54	11.0	.71	
Bm	4-28	96.0	3.0	1.0	.66	.80	50	20.0	1.46	
Bc	28-58	97.0	1.0	0.0						
C1	58-84	98.5	1.5	0.0	.36	.40	67	7.5	.76	
C2	84-102	96.5	3.5	0.0						

Table 3. Texture and concentration of Fe, Al, Mn and Zn of a Dystric Brunisol (Soil No. 2).

Horizon	Depth (cm)	Texture				Total				
		Sand (%)	Silt (%)	Clay (%)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Fe + Al (%)	
L-H	4-0									
Ae	0-7.5	76.0	20.5	3.5	.67	.62	96	27.5	1.29	
Bm1	7.5-25	75.0	20.0	5.0	1.42	1.19	115	35.0	2.61	
Bm2	25-35	83.5	15.0	1.5	1.24	1.14	108	30.0	2.38	
BC	35-61	86.0	14.0	0.0	.77	.63	78	30.0	1.40	
BCa1	61-76	83.5	16.5	0.0	.70	.46	87	17.5	1.16	
BCa2	76-85	88.0	12.0	0.0	.86	.69	100	17.5	1.55	
C	85+	80.0	19.0	1.0	.74	.45	85	17.5	1.19	

Table 4. Texture and concentration of Fe, Al, Mn and Zn of a Dystric Brunisol (Soil No. 3).

Horizon	Depth (cm)	Texture			Total					
		Sand (%)	Silt (%)	Clay (%)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Fe + Al (%)	
L-H	5-0									
Ae	0-7.5	68.0	27.0	5.0	.62	.61	280	30.0	1.23	
Bm ₁	7.5-18	82.5	10.5	7.0	1.00	1.20	80	30.0	2.20	
Bm ₂	18-43	87.5	7.5	5.0	1.25	1.82	134	32.5	3.07	
BC	43-61	68.0	25.0	7.0	1.13	1.24	130	30.0	2.37	
BCa ₁	61-86	73.0	23.0	4.0	1.00	.82	136	27.5	1.82	
BCa ₂	86-106	68.0	27.0	5.0	1.13	.90	173	32.5	2.03	
C	106+	72.0	25.5	2.5	.90	.66	154	30.0	1.56	

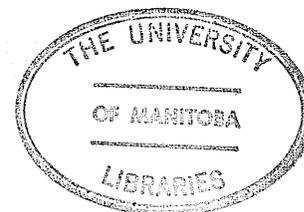


Table 5. Texture and concentration of Fe, Al, Mn and Zn of a Dystric Brunisol (Soil No. 4).

Horizon	Depth (cm)	Texture				Total			
		Sand (%)	Silt (%)	Clay (%)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Fe + Al (%)
L-H	4-0								
Bm1	0-10	41.0	39.0	20.0	2.10	3.08	168	82.5	5.18
Bm2	10-20	46.0	30.5	23.5	2.10	3.10	185	76.0	5.20
Bm3	20-31	54.0	32.0	14.0	1.91	2.89	150	52.5	4.80

Table 6. Texture and Concentration of Fe, Al, Mn and Zn of an Orthic Gray Luvisol (Soil No. 5).

Horizon	Depth (cm)	Texture				Total				
		Sand (%)	Silt (%)	Clay (%)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Fe + Al (%)	
L-H	0-2.5				1.32	0.95	1420	114	2.27	
Ae	2.5-10	51.1	38.1	10.8	1.52	1.25	1100	34	2.77	
BA	10-17.5	33.0	31.0	36.0	2.75	3.07	800	70	5.82	
Bt1	17.5-25	31.4	24.3	44.3	3.50	3.65	780	83	7.15	
Bt2	25-32	31.1	24.4	44.5	5.85	3.48	750	137	9.33	
BC	32-42	35.8	32.2	31.9	2.90	3.07	760	74	5.97	
CK1	42-85	36.2	34.3	29.5	1.89	1.43	480	36	3.32	
CK2	85+	40.6	35.1	24.2	2.10	1.67	870	47	3.77	

Table 7. Texture and concentration of Fe, Al, Mn and Zn of a Gray Luvisol (Soil No. 6).

Horizon	Depth (cm)	Texture					Total			
		Sand (%)	Silt (%)	Clay (%)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Fe + Al (%)	
Ae	*	51.8	29.6	18.5	1.20	1.00	320	35.0	2.20	
BA		12.0	24.8	63.1	3.18	3.70	275	82.5	6.88	
Bt ₁		4.3	21.9	73.7	3.55	3.70	400	95.0	7.25	
Bt ₂		1.4	31.7	66.9	3.00	2.93	563	87.5	5.93	
Ck ₂		7.6	47.4	45.0	2.55	2.40	413	92.5	4.95	

* depths were unavailable.

Table 8. Texture and concentration of Fe, Al, Mn and Zn of an Orthic Dark Gray (Soil No. 7).

Horizon	Depth (cm)	Texture			Total				
		Sand (%)	Silt (%)	Clay (%)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Fe + Al (%)
L-H					1.86	1.55	680	89	3.41
Ah	5-15	35.2	35.4	29.4	2.18	2.38	800	73	4.56
Bt ₁	15-28	32.5	30.8	36.7	2.68	2.83	550	68	5.51
Bt ₂	28-35	32.5	32.0	35.5	2.75	2.88	530	85	5.63
BC	35-50	33.3	36.2	30.5	2.13	1.70	520	54	3.83
C	50-75	31.5	39.5	29.0	2.13	2.03	510	54	4.16

Table 9. Texture and concentration of Fe, Al, Mn and Zn of a Gleyed Rego Black (Soil No. 8).

Horizon	Depth (cm)	Texture				Total			
		Sand (%)	Silt (%)	Clay (%)	Fe (%)	Al (%)	Mn (ppm)	Zn (ppm)	Fe + Al (%)
Ap	0-18	19.6	18.2	62.2	2.90	3.15	500	97.5	6.05
Cg	18-30	21.6	9.7	68.7	3.43	4.10	400	105.0	7.53
Ck81	30-51	17.6	16.0	66.4	2.93	3.70	325	85.0	6.63
Ck82	51+	10.6	14.9	74.5	2.93	3.70	313	86.5	6.63

Statistical analyses were conducted to correlate total Fe, Al, Mn and Zn concentrations and particle size distribution. Total population consisted of 41 soil samples. Results of this correlation analysis (r values) are given in Table 10. There were highly significant correlations (significant at the 0.1% probability level) between total Fe, Al, or clay content and Zn concentration ($r = 0.86, 0.95$ and 0.91 , respectively). Significant correlation between Zn concentration and clay content might have been caused by the inter-relation of Fe and Al with clay content ($r = 0.84, 0.88$). There was also a significant negative correlation between the sand content and Zn concentration ($r = -0.91$) which was probably due to the negative correlation of the sand content with total Fe, Al and clay content ($r = -0.83, -0.85, -0.93$). There was also a correlation between total Zn and Mn ($r = 0.51$). However, it was not as significant as the correlation between Zn and either Fe or Al (Table 10). The above findings confirmed that of Nair and Cottenie (1971). They presented convincing statistical proof to show that amorphous Fe_2O_3 may retain a large proportion of the micro-elements including Zn possibly by coating the surface of finer particles.

Zinc enriched horizons in the soil profiles were often enriched with clay (Tables 6 and 7). However, for horizons into which there was very little clay movement or in which very little clay existed, enrichment of Zn occurred and followed closely accumulation of Fe and Al (Tables 2 and 3) indicating that hydrous oxides of Fe and Al rather than clay were probably the matrices accommodating Zn. In the Bm horizon of soil number one (Table 2) which was almost pure sand there were substantial accumulations of Zn, Fe and Al but no accumulations of either clay or Mn. On the other hand, in the B horizon of

Table 10. "r" values for relations between zinc concentration, texture and concentration of Fe, Al and Mn.

	Sand	Silt	Clay	Fe	Al	Mn	Fe + Al	Zn
Sand		-0.57 ⁺⁺	-0.93 ⁺⁺	-0.83 ⁺⁺	-0.85 ⁺⁺	-0.63 ⁺⁺	-0.87 ⁺⁺	-0.91 ⁺⁺
Silt			0.23	0.34	0.28	0.58 ⁺⁺	0.32	0.40 ⁺
Clay				0.84 ⁺⁺	0.88 ⁺⁺	0.48 ⁺	0.88 ⁺⁺	0.91 ⁺⁺
Fe					0.89 ⁺⁺	0.62 ⁺⁺	0.97 ⁺⁺	0.86 ⁺⁺
Al						0.48 ⁺	0.97 ⁺⁺	0.95 ⁺⁺
Mn							0.57 ⁺⁺	0.51 ⁺⁺
Fe + Al								0.93 ⁺⁺

+ significant at the 1% probability level

++ significant at the 0.1% probability level

of soil number five (Table 6) there were accumulations of clay, Zn, Fe and Al, but not Mn. These results agreed well with findings of Stanton and Burger (1966b) who found that total Zn in soil profiles of South Africa followed closely the distribution of soil colloids, both values increasing markedly with depth. They felt that increases in Zn concentration in the sand fraction with depth resulted from an increase with depth of ferruginous concentrations in the sand fraction.

The L-H horizons in soils five and seven (Tables 6 and 8) were enriched in Zn. This was evidence for adsorption and fixation of Zn by organic matter. Although the organic horizon (L-H) contained very little inorganic material, it did contain significant amounts of Fe and Al (Tables 6 and 8). Therefore, it might be speculated that Zn accumulation in the organic horizon was also associated with hydrous oxides of Fe and Al. Conclusions from the correlation analysis may be outlined as follows:

1. Total soil Zn concentration was correlated with Fe and Al concentration and with percent clay content.
2. Zinc was also significantly correlated with Fe and Al concentration when the clay size fraction was very small.
3. The correlation between Zn and percent clay content may have resulted from correlation between clay and the hydrous oxides of Fe and Al.
4. Correlation between Zn and Mn concentration was comparatively relatively small and might have been caused by the correlation between Mn and clay content.
5. Accumulation of Zn in organic horizons (L-H) might have been related to enrichments of Fe and Al in those horizons.

d. Extraction of Fe, Al and Associated Zn from Soils.

Similarities between concentration versus pH diagrams for Zn and Fe (Figures 2 and 3) suggested an association between Zn and hydrous oxides of Fe. Although they were conducted on different soils, the statistical correlation analysis (Table 10) confirmed that hypothesis. Those analyses also suggested the possible involvement of Fe as well as Al. However, although both of those led to similar conclusions, they were only indirect approaches and were not conducted on the same soils. Therefore, a more direct approach was required to reinforce the above findings and clarify the inter-relationships.

The more direct approach included two extraction methods both of which were conducted on the four soils studies in the acidification experiment (Table 1). The first extraction method was designed to measure exchangeable Zn, Fe and Al. Five successive extractions with a solution of 1 M KCl + 0.01 M Na₂EDTA were conducted. Na₂EDTA was included in the extractant to prevent readsorption or precipitation of Zn, Fe or Al displaced from the exchange sites. Air-dried samples of four soils (Table 1) were ground to pass a 100 mesh sieve. Duplicate 5.0 g samples of each soil were shaken with 50 ml of 1.0 M KCl + 0.01 M Na₂EDTA for two hours in centrifuge tubes. pH of the supernatant above the sediment was measured after each extraction. The suspensions were then centrifuged for 15 minutes at 2000 RPM. The clear centrifugates were decanted into another set of tubes and saved for Zn, Fe and Al analysis. The procedure was repeated five times on the same soil sample. Exchangeable Zn, Fe and Al were calculated on a soil basis using the sum of metal cation extracted in the five extractions.

Much of the exchangeable Fe and Al and nearly all of the exchangeable Zn was extracted in the first extraction (Table 11). Except for the Plum Ridge soil, the amount of exchangeable Zn was small and constituted only a small proportion of the total soil Zn concentration (5.3% in Stockton, 2.6% in Newdale and 1.1% in Lakeland) (Table 11). The exceptionally high exchangeable Zn level in the Plum Ridge soil (26% of the total) was not surprising considering that the Zn concentration for the Plum Ridge soil solution in the Zn concentration vs pH study was higher than for the other three soils (Figure 2). The reason for the high exchangeable Zn in the Plum Ridge soil is not clear. However, it is possible that the soil sample was taken from a location which had been fertilized with Zn. Amounts of exchangeable Fe and Al were also small and each constituted a very small fraction of the total Fe or Al (Table 11). As with Zn, this was particularly true for the calcareous Lakeland soil.

The pH of the extracting solution (1 M KCl + 0.01 M Na₂EDTA) was about four. However, it increased markedly when the solution was added to the calcareous soils (Table 11). It was thought that the comparatively low quantities of Fe, Al and especially Zn extracted from the Lakeland soil were due to the high carbonate content and resultant high buffer capacity. However, high carbonate content in the Plum Ridge soil did not prevent extraction of relatively large quantities of Zn (Table 11). Furthermore, the low pH of extracting solution in the non-calcareous Stockton and Newdale soil did not greatly increase the amount of Zn extracted indicating that pH did not greatly influence the extracting power of the solution (Table 11).

Soils (Table 1) were extracted successively with a solution of

Table 11. Exchangeable Zn, Fe and Al extracted by 1 M KCl + 0.01 M EDTA. (1:10 soil:sol'n)

Extraction No.	Stockton LS-SL			Newdale CL			Plum Ridge SL			Lakeland SiL						
	pH (1:10)	(ppm soil basis)		pH (1:10)	(ppm soil basis)		pH (1:10)	(ppm soil basis)		pH (1:10)	(ppm soil basis)					
		Zn	Fe		Al	Zn		Fe	Al		Zn	Fe	Al	Zn	Fe	Al
1	4.1	2.8	121	142	4.6	2.0	121	200	6.7	10.0	35	28	7.0	0.6	21	32
2	4.2	0.1	35	65	4.5	0.1	60	103	6.2	1.3	60	45	7.1	0.0	21	28.
3	4.3	0.2	40	30	4.8	0.0	60	82	6.2	0.6	40	60	7.2	0.0	24	25
4	4.4	0.3	31	35	4.9	0.0	42	34	6.0	0.3	32	70	7.1	0.0	24	30
5	4.4	0.0	11	15	4.8	0.0	13	8	5.7	0.0	21	65	7.0	0.0	23	35
Total Extracted		3.1	238	287		2.1	296	427		12.2	187	268		0.6	113	150
% of Total*		5.3	1.87	1.64		2.6	1.22	1.15		25.96	2.08	2.55		1.15	0.66	0.65

* Total extracted with 1 M KCl + 0.01 M EDTA x 100/Total metal content of soil.

oxalic acid + NH_4 -oxalate (pH = 3) in a second extraction study. A 0.2 M solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (ammonium oxalate) and a 0.2 M solution of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (oxalic acid) were prepared. About 700 ml of the former and 535 ml of the latter were mixed and the pH adjusted to 3.0 by adding either ammonium oxalate or oxalic acid.

Air-dried samples of soils (Table 1) were ground to pass a 100-mesh sieve. Duplicate one g samples of each soil were shaken with 40 ml of the acid oxalate solution in centrifuge tubes for four hours (McKeague and Day, 1966). pH of the supernatant was measured, the suspensions centrifuged for 15 minutes at 2000 RPM and the clear centrifugates decanted into another set of tubes. Another 40 ml of acid ammonium oxalate was added to the samples and the procedure repeated. Five successive extractions were conducted. Zinc, Fe and Al concentrations of the clear centrifugates were measured. The amounts of Zn, Fe and Al extracted in the five extractions were calculated on a soil basis. The portion of total soil Zn, Fe and Al extracted by the oxalate solution was calculated (Table 12) using values for total Zn, Fe and Al shown in Table 1.

Oxalate extraction removed amorphous inorganic Fe and Al and organic-complexed Fe and Al from soils (Blume and Schwartzmann, 1969). Data (Table 12) clearly showed that large quantities of Zn were extracted along with Fe and Al. In addition, for each of the three elements the proportion of the total which was extracted with oxalate was considerably higher than the proportion of the total which was exchangeable (Tables 11 and 12). Total Zn extracted in the five successive extractions varied considerably among the soils. Total oxalate extractable Zn varied between 45 and 71% of the total Zn content of the soils (Table 12). Oxalate extractable Zn was greater for coarse-textured soils than

Table 12. Successive extraction of amorphous and organic-complexed Fe and Al and Zn associated with them by oxalic acid + NH₄⁺-oxalate (pH = 3).

Extraction No.	Stockton LS-SL				Newdale CL				Plum Ridge SL				Lakeland SiL			
	pH (1:40) (Soil: soln)	Zn (ppm)	Fe (%)	Al (%)	pH (1:40) (Soil: soln)	Zn (ppm)	Fe (%)	Al (%)	pH (1:40) (Soil: soln)	Zn (ppm)	Fe (%)	Al (%)	pH (1:40) (Soil: soln)	Zn (ppm)	Fe (%)	Al (%)
1	3.1	16.0	0.20	0.12	3.0	23.2	0.22	0.12	3.2	32.0	0.13	0.10	4.0	10.0	0.10	0.12
2	3.0	10.5	0.10	0.08	3.0	4.0	0.07	0.02	3.0	6.4	0.02	0.01	3.2	6.4	0.03	0.03
3	3.0	7.0	0.05	0.04	3.0	5.2	0.11	0.02	3.0	5.2	0.03	0.02	3.1	4.6	0.04	0.02
4	3.0	4.0	0.02	0.01	3.0	4.0	0.03	0.01	3.0	2.1	0.01	0.01	3.0	4.2	0.02	0.02
5	3.0	1.0	0.00	0.00	3.0	2.0	0.01	0.00	3.0	0.0	0.00	0.00	3.0	2.0	0.00	0.01
a) Total Extracted		38.5	0.37	0.25		38.4	0.44	0.17		45.7	0.19	0.14		27.2	0.27	0.29
b) Exchange-able Table 10		3.1	0.02	0.03		2.1	0.03	0.04		12.2	0.02	0.03		0.6	0.01	0.01
a - b		35.4	0.35	0.22		36.3	0.41	0.13		33.5	0.17	0.11		26.6	0.26	0.28
% of total*		61.0	27.5	12.6		45.4	16.9	3.5		71.3	18.9	10.5		51.1	15.1	12.2

* (Total extracted with oxalate - total exchangeable) x 100/Total metal content of soil.

fine-textured soils. Total oxalate extractable Fe and Al were 15 to 27% and 3.5 to 12% of total Fe and Al concentrations in the soils, respectively. Those values were significantly lower than for Zn (Table 12). The proportions of total Zn and Fe extracted by oxalate were greater in the coarse-textured Stockton and Plum Ridge soils.

The extracting power of the oxalate solution is mainly due to complexing of Fe and Al with oxalate rather than acid dissociation (McKeague and Day 1966). This was confirmed in an acidification experiment in which very little Zn and Fe were extracted from the soils which had been acidified to pH values of three (Figures 2 and 3). Regardless of the mechanism(s) involved, relatively large quantities of Zn were in some way associated with hydrous oxides of Fe and Al.

The oxalate solution contained NH_4^+ and therefore extracted not only Fe, Al and associated Zn, but also exchangeable Fe, Al and Zn. Thus, corrections were made by subtracting the exchangeable values from the oxalate extractable Fe, Al and Zn (Table 12). Corrected values were employed to calculate the percent of the total Fe and Al which were amorphous and organic complexed Fe and Al as well as percent of total Zn associated with this fraction of Fe and Al (Table 12). These results confirmed findings of White (1957) who used 1 M $\text{CH}_3\text{-COONH}_4$ (pH = 7.0) for exchangeable and dithionite-citrate for removal of Fe and Al. He found that 30-60% of the total Zn was associated with Fe oxides, 20-45% was held in the lattice position of the clay minerals and one to seven percent was exchangeable.

It may be concluded that probably no Zn mineral exists in soils as have been previously postulated by some researchers. Furthermore Zn in soils is most likely associated in some way with hydrous oxides of Fe and Al.

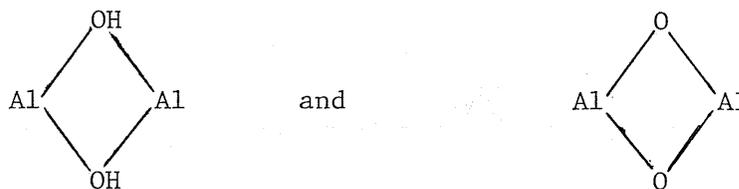
B. Zinc Adsorption by Fe & Al Oxides

From an agricultural and an environmental standpoint, the need to understand the factors moderating the partition of ions between solid interfaces and aqueous solution is of considerable importance. The almost ubiquitous occurrence of oxides means that they play a significant role in controlling the concentrations of various ions in soil solutions and natural water systems.

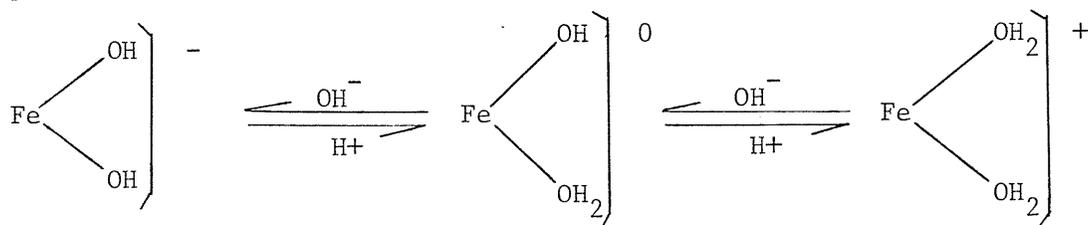
It was well established in the previous section that Fe and Al hydrous oxides are the major matrices accommodating soil Zn and probably some of the other micronutrients. A strong association between Zn, Fe and Al was shown to exist in the soils studied. This association may be the reason for both the unavailability of native Zn forms and fixation of applied Zn into unavailable form(s). Although association undoubtedly exists, the mechanisms involved have remained challenging problems yet to be satisfactorily explained. Further progress in the field of Zn nutrition of plants will depend on our ability to recognize and alleviate the causative factors of Zn unavailability. Attempts have been made in this section to clarify some aspects of the mechanisms of Zn sorption by Fe and Al hydrous oxides.

The greater portion of reactive Fe in most soils is in the form of variably hydrated ferric oxides (Merkle, 1955). Except in very acid soils, the amount of Fe in solution is generally small. Similarly, Al occurs mainly as the solid phase, but is also present as exchangeable ions (Wild, 1950).

Hydrous oxides of Fe and Al have a structure in which Fe and Al atoms are linked by



groups (Hem and Roberson, 1967; 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 in turn determines the surface charge:



Thus, at any pH value, there will be present on the surface three types of sites: positive, negative and neutral. There will be a pH at which the number of positive sites equals the number of negative sites when the surface as a whole will be electrically neutral. This pH value is termed the isoelectric point - IEP (Parks, 1965).

It is necessary in Zn sorption studies to exclude the precipitation of Zn as $\text{Zn}(\text{OH})_2$. Concentrations of Zn^{2+} and OH^- sufficiently low to preclude the ionic concentration products exceeding the solubility product of $\text{Zn}(\text{OH})_2$ were therefore employed. It is also desirable to know the conditions under which complex ions of Zn are formed so that complex ion sorption can be taken into account. From a consideration of the hydrolysis reaction of Zn^{2+} , the role of the ZnOH^+ form appears to be insignificant. The hydrolysis constant for the Zn^{2+} ion is $(\text{ZnOH}^+)(\text{H}^+)/(\text{Zn}^{2+}) = 10^{-10}$ (Charlot, 1954). The variation of the ionic ratio of $\text{Zn}^{2+}/\text{ZnOH}^+$ with pH as predicted from the hydrolysis constant is as follows:

pH	$\frac{\text{Zn}^{2+}}{\text{ZnOH}^+}$
4	10^6
5	10^5
6	10^4
7	10^3

In acid and neutral solutions, the ionic ratio of $Zn^{2+}/ZnOH^+$ is so large that it tends to preclude any significant sorption of $ZnOH^+$.

Zinc also forms complexes with the Cl ion. The ionic ratios of $ZnCl^+/Zn^{2+}$ increase with increasing concentration of the salt solutions. Short and Morris (1961) established the existence of the complex species $ZnCl^+$, $ZnCl_2^0$, $ZnCl_3^-$ and $ZnCl_4^{2-}$ in aqueous solution and measured their stability constants. They reported the following values for 0.691 M Cl^- at 20C:

$$K_1 = (ZnCl^+)/([Zn^{2+}][Cl^-]) = 5.3 \text{ moles}^{-1} \text{ litre.}$$

$$K_2 = (ZnCl_2)/([ZnCl^+][Cl^-]) = 0.58 \text{ moles}^{-1} \text{ litre.}$$

$$K_3 = (ZnCl_3^-)/([ZnCl_2][Cl^-]) = 0.20 \text{ moles}^{-1} \text{ litre.}$$

$$K_4 = (ZnCl_4^{2-})/([ZnCl_3^-][Cl^-]) = 2.34 \text{ moles}^{-1} \text{ litre.}$$

Using these constants the percentages of ionic species were calculated to be:

Concentration	Zn^{2+}	Percentage of ionic species			
		$ZnCl^+$	$ZnCl_2$	$ZnCl_3^-$	$ZnCl_4^{2-}$
0.001 M	99.0	1.0	-	-	-
0.01 M	88.6	8.87	0.52	-	-
0.1 M	53	45	4	-	-

Values in the above table indicated that with the Zn and Cl concentrations (1.23×10^{-3} and 2.46×10^{-3} M respectively) used in this experiment, the role of all Zn species except Zn^{2+} would be insignificant.

An adsorption study was conducted using samples of pure Reagent Grade Fe_2O_3 and Al_2O_3 obtained from Fisher Scientific Co. The oxides were x-rayed and found to be crystalline α - Fe_2O_3 (hematite) and α - Al_2O_3 (corundum). Both minerals are known to occur naturally with hematite being the most common naturally occurring form of anhydrous oxide.

Triplicate sets of 0.2g-samples of 270-mesh Al_2O_3 and Fe_2O_3 were placed in centrifuge tubes. Ten ml of a 400 ppm Zn solution made of Reagent Grade ZnCl_2 in deionized H_2O was added to all but control solutions. Increasing volumes of 0.01 N NaOH ranging from one to 12 ml were added to the tubes and the final volumes adjusted to 50 ml with deionized H_2O . The suspensions were shaken for 24 hours after which the pH of the suspension was measured. The suspensions were filtered immediately after pH measurements using Whatman number five filter paper, and the Zn, Na, Fe or Al and Cl ion concentrations of the filtrates measured.

The proportion of adsorbed Zn which was held in exchangeable form was measured using a second set of duplicate samples prepared in the same manner as above except that after the pH measurements, the samples were centrifuged at 2000 RPM for 20 minutes. The centrifugates were decanted into another set of tubes and saved for Zn measurements. Fifty ml of 1.0 M BaCl_2 were then added to the oxide sediments and the suspensions equilibrated for 24 hours with shaking. The suspensions were filtered and the Zn concentrations of the filtrates measured. The proportion of total adsorbed Zn, exchanged or displaced by 1.0 M BaCl_2 was considered to be the portion of exchangeable Zn.

Initial Zn concentrations in all solutions were 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 7.2 or greater. Amounts of Zn adsorbed was calculated from the difference between Zn concentration after equilibration and the initial concentration of Zn added (80 ppm).

Decrease in pH concomitant with Zn adsorption revealed the release of H^+ ions as a result of Zn adsorption. In order to measure the amount of hydrogen ions released upon Zn adsorption, titration curves for Fe_2O_3 and

Al_2O_3 were constructed. Air-dried samples of Reagent Grade Al_2O_3 and Fe_2O_3 were ground to pass a 270 mesh sieve. Duplicate 0.2g-samples of Fe_2O_3 and Al_2O_3 were treated with increasing volumes of either 0.01 N HCl or 0.01 N NaOH. The final volume was adjusted to 50 ml by deionized water and the pH of the suspension measured after two hours, one, four and ten days of equilibration in centrifuge tubes. Final pH values were plotted versus milliequivalents of HCl or NaOH used (Figure 5).

The quantity of H ions released on Zn adsorption was calculated from the amount of base consumed in the reaction. The final pH values obtained for samples treated with Zn and NaOH were higher or lower than for non-treated oxides in deionized H_2O . The amount of base consumed in samples treated with zinc and having final equilibrium pH values greater than that for the oxides in deionized water was calculated as follows:

meq. of base added to sample treated with Zn - meq. of base required to increase pH of the nontreated sample to the pH values of the sample treated with Zn. The latter value was obtained from the titration curves shown in Figure 5. The amount of base consumed in samples treated with Zn but having final pH values less than that for the oxides in distilled water was calculated as follows:

meq. of base added to sample treated with Zn + meq. of acid required to decrease the pH of the nontreated sample to the pH value of the sample treated with Zn.

Increase in pH of untreated Fe_2O_3 and Al_2O_3 with shaking time indicated the protonation of surface Al-O groups to Al-OH or Al-OH₂ groups (Figure 5). Increase in pH with time was slightly greater for Al_2O_3 than Fe_2O_3 particularly at low pH's. The increase of pH decreased with time and approached zero after 4 days of equilibration (Figure 5). At lower pH values protonation was favored as a result of higher H^+

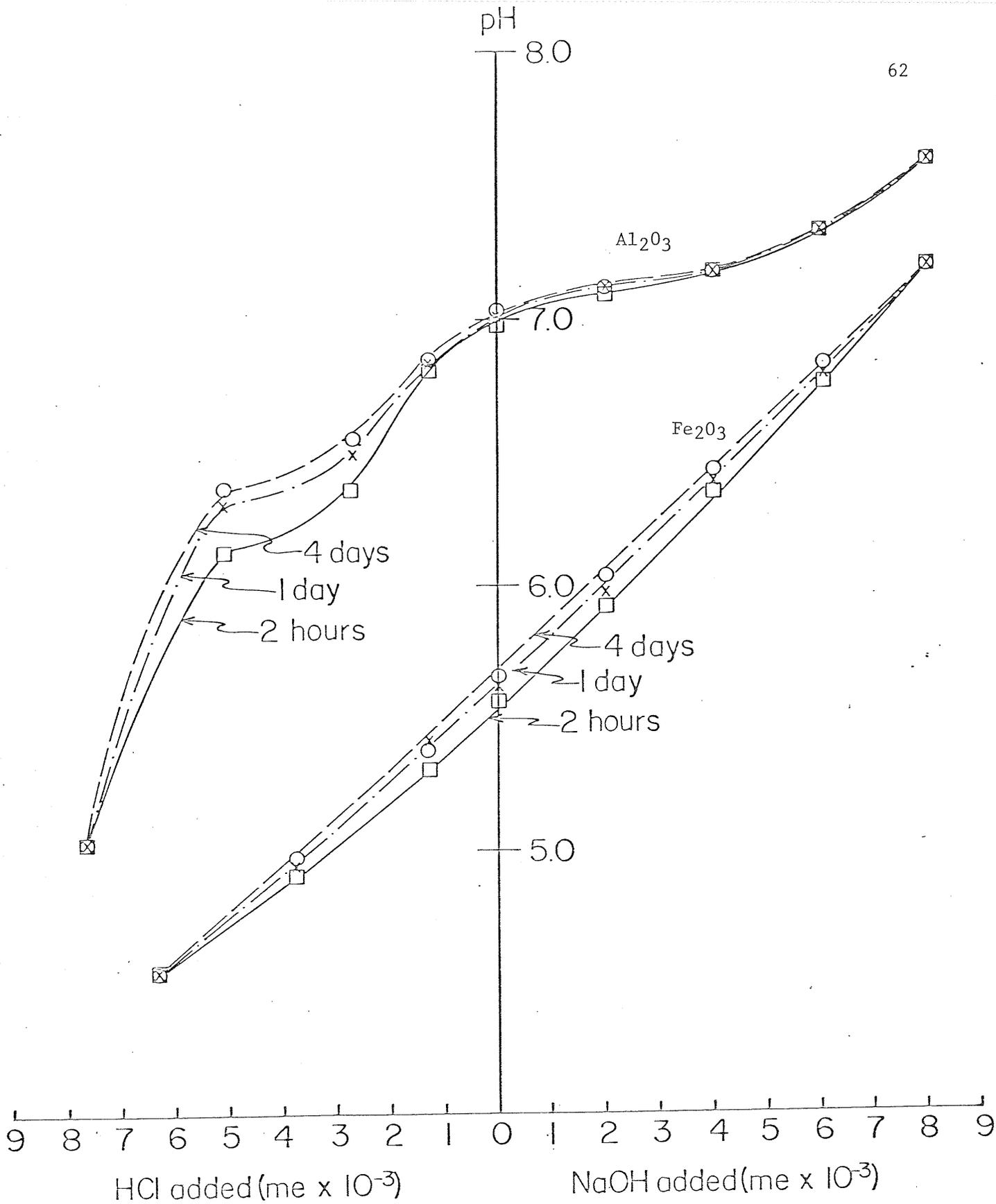


Figure 5. Titration curves for α - Al_2O_3 and α - Fe_2O_3 . Effect of time of equilibration on final pH values for each oxide is shown by the various curves.

ion concentration in the solution. At very low pH's, however, the H^+ ion concentration was high enough so that H^+ uptake by the mineral did not change the pH significantly (Figure 5). Since pH did not increase significantly after one day, 24 hours shaking was adopted as equilibrium time for the Zn adsorption study.

Adsorption of Zn by hydrated Al_2O_3 and Fe_2O_3 was conducted at pH values ranging from 6.42 to 6.92 for Al_2O_3 and from 5.93 to 6.96 for Fe_2O_3 (Table 13). Sorption increased markedly with pH for both Fe and Al oxides probably due to a reduction in net positive charge and development of new neutral and negative adsorption sites on the mineral's surface. Also H^+ from $-OH_2$ groups could be more easily replaced at the higher pH's. 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. This was probably due to the lower isoelectric pH of Fe_2O_3 as compared to Al_2O_3 (Chu, 1960).

An extremely significant feature was the concomitant desorption of H^+ when Zn was sorbed. The quantity of H^+ released was a function of both pH and Zn adsorbed (Table 13). The molar ratio of H^+ released to Zn adsorbed, increased with pH and amount of Zn adsorbed and had a range from 1.58 to 1.87 with an average of 1.71 for Al_2O_3 and from 1.53 to 1.94 with an average of 1.75 for Fe_2O_3 . In other words for each mole of Zn adsorbed an average of about 1.73 protons were desorbed. This agreed with the findings of Forbes (1973) who suggested that for each Cu (II) adsorbed on goethite, 1.78 protons were released. The fact that this value was less than two was attributed to monodentate bondings. If Zn sorption could be viewed as a straight surface adsorption with release of H^+ from aquo or hydroxo groups, then two H^+ ions should be released on adsorption of one mole of Zn in order for the solution to remain electrically neutral. If less than two H^+ were

Table 13. Adsorption of Zn by Fe and Al Oxides Suspended in Aqueous Solutions of Varying pH.

Susp. pH	Zn Adsorbed (A)	H ⁺ Released (B)	Cl ⁻ Adsorbed (C)	Na ⁺ Adsorbed (D)	Molar Ratio			Proportion of Adsorbed Zn Replaced by Ba ²⁺
					B/A	C/A	B-C/A-C	
Aluminum Oxide								
6.42	7.26	5.75	1.41	0.00	1.58	0.39	1.95	0.35
6.59	13.02	10.05	2.42	0.00	1.62	0.37	1.80	0.33
6.70	17.58	15.00	2.60	0.00	1.70	0.29	2.00	0.28
6.85	26.82	24.14	2.21	0.00	1.80	0.16	1.96	0.20
6.92	37.05	34.65	2.70	0.43	1.85	0.14	2.02	0.17
Iron Oxides								
5.93	12.77	9.80	2.82	0.00	1.53	0.44	1.96	0.37
6.42	22.18	18.30	3.75	0.00	1.65	0.34	1.98	0.30
6.66	31.36	27.55	3.82	0.00	1.76	0.24	2.00	0.23
6.79	41.20	37.10	3.11	0.65	1.80	0.15	1.94	0.19
6.86	51.35	47.50	3.60	0.00	1.85	0.14	1.99	0.16
6.96	58.13	56.45	2.40	0.00	1.94	0.08	2.03	0.10

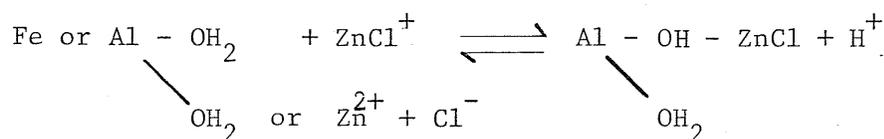
released as appeared to be the case for this experiment, then an anion should have been counter adsorbed to balance off the charge imbalance caused by Zn adsorption. Chloride was the only other anion that existed in the system which could have been adsorbed. Very few or no Cl concentration differences were detected among the Zn treated samples. However, when Cl concentration values were compared with control determinations a small and uniform Cl adsorption was recognized (Table 13). In contrast to Zn adsorption which was highly pH dependent, Cl adsorption did not vary with pH. The molar ratio of Cl to Zn sorbed, however, decreased markedly with increasing pH (Table 13). The ratio of moles of Cl to moles of zinc adsorbed decreased from 0.39 at low pH values to 0.08 at high pH values (Table 13). The chloride adsorbed with Zn might have been adsorbed onto the same sites as Zn or adsorbed onto separate sites. Evidence presented here indicates that Cl^- ions were adsorbed onto the same sites as Zn. Another way of regarding this process is to assume that the surface had a strong affinity for a complex species such as ZnCl^+ . Even though concentrations of such a species would have been very low because of the low Zn and Cl concentrations, the removal of ZnCl^+ by the surface would have caused displacement of the solution equilibrium forming new complex species to be adsorbed. The affinity of the surface for the complex form must have decreased markedly with increasing pH since the Cl to Zn molar ratio was always less than one. Perhaps two kinds of sites for adsorption of Zn existed, one with and one without Cl and the proportion of sites with Cl decreased as pH increased (Table 13). Decrease in the proportion of sites with Cl might have been due to the development of new neutral or negative sites with an increase in pH. These new sites would have provided the mineral with new locations to preferentially adsorb Zn^{2+} rather than ZnCl^+ .

Comparison of Na concentrations in solution with control determinations indicated that no Na adsorption occurred (Table 13). Concentrations of Fe and Al in solution were below the detection limit of atomic absorption spectrometry. Zinc and Cl were the only ions adsorbed and H^+ the only ion desorbed in measureable amounts. Thus, if the solution were to remain electrically neutral, the sum of H^+ released plus Cl^- adsorbed in milliequivalents should have been equal to total Zn adsorbed in milliequivalents. The data (Table 13) indicated that this was the case.

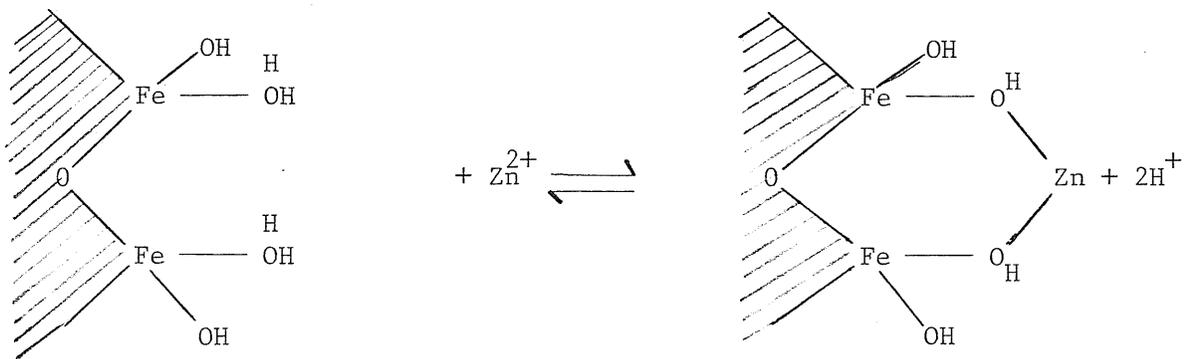
If adsorption of both $ZnCl^+$ and Zn^{2+} occurred, there probably would have been two different sites and adsorption mechanisms. Since $ZnCl^+$ is a monovalent cation as opposed to Zn^{2+} which is a divalent cation, one H^+ would have been released upon adsorption of $ZnCl^+$ and two H^+ for Zn^{2+} . In other words, if the number of moles of Cl adsorbed were subtracted from both the moles of H^+ released and Zn adsorbed, the molar ratio of the remainder of H released to Zn adsorbed should be equal to two. Data (Table 13) indicated values for this quantity ranging from 1.80 to 2.03 with an average of 1.97 which could be considered as support for the above hypothesis. If different mechanisms had been involved in adsorption of Zn^{2+} and $ZnCl^+$, then Zn^{2+} and $ZnCl^+$ would likely have been adsorbed with varying strengths. Or, if they were adsorbed with different strengths, then this would have been a reason for the different mechanisms being involved.

Preliminary experiments indicated that only a portion of total Zn adsorbed on Fe_2O_3 and Al_2O_3 were exchangeable by Ba^{2+} , Ca^{2+} and Mg^{2+} . These experiments also showed that the amount of Zn replaced by 1.0 M $BaCl_2$, $CaCl_2$ and $MgCl_2$ were not significantly different and did not change with time of extraction after 24 hours. Thus, 24 hours extraction with 1.0 M $BaCl_2$ was adopted for measurement of exchangeable Zn. An interesting

point was that exchangeable Zn which was displaced with 1.0 M BaCl₂ was in close agreement with the proportion of sites occupied by Cl⁻ or the proportion of Zn which was adsorbed as ZnCl⁺ (Table 13). The fact that a relatively high concentration of Ba²⁺ and 24 hours of extraction period could displace only a portion of Zn adsorbed and that this portion decreased with increasing pH exactly in the same manner that the molar ratio of Cl to Zn decreased, once more supported the hypothesis that two mechanisms of Zn adsorption existed. The first mechanism likely involved adsorption of Zn²⁺ and Cl⁻ or ZnCl⁺ along with release of one H⁺ for each ZnCl⁺. This portion which was relatively high at low pH values and decreased markedly as pH increased consisted of 39 to 14% and 44 to 8% of total Zn absorbed by Al₂O₃ and Fe₂O₃, respectively (Table 13). Adsorption of ZnCl⁺ was nonspecific for Zn in that it could be replaced by Ba²⁺, Ca²⁺ and Mg²⁺. The exact mechanism and location of ZnCl⁺ adsorption on the surface is not clear. However, due to its lower positive charge as compared to Zn²⁺ and also its much stronger polarity, the probability of ZnCl⁺ being adsorbed onto positive sites was better than for Zn²⁺. Since adsorption of ZnCl⁺ was accompanied with release of one H⁺ ion, ZnCl⁺ adsorption cannot be considered as purely electrostatic. This adsorption was only significant at low pH's, thus it may have only involved aquo groups. This might be considered as monodentate adsorption of Zn as described by Forbes (1973). Considering the experimental evidence presented here the following mechanisms of adsorption of ZnCl⁺ on the surfaces of Al₂O₃ and Fe₂O₃ were postulated:



The second mechanism likely involved adsorption of Zn^{2+} and release of two H^+ for each Zn^{2+} . This portion increased with pH from 61 to 86% for Al_2O_3 and 56 to 92% for Fe_2O_3 , respectively (Table 13). In contrast to $ZnCl^+$, adsorption of Zn^{2+} was specific for Zn in that Ca^{2+} , Ba^{2+} and Mg^{2+} could not replace it from the mineral surface. In this mechanism, Zn^{2+} was likely adsorbed at pH values (6 to 7) below the IEP of both Al_2O_3 and Fe_2O_3 (Kinniburgh, et al 1975). Thus adsorption probably took place despite an unfavorable electrical potential due to the large chemical affinity. Therefore, the Zn was held by strong chemical bonding. Quirk and Posner (1975) suggested the following mechanism for adsorption of Zn^{2+} on the goethite surface:



In this scheme an olation bridge and ring structure is postulated to form. Such adsorption can be viewed as a growth or an extension of the surface and its properties would accord with the lack of reversibility of such an adsorption. The adsorption of Zn^{2+} was represented as a bridging ligand between two neutral sites, however, Zn^{2+} could be adsorbed to two positive or a positive and a neutral site similar to the above scheme. This mechanism fitted the experimental evidence found for Zn specifically adsorbed i.e. the portion which was not exchangeable with Ba^{2+} . Release of two H^+ for each Zn^{2+} adsorbed and lack of reversibility were both shown to be the characteristics of this portion of adsorbed Zn^{2+} adsorbed on Al_2O_3 and Fe_2O_3 .

The source of desorbed H^+ could have been either hydroxo or aquo groups. Aquo groups, however, as was postulated by Quirk and Posner (1975) were more likely the source of H^+ because they were more abundant at pH's lower than the IEP. Furthermore, H^+ would have been more easily dissociated from aquo groups than from hydroxo groups.

Iron and Al hydrous oxides revealed a tremendous capacity for adsorption of Zn. Adsorption was highly pH dependent and consisted of specific and non-specific portions. The nonspecific portion decreased whereas the specific portion increased markedly with increasing pH. Specifically adsorbed Zn accounted for 60 to 90% of total adsorption and may explain, at least to some extent, the significant association found between Zn and Fe or Al content of some soils studied in the previous chapter.

C. Reaction Products of $ZnSO_4$, ZnEDTA, ZnS and $ZnSO_4 + NH_4H_2PO_4$
Banded in Soils

The solid-phase crystalline reaction products formed when Zn fertilizers are added to calcareous and noncalcareous soil, have been inferred, by several researchers, using solubility criteria. However, no direct evidence, for the existence of these compounds in the soil, were reported or were found in the literature. It is therefore of interest to determine if Zn compounds could form in calcareous and non-calcareous soils when microregions in soils are saturated with respect to Zn fertilizer.

A method similar to that of Bell and Black (1970) was selected to determine the reaction products of Zn compounds applied as a band. Air-dried duplicate samples of Lakeland, Newdale, Stockton and Plum Ridge soils (Tables 1 and 14) were placed in plastic cylinders (2.5 cm diameter and 5 cm high) and wetted to field capacity by capillarity using distilled water. One-tenth g of Zn as $ZnSO_4$, ZnS or ZnEDTA was placed on the surface of the soil and the tops of the columns sealed with parafilm. The columns were inverted and incubated at room temperature in a glass container maintained near 100% relative humidity.

In a second study, samples of Lakeland and Newdale soil were treated with both Zn and P. The procedure followed was as outlined above except that 0.3 g phosphorus as $NH_4H_2PO_4$ was added and only $ZnSO_4$ was used as a source of Zn.

After incubation for 2, 4, 8, 16 and 32 weeks a very small sample of soil immediately adjacent to the placement site was taken, air dried and finely ground for powder x-ray diffraction analysis. The "d" spacings for treated soils and soil without added Zn were determined. "d"

TABLE 14. Some Characteristics of Soils Studied.

Soil	Texture	pH 1:10 (Soil:H ₂ O)	Inorganic CO ₃ (%)	Organic C (%)	Conc. (1:10 Soil:H ₂ O)		NH ₄ Ac - Displaceable		Cation Exchange Capacity (me/100 g)	Total Zn (ppm)
					HCO ₃ (me/L)	Zn (ppm)	Ca (me/100 g)	Mg (me/100 g)		
Stockton	LS-SL	7.2	0.3	2.0	0.15	0.03	8.0	3.8	12.6	58
Newdale	CL	8.2	0.4	3.5	1.40	0.04	27.1	5.6	29.6	80
Lakeland	SIL	8.3	15.6	2.6	1.60	0.02	25.2	11.6	22.0	52
Plum Ridge	SL	8.2	7.5	1.5	1.50	0.02	21.9	8.4	11.6	47

spacings that occurred in the treated soil, and not found in the soil without added Zn, were taken to be those of the reaction products. Some of the "d" spacings obtained for the soil-Zn reaction products and the "d" spacings (most intense lines) listed for these products in the ASTM (American Society for Testing Materials X-ray powder data files) are shown in Table 15. The experimental values, usually with $\pm 0.03\text{\AA}$ of the known values, are means of values obtained for several analyses. Five or six "d" spacings were usually identified for a particular reaction product before it was listed as being present in the soil.

A two-cm layer of soil adjacent to the fertilizer band was cut, air dried, and ground for pH and solubility measurements. Five g of soil was shaken in 50 ml of deionized water for 24 hours. pH was measured on the supernatant, using glass and calomel electrodes attached to a Beckman pH meter. Zinc concentration in the filtrate was measured by atomic absorption spectrometry.

a. Reaction Products and Solubility of Banded ZnSO_4

1) Newdale CL.

Zinc hydroxide $\text{Zn}(\text{OH})_2$ was identified as a reaction product of banded ZnSO_4 in the Newdale soil after two and four weeks of incubation (Table 16). The soil pH adjacent to the ZnSO_4 band was 6.35 and 6.60 at two and four weeks of incubation, respectively (Table 17). This agrees with the findings of Bingham et al (1964) in which precipitation of $\text{Zn}(\text{OH})_2$ in a H-montmorillonite occurred only when the pH of the system was above 5.5 to 6.5 and added Zn was in excess of the NH_4^+ -exchange capacity of the clay. Zinc hydroxide $\text{Zn}(\text{OH})_2$ was not detected after more than four weeks of incubation in the Newdale soil treated with ZnSO_4 . Thus, it appears that $\text{Zn}(\text{OH})_2$ was a metastable reaction

TABLE 15. "d" Spacings (A) For Soil-Zinc Reaction Products*

Zn(OH) ₂	Relative Intensity	ZnCO ₃	Relative Intensity	ZnS	Relative Intensity	Zn ₅ (CO ₃) ₂ (OH) ₆	Relative Intensity
7.57 (7.56)	40	3.54 (3.55)	50	3.31 (3.31)	2	3.98 (3.99)	20
3.28 (3.27)	100	2.73 (2.75)	100	3.12 (3.12)	100	3.68 (3.66)	40
3.23 (3.26)	100	2.33 (2.33)	25	2.72 (2.71)	4	2.99 (3.00)	10
3.06 (3.03)	90	1.95 (1.95)	25	1.91 (1.90)	50	2.86 (2.85)	30
2.77 (2.76)	60	1.70 (1.70)	45	1.76 (1.76)	4	2.72 (2.72)	60
2.68 (2.69)	10	1.49 (1.49)	14	1.67 (1.68)	2	2.64 (2.69)	20
2.08 (2.09)	10			1.63 (1.63)	35	2.43 (2.39)	70
2.01 (2.01)	30			1.60 (1.60)	2	1.86 (1.84)	10
				1.35 (1.35)	2	1.72 (1.69)	40
NH ₄ ZnPO ₄							
		Zn ₃ (PO ₄) ₂ · 4H ₂ O		Zn ₃ (PO ₄) ₂ · 2H ₂ O		Ca[Zn(OH) ₃] ₂ · 2H ₂ O	
4.66 (4.65)	100	4.83 (4.85)	20	4.58 (4.55)	10	4.13 (4.12)	100
2.72 (2.72)	55	3.04 (3.03)	10	3.05 (3.06)	5	3.66 (3.57)	16
2.76 (2.76)	12	2.31 (2.27)	30	2.77 (2.78)	-	3.09 (3.12)	100
2.07 (2.07)	4	1.93 (1.94)	40	2.72 (2.74)	-	3.00 (3.00)	2
2.02 (2.01)	4	1.75 (1.77)	5	2.33 (2.33)	-	2.86 (2.88)	50
1.79 (1.78)	8	1.72 (1.73)	10	1.92 (1.93)	15	2.72 (2.73)	10

TABLE 15 (Contin)

1.57 (1.57)	6	1.69 (1.69)	10	1.88 (1.88)	5	2.48 (2.49)	4
				1.74 (1.72)	-	1.96 (1.96)	6
				1.71 (1.69)	-		
				1.62 (1.63)	-		
				(1.60) (1.59)	5		

*Numbers in parentheses indicate values listed in the ASTM X-ray powder data file.

TABLE 16. Reaction Products of Zinc Compounds Banded in Soil.

Applied Compound	Incubation Time (weeks)	Stockton	Newdale	Lakeland SIL	Plum Ridge SL
ZnSO ₄	2	*	Zn(OH) ₂	ZnCO ₃	-
	4	-	Zn(OH) ₂	ZnCO ₃	Zn ₅ (CO ₃) ₂ (OH) ₆
	8	-	-	-	Zn ₅ (CO ₃) ₂ (OH) ₆
	16	-	-	ZnCO ₃	Zn ₅ (CO ₃) ₂ (OH) ₆
	32	-	-	-	-
Zn EDTA	2	-	-	-	-
	4	-	-	-	-
	8	-	-	-	-
	16	-	-	-	-
	32	-	-	-	-
ZnS	2	ZnS	ZnS	ZnS	ZnS
	4	ZnS	ZnS	ZnS	ZnS
	8	ZnS	ZnS	ZnS	ZnS
	16	ZnS	ZnS	ZnS	ZnS
	32	ZnS	ZnS	ZnS	ZnS + Zn ₅ (CO ₃) ₂ (OH) ₆ + Ca[Zn(OH) ₃] ₂ · 2H ₂ O
ZnSO ₄ + NH ₄ H ₂ PO ₄	2	X. **	Zn ₃ (PO ₄) ₂ · 4H ₂ O	NH ₄ ZnPO ₄ Zn ₃ (PO ₄) ₂ · 4H ₂ O	X X
	4	X	Zn ₃ (PO ₄) ₂ · 4H ₂ O	Zn ₃ (PO ₄) ₂ · 2H ₂ O Zn ₃ (PO ₄) ₂ · 4H ₂ O	X X
	8		Zn ₃ (PO ₄) ₂ · 4H ₂ O	Zn ₃ (PO ₄) ₂ · 4H ₂ O	X
	16	X	Zn ₃ (PO ₄) ₂ · 4H ₂ O	Zn ₃ (PO ₄) ₂ · 4H ₂ O + ZnCO ₃	X
	32	X	Zn ₃ (PO ₄) ₂ · 4H ₂ O	Zn ₃ (PO ₄) ₂ · 4H ₂ O + ZnCO ₃	X

* no reaction product detected.

** study not conducted.

TABLE 17. pH of Soils Banded With Zinc Compounds.

Compound Applied	Incubation Time (week)	Soil pH (1:10 soil - H ₂ O)		
		Stockton LS-SL	Newdale CL	Lakeland SIL Plum Ridge SL
ZnSO ₄	2	5.10	6.35	7.25 6.60
	4	5.40	6.60	7.30 6.85
	8	5.60	6.70	7.40 6.95
	16	5.65	6.75	7.40 7.00
	32	5.55	6.80	7.45 7.10
Zn EDTA	2	7.20	7.60	8.25 8.05
	4	7.30	7.75	8.35 8.15
	8	7.45	7.85	8.40 8.20
	16	7.10	7.70	8.30 8.10
	32	7.00	7.90	8.30 7.90
ZnS	2	6.25	7.70	8.00 7.90
	4	6.45	7.85	8.10 8.05
	8	6.60	7.75	8.10 7.95
	16	6.70	7.70	8.00 7.60
	32	6.10	7.40	7.55 7.50
ZnSO ₄ + NH ₄ H ₂ PO ₄	2	X*	5.80	7.65 X
	4	X	6.10	7.80 X
	8	X	6.40	7.90 X
	16	X	6.70	8.05 X
	32	X	6.60	8.15 X

*--study not conducted.

product which persisted only for a short period of time. This is in agreement with the report of Krauskopf (1972). He found precipitated $\text{Zn}(\text{OH})_2$ to be unstable, decomposing under both natural and laboratory conditions to zincite, ZnO . Dhillon *et al.* (1975) also suggested that $\text{Zn}(\text{OH})_2$, formed upon addition of supplementary Zn to soil, converts into more sparingly soluble compounds upon aging.

Reported solubility product data for $\text{Zn}(\text{OH})_2$ vary from 10^{-14} to 10^{-18} (Sillen & Martel 1964). However, values near 10^{-17} are most frequently reported. Thus, a value of $10^{-17.15}$ at 25°C from Sillen and Martell (1964) was chosen for solubility calculations. Using this value and measured pH's, Zn concentrations for the various incubation times were calculated and compared to measured values for Zn concentration (Table 18). The activity coefficient, in those calculations was assumed to be unity. Except for the sample obtained after two weeks of incubation in which the measured Zn concentration was lower than the calculated value, the measured and calculated values agreed reasonably well (Table 18), suggesting that the Zn concentration was controlled by the solubility of $\text{Zn}(\text{OH})_2$. However, uncertainty regarding the solubility product of $\text{Zn}(\text{OH})_2$ precludes further speculation regarding the existence of $\text{Zn}(\text{OH})_2$ beyond four weeks of incubation. The difference between the measured and calculated Zn concentrations for the sample obtained after two weeks of incubation indicated the soil solution was undersaturated with respect to $\text{Zn}(\text{OH})_2$. However, errors involved in pH measurement or in choosing the solubility product value might have been partially responsible for the difference.

Solubility of Zn (concentration of Zn in the soil extract) when applied as ZnSO_4 to the Newdale soil decreased with time, with the

TABLE 18. Measured Zinc Concentrations in Newdale Soil Banded With ZnSO_4 Compared to Zinc Concentrations Calculated Assuming Equilibrium with $\text{Zn}(\text{OH})_2$.

Incubation Time (week)	pH 1:10 (Soil- H_2O)	Calculated* Zinc Concentration (ppm)	Measured Zinc Concentration (ppm)
2	6.35	904	346
4	6.60	286	260
8	6.70	180	188
16	6.75	143	141
32	6.80	114	97

* Calculated from $[\text{Zn}^{2+}] = 10^{-\frac{17.15}{[\text{OH}]^2}}$ (Sillen and Martell 1964).

largest decrease occurring during the first eight weeks of incubation (Figure 6). Decrease in Zn solubility may have been caused by the formation of more sparingly soluble Zn compounds. This conforms to the x-ray diffraction data in which Zn(OH)_2 was not detected after four weeks of incubation (Table 16) indicating the possible conversion of Zn(OH)_2 to other Zn compounds. The decrease in Zn solubility could also be attributed to the increase in the pH of soil solution, causing the concentration of Zn in the soil extract to decrease: this hypothesis is supported by the agreement between calculated and measured values of Zn concentration in the soil solution (Table 18). However, both mechanisms could have been operative.

Decrease in solubility of Zn added as ZnSO_4 to the Newdale soil, contrary to the other soils, continued after 16 weeks of incubation (Figure 6), indicating either continuous changes in the Zn solid phase, or in the pH of the soil-water system or both.

Solubility of Zn in the Newdale soil decreased more than three fold from 350 ppm at two weeks incubation time to about 100 ppm after 32 weeks of incubation (Figure 6). Nevertheless, Zn solubility, even after 32 weeks of incubation was much greater than for the untreated soil (0.04 ppm) and great enough such that ZnSO_4 would be a good Zn fertilizer. Zinc concentration in the Newdale soil solution was higher, at all incubation times than in the calcareous Plum Ridge and Lakeland soils and lower than in the non-calcareous Stockton soil.

2) Stockton LS-SL

No reaction product was detected in the Stockton soil treated with ZnSO_4 (Table 16). This was probably a result of the relatively low soil pH near the fertilizer band (Table 17) or due to the formation

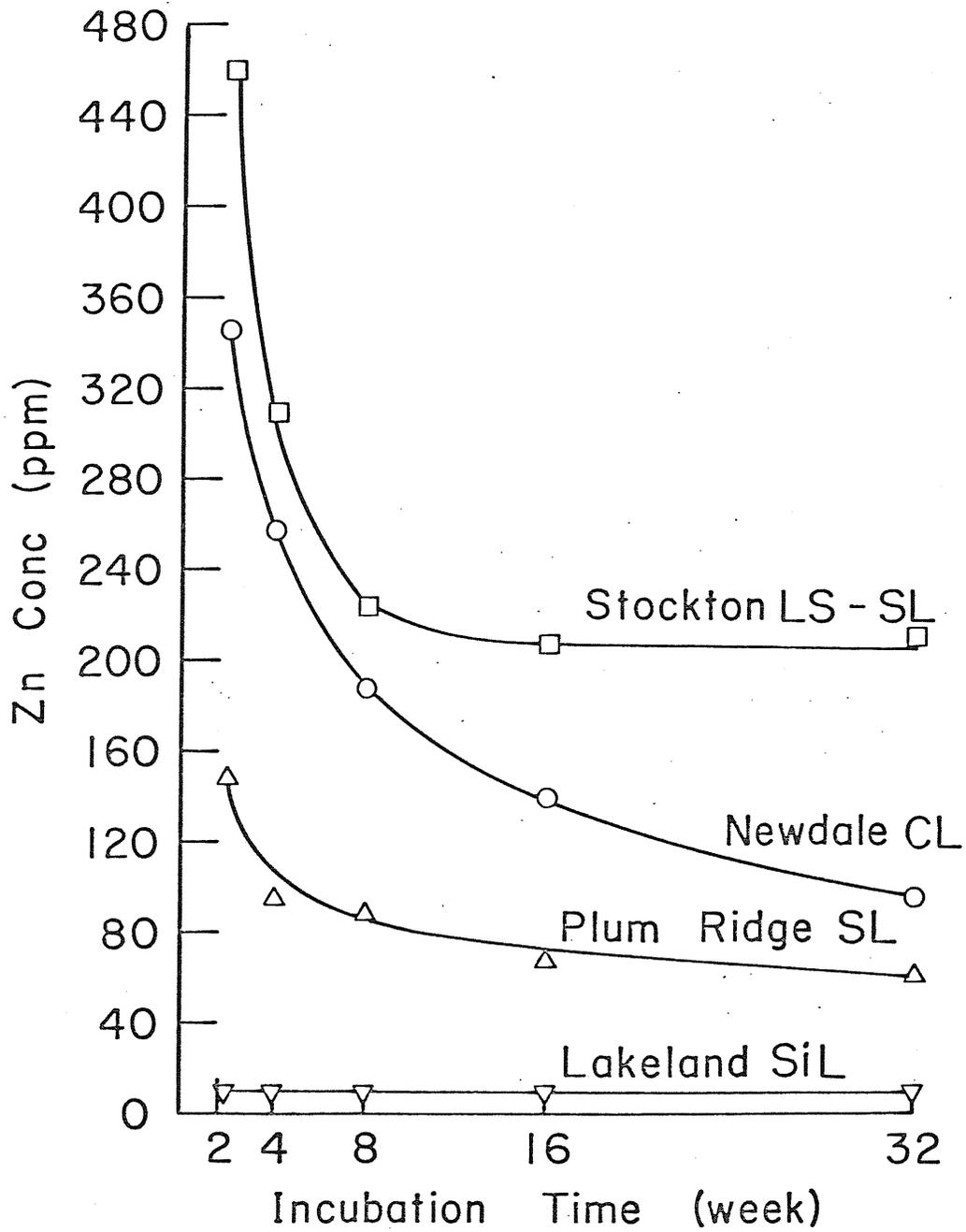


Figure 6. Zinc Concentrations in Water-extracts of Soils Banded with $ZnSO_4$.

of a reaction product in very low concentration and thus not detected by x-ray diffraction analysis. Precipitation of a new Zn solid phase was unlikely as the treated soil exhibited no "d" spacings other than those found in the untreated soil. Solubility of Zn in the Stockton soil treated with ZnSO_4 was higher at all incubation times than in the other soils, especially the calcareous Plum Ridge and Lakeland soils (Figure 6). Zinc concentration in the soil solution declined very sharply from 460 ppm at two weeks of incubation time to 220 ppm at eight weeks of incubation time. The rapid decrease in Zn solubility was probably due to both adsorption and formation of new Zn compounds. Increasing pH with incubation time (Table 17) may have also decreased the solubility of Zn through its influence on both adsorption and solubility of newly formed Zn compounds. The pH as well as Zn concentration in the soil extract remained relatively constant after eight weeks of incubation (Figure 6, Table 17).

Stockton LS-SL soil is non-calcareous and has a low buffer capacity due to its coarse texture (Table 1). Consequently, the pH of the soil decreased markedly when ZnSO_4 was added. The pH of soil adjacent to the ZnSO_4 band was 5.10 to 5.65 during incubation. Precipitation of Zn(OH)_2 under this pH range would require Zn^{2+} concentrations of at least 2.3×10^4 ppm which is much greater than the Zn concentration in the Stockton soil at any incubation time (Figure 6). Therefore, Zn(OH)_2 could not have precipitated in the Stockton soil. However, the possibility of formation of very small amounts of more sparingly soluble Zn compounds (not detectable by x-ray analysis) should not be excluded.

3) Lakeland SiL

Zinc carbonate (ZnCO_3) was the only reaction product identified after ZnSO_4 had been added to the calcareous Lakeland soil (Table 16). The soil pH adjacent to the ZnSO_4 band was 7.25 to 7.45 (Table 17). This confirms the findings of Udo et al. (1970), Hoover (1966) and Dhillon et al. (1975) who suggested ZnCO_3 formed as a reaction product when ZnSO_4 was added to calcareous soils. However, none of the above researchers identified ZnCO_3 by x-ray analysis, but only inferred its possible precipitation using solubility criteria. Zinc carbonate (ZnCO_3) was detected in the Lakeland soil after 16 weeks of incubation (Table 16) indicating that it was more stable than Zn(OH)_2 which persisted for only eight weeks in the Newdale soil.

Solubility of ZnCO_3 is not only a function of pH but also depends upon the partial pressure of CO_2 (PCO_2) in the medium, making the calculation of Zn concentration in solution in equilibrium with solid phase ZnCO_3 somewhat complicated. Critical control of PCO_2 in the soil solution was not exercised. However, calculations were conducted assuming that the PCO_2 in the soil-water system was in equilibrium with atmospheric CO_2 . Dissociation constants for H_2CO_3 reported by Garrels and Christ (1965) and the ZnCO_3 solubility product reported by Sillen and Martell (1964) were used. The activity coefficients were assumed to be unity. Calculated Zn concentrations assuming equilibrium with solid phase ZnCO_3 and a PCO_2 of $10^{-3.5}$ (atmospheric partial pressure of CO_2) are compared to measured Zn concentrations in Table 19. Measured and calculated values agreed reasonably well except for samples obtained after two weeks of incubation. The calculated value was about twice as large as the measured value for samples obtained after two weeks

TABLE 19 Measured Zinc Concentrations in Lakeland Soil Banded With $ZnSO_4$ Compared to Zinc Concentrations Calculated Assuming Equilibrium with $ZnCO_3$.

Incubation Time (week)	pH { 1:10 Soil-H ₂ O}	Calculated* Zinc Concentration (ppm)	Measured Zinc Concentration (ppm)
2	7.25	21.6	10.6
4	7.35	13.7	10.9
8	7.40	10.8	10.1
16	7.40	10.8	8.10
32	7.45	8.6	9.6

* Calculated Using $10^{-10.68}$ (Sillen and Martel 1964) and $10^{-3.7}$ (Garrels and Christ 1965) as values for Ksp for $ZnCO_3$ and Pco_2 , respectively.

of incubation. Agreement between calculated and measured Zn concentrations indicates that ZnCO_3 was likely the solid phase controlling the solubility of Zn in the Lakeland soil treated with ZnSO_4 . Furthermore, it shows that ZnCO_3 existed at eight weeks and probably persisted for 32 weeks even though ZnCO_3 was not detected by x-ray analysis after eight and 32 weeks of incubation. The difference between calculated and measured Zn concentrations for the samples obtained after two weeks of incubation may have been caused by a PCO_2 value in the soil solution higher than that in the atmosphere. This can happen if a soil-water system is shaken in stoppered bottles. Increasing PCO_2 would increase the concentrations of H_2CO_3 , HCO_3^- and $\text{CO}_3^{=}$ in the calcareous soil solution suppressing the solubility of ZnCO_3 and causing Zn^{2+} concentration in the soil solution to decrease.

Solubility of Zn in a soil solution, in equilibrium with ZnCO_3 is also extremely pH sensitive. Errors as large as 0.1 pH unit are quite common in soil pH measurements and are large enough to result in Zn^{2+} concentration changes of about 80%. Therefore, inherent errors involved in pH measurements could have also contributed to differences between measured and calculated values of Zn^{2+} concentration.

Solubility of Zn from ZnSO_4 was lower in the Lakeland soil than in the other soils (Figure 6). In contrast to the other soils in which there was a considerable decrease in Zn solubility between two and 32 weeks, there was little or no variation in solubility of Zn from ZnSO_4 in the Lakeland soil (Figure 6). This likely was caused by rapid formation of ZnCO_3 and its persistence throughout the entire incubation period.

Zinc solubility from ZnSO_4 in the Lakeland soil was relatively low compared to the other soils. Nevertheless, Zn concentrations in

the soil solution were much greater than for the untreated soil and high enough to supply Zn to plants. Therefore, banded $ZnSO_4$ would likely be a good source of fertilizer Zn in the calcareous Lakeland soil.

4) Plum Ridge SL

Banding $ZnSO_4$ in the Plum Ridge soil resulted in the formation of $Zn_5(CO_3)_2(OH)_6$ (Table 16). The soil pH adjacent to the $ZnSO_4$ band varied from 6.60 to 7.10 (Table 17). This agrees with Misra and Tiwari (1966) who hypothesized that under conditions of high pH and the presence of free carbonates both $Zn(OH)_2$ and $Zn_5(CO_3)_2(OH)_6$ should precipitate. Although $Zn_5(CO_3)_2(OH)_6$ was not detected after two and 32 weeks of incubation (Table 16) relatively small changes in both soil pH and concentration of Zn in soil solution (Figure 6, Table 17) throughout the incubation period indicate that $Zn_5(CO_3)_2(OH)_6$ probably persisted beyond 16 weeks of incubation.

Solubility product data for $Zn_5(CO_3)_2(OH)_6$ were not found in the literature. However, since it is both a carbonate and a hydroxide its solubility would depend both on pH and PCO_2 . Decrease in Zn solubility particularly in the first eight weeks of incubation (Figure 6) was probably due to the slight increase in soil pH (Table 17). The data also indicates that the solubility of Zn from the $ZnSO_4$ banded in the Plum Ridge soil was greater than in the Lakeland soil but less than in the Newdale. The relatively high solubility of Zn after 32 weeks of incubation indicates that $ZnSO_4$ would also be a good Zn fertilizer on the Plum Ridge soil.

Solubility of Zn from banded $ZnSO_4$ was great enough on all four soils to supply sufficient Zn to plants (Figure 6). Nevertheless, it

is obvious that the availability of Zn from ZnSO_4 would be much higher in noncalcareous than in calcareous soils. Furthermore, that availability of Zn from ZnSO_4 would be lower on fine-textured soils than on coarse textured soils, probably because of a more rapid reaction of Zn with soil constituents in the fine textured soils.

b. Reaction Products and Solubility of Banded ZnEDTA

No reaction products were detected when ZnEDTA was banded in the soils (Table 16). This was probably caused by Zn persisting in the soil as ZnEDTA resulting in low concentrations of ionic Zn^{2+} in soil solution and therefore little or no precipitation of Zn compounds near the ZnEDTA band. In addition, the greater solubility of ZnEDTA would allow it to diffuse through the soil such that the amounts precipitated in any particular volume of soil would be small and not detectable by x-ray analysis.

Concentrations of Zn in extracts of soils treated with ZnEDTA were much higher than the concentrations of Zn in extracts of soils treated with ZnSO_4 (Figures 6 and 7) indicating that Zn probably remained in chelated form even after 32 weeks of incubation (Figure 7). Thus, ZnEDTA was sufficiently stable to hold a large portion of the Zn in solution in spite of the high pH and carbonate content of soils and the affinity of soil constituents for Zn.

Solubility of Zn from ZnEDTA was highest in the Lakeland soil whereas solubility of ZnSO_4 was the lowest in this soil (Figures 6 and 7). This was probably due to the higher stability of ZnEDTA at higher pH's. The pH of soil adjacent to the fertilizer band was highest in the Lakeland soil ranging from 8.35 to 8.45 and lowest in Stockton LS to SL ranging from 7.10 to 7.45 (Table 17). This, however, contradicted

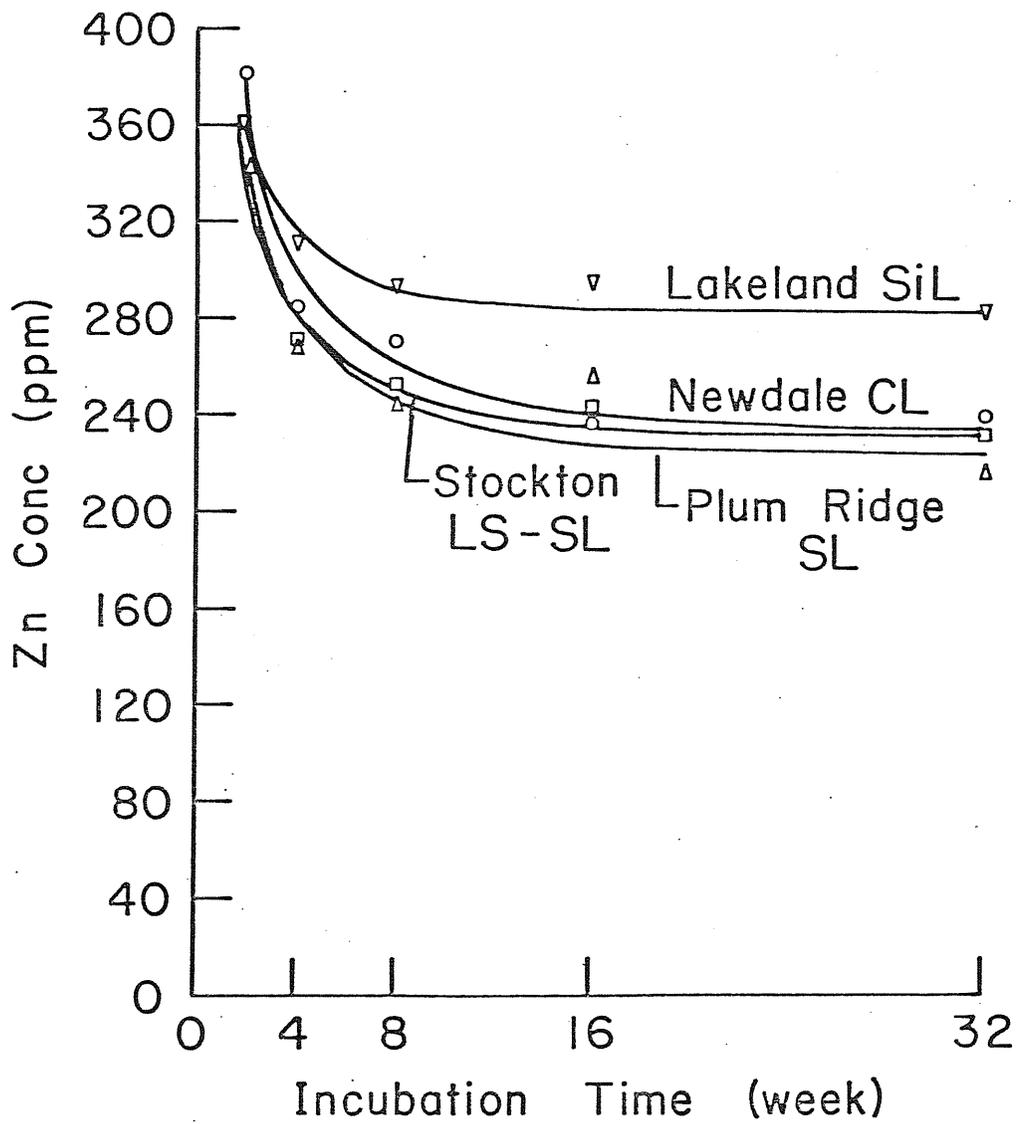


Figure 7. Zinc Concentrations in Water-extracts of Soils Banded with ZnEDTA.

the findings of Lindsay and Norvell (1969) who found that ZnEDTA had a maximum stability at pH 6.5 where approximately 70% of the EDTA ligand was chelated with Zn^{2+} .

The loss of the EDTA ligand from soil solution is thought to result primarily from its adsorption by soil particles. The rate of adsorption or fixation is usually rapid initially and decreases sharply with time. Zinc solubility from ZnEDTA decreased very rapidly until eight weeks and then became nearly constant with time (Figure 7). This is in accordance with reports by Norvell and Lindsay (1969) who found the rate of Zn loss from the reaction of ZnEDTA with soil solution, having pH's near neutral, very rapid initially. Further loss occurred, however, quite slowly and in most cases the percentage of ZnEDTA became nearly constant with time.

Very high solubility of Zn in soils treated with ZnEDTA stability in soils especially after eight weeks of incubation indicates that ZnEDTA when banded will maintain high concentrations of Zn in soil solution in both calcareous and noncalcareous soils and thus would be excellent Zn fertilizer.

c. Reaction Products and Solubility of Banded ZnS

Zinc sulfide (ZnS), a sparingly soluble salt, dissolved very slowly such that ZnS persisted in the soils at all sampling dates (Table 16). However, x-ray analysis showed the formation of $Zn_5(CO_3)_2(OH)_6$ and $Ca[Zn(OH)_3]_2 \cdot 2H_2O$ in the Plum Ridge soil after 32 weeks of incubation (Table 16).

Solubility measurements (Figure 8) revealed two distinct differences in the solubility behaviour of ZnS as compared to $ZnSO_4$ and ZnEDTA:

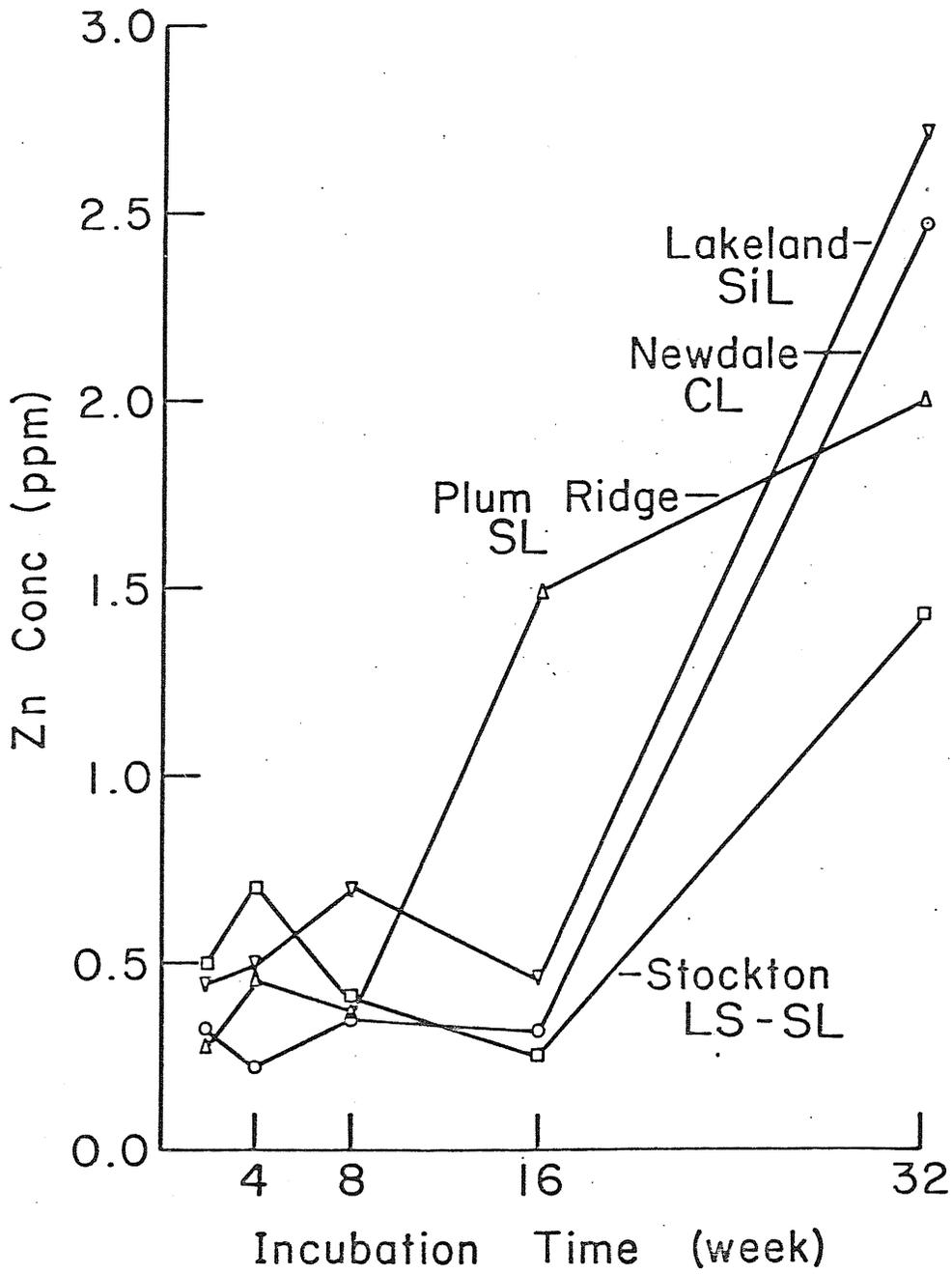


Figure 8. Zinc Concentrations in Water-extracts of Soils Banded with ZnS.

i) - Concentrations of Zn in solution of soils treated with ZnS were very low as compared to soils treated with ZnSO_4 or ZnEDTA. Nevertheless, it was at least ten times greater than for untreated soils (Figure 8, Table 14).

ii) - Zinc concentrations in solution of soils treated with ZnSO_4 or ZnEDTA decreased with time whereas Zn concentrations in extracts of soils treated with ZnS increased with time (Figure 6, 7, 8). However, the increases in Zn concentrations with time in solutions of soils treated with ZnS were irregular, probably due to pH fluctuations (Table 17). Most of the increases in Zn concentrations occurred after 16 weeks of incubation.

Zinc sulfide (ZnS) has a solubility product of about 10^{-25} (Sillen and Martell, 1964) and is therefore highly insoluble in the presence of even trace quantities of H_2S . However, under aerobic conditions in which H_2S is thermodynamically unstable ZnS is oxidized to soluble compounds such as ZnSO_4 with the release of Zn^{2+} into solution. Reports of Krauskopf and Lindsay (1972) support this theory. They suggested that ZnS is unstable under normal oxidizing conditions. Formation of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and $\text{Ca}[\text{Zn}(\text{OH})_3]_2 \cdot 2\text{H}_2\text{O}$ in the Plum Ridge soil (Table 16) and the increase in zinc concentration with time in soils treated with ZnS (Figure 8) are evidence for at least partial oxidation of ZnS to less sparingly soluble compounds. However, the oxidation reaction was apparently slow, becoming significant only after 32 weeks on incubation (Figure 8). Furthermore, detection of ZnS by x-ray analysis even after 32 weeks of incubation indicated that only partial oxidation occurred. Increases in solubility of applied ZnS with time were also reported by McGregor (1972). He found Zn concentrations

increased by about 10 ppm (on soil basis) during three weeks of incubation when ZnS was mixed with calcareous soils.

Zinc sulfide can still be considered a good Zn fertilizer, despite its low solubility compared to ZnSO_4 and ZnEDTA. Zinc concentrations were about ten times higher in soil solutions receiving ZnS than in soils receiving no supplementary Zn. Solubility of ZnS increased with time indicating that ZnS would maintain high Zn concentrations in soil solutions for an extended period of time whereas solubility of Zn in soil solution from ZnSO_4 and ZnEDTA decreased with time. In addition, ZnS is a less costly source of Zn fertilizer than either ZnSO_4 or ZnEDTA.

d. Reaction Products and Solubility of $\text{ZnSO}_4 + \text{NH}_4\text{H}_2\text{PO}_4$ Banded in Newdale CL and Lakeland SiL.

Zinc orthophosphate ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) was detected in the Newdale soil treated with ZnSO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ at all incubation durations and was the only reaction product detected. In the Lakeland soil, however, NH_4ZnPO_4 and ZnCO_3 were identified in addition to $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Table 16). These results agreed with those of Dhillon *et al.* (1975), Jones (1936) and Hossner and Blanchar (1969) who indicated that ZnNH_4PO_4 and $\text{Zn}_3(\text{PO}_4)_2$ were probable reaction products when Zn and P were applied simultaneously in a band.

A large portion of the applied fertilizer mixture remained at the site of addition even after 32 weeks of incubation. The portion which did not move into the soil was x-rayed and identified as $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ for both soils. Since that was the case even after two weeks of incubation, it may be deduced that most of the Zn reacted with phosphate in the fertilizer band prior to diffusing into the soil.

Zinc concentrations decreased with time in both soil solutions (Figure 9) whereas soil pH increased (Table 17). Since the reaction

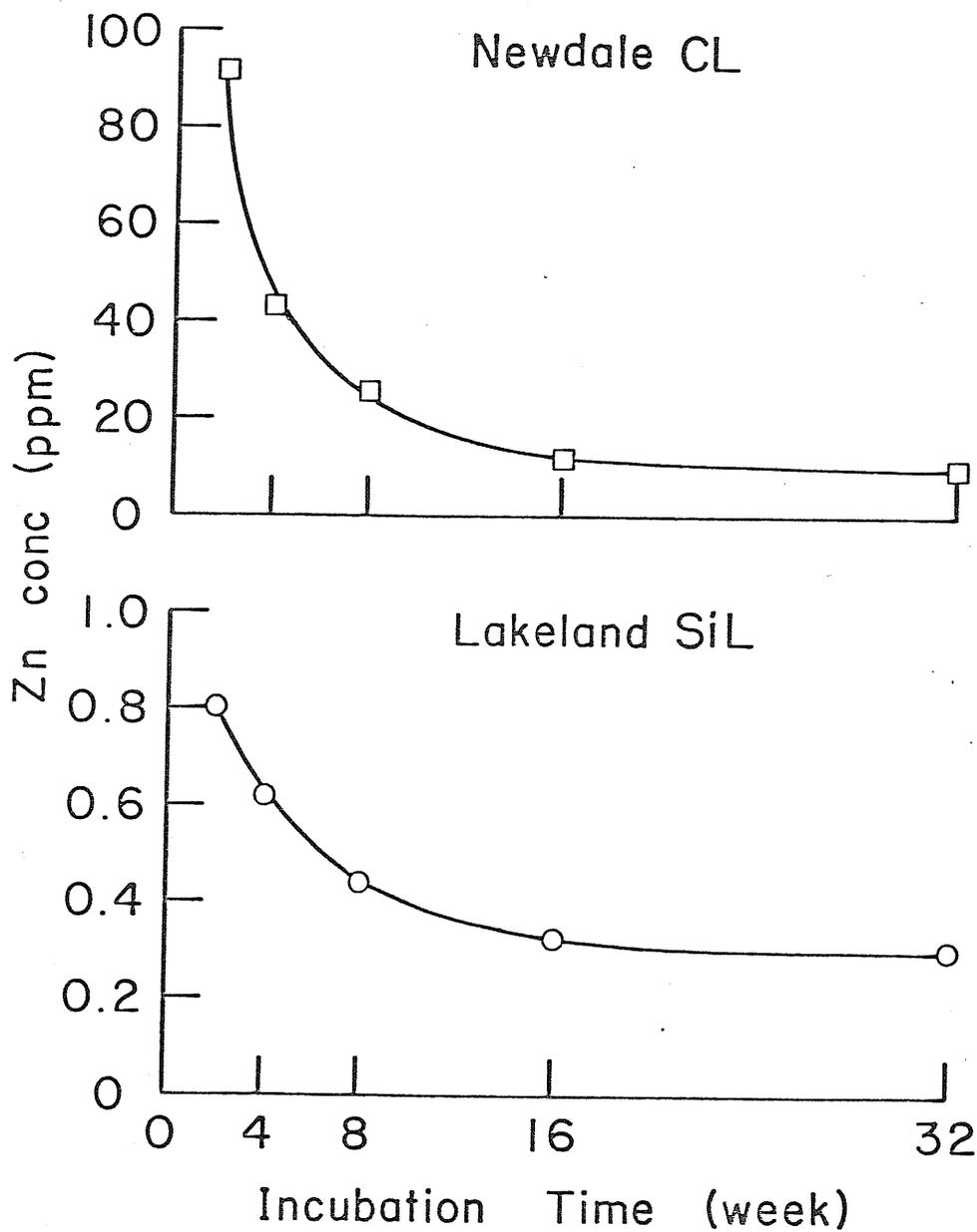


Figure 9. Zinc Concentrations in Water-extracts of Soils Banded with $ZnSO_4$ Plus $NH_4H_2PO_4$.

products, particularly $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, persisted in both soils for the total incubation period of 32 weeks, it may be concluded that decreases in Zn concentration in both soil solutions was due primarily to increasing pH. Zinc concentrations in the Newdale soil solution were about 100 fold higher than in the Lakeland soil (Figure 9). This was probably due to the large difference in pH between the two soils (Table 17). Decreases in Zn concentration with time were initially sharp in both soil solutions. However, after eight weeks of incubation zinc concentration in the soil solutions became relatively constant with time.

Concentration of Zn in a solution in equilibrium with pure solid phase $\text{Zn}_3(\text{PO}_4)_2$ is governed only by the pH of the system. However, application of orthophosphates to soils results in formation of various phosphate compounds. Racz (1966) identified $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ in some Manitoba soils treated with orthophosphate. The concentration of phosphorus in soil solution would be governed by the most soluble compound, such as $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$. The presence of phosphate ions from the dissolution of the calcium and magnesium phosphates would affect the solubility of $\text{Zn}_3(\text{PO}_4)_2$ through the common ion effect. Due to the common ion effect, calculation of Zn solubility in soils treated with both Zn and P without knowing the concentrations of the various phosphate species was not possible.

It is interesting to note the concentrations of Zn in the solution of soils treated with both Zn and P were much less than for the soils treated only with Zn (Figures 6 and 9). This indicates that phosphate fertilizers applied with Zn fertilizers such as ZnSO_4 may decrease the solubility of both Zn and P. However, although depression in Zn availability occurred in these experiments, concentration of Zn in solution

of soils treated with both Zn and p were still much greater than untreated soils (Figures 9 and 14).

V. SUMMARY AND CONCLUSIONS

Sphalerite (ZnS), hemimorphite ($\text{Zn}_4(\text{OH})_2\text{SiO}_7 \cdot \text{H}_2\text{O}$) and willomite (Zn_2SiO_2) have been postulated to occur in soils as native Zn compounds. In order to test this postulation, Zn concentration in saturated solutions of these minerals adjusted to varying pH values was compared with the concentration of Zn in soil solutions adjusted to equivalent pH values. Concentration of Zn in solution from these minerals particularly hemimorphite and willomite were much greater than the concentration of Zn in soil solutions indicating that these minerals were too soluble to persist in soils as solid phases. Although the solubility of sphalerite was much less than that of willomite and hemimorphite, the solubility of sphalerite was still much greater than that of soil Zn. Sphalerite is also unstable under the oxidizing conditions normally prevailing in soils and converts to more soluble compounds upon oxidation. Furthermore, when ZnS was banded in soils, Zn concentration in solution of all the soils increased. Thus it appears that ZnS does not exist as a solid phase in soil.

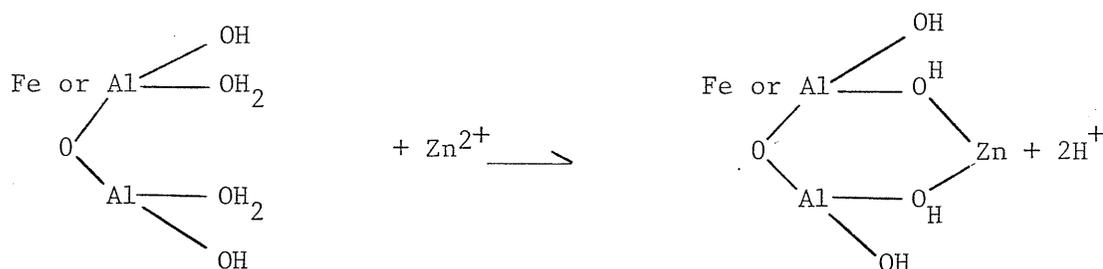
Acidification of the soils resulted in the release of both Fe and Zn. Release of relatively large amounts of Zn at about the same pH as Fe suggested a possible association of Zn with Fe oxides or other oxides in the soil. In order to investigate the association of Zn with these oxides, eight soils in Manitoba, varying in texture and in amount of clay movement were analyzed. Percent sand, silt and clay as well as total content of Fe, Al, Mn and Zn were measured in every horizon of each soil. Statistical analyses were conducted to correlate total Fe, Al, Mn and Zn concentrations and particle size distribution. There were highly significant correlations between total Fe, Al or clay content and Zn concentration ($r = 0.86, 0.95$ and 0.91 , respectively). Zinc was

also significantly correlated with Fe and Al concentration when the clay size fraction was very low or absent.

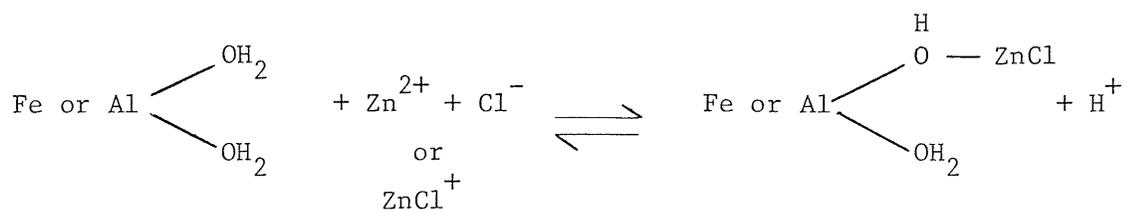
Similarities between concentration versus pH diagrams for Zn and Fe suggested an association between Zn and oxides of Fe. The statistical correlation analysis supported this hypothesis. Nevertheless, a more direct approach was required to confirm the above findings. The more direct approach included two extraction methods both of which were conducted on the four soils studied in the acidification experiment. Exchangeable Zn, Fe and Al were measured after extraction with a solution of 1 M KCl + 0.01 M Na₂EDTA. Except for the Plum Ridge soil, the exchangeable Zn was small and constituted only a small proportion of the total soil Zn concentration (5.3% in Stockton, 2.6% in Newdale, 1.1% in Lakeland and 26% in the Plum Ridge soil). The soils were extracted with a solution of oxalic acid + NH₄-oxalate (pH = 3) in a second study. Oxalate extraction removed amorphous inorganic Fe and Al and organic complexed Fe and Al from soils. Large quantities of total Zn (61% in Stockton, 45% in Newdale, 51% in Lakeland and 71% in the Plum Ridge soil) were extracted along with Fe and Al indicating, once more that Zn was in some manner associated with oxides of Fe and Al in the soil.

Following the establishment of an association between Zn and oxides of Fe and Al in soils, studies were conducted to investigate the mechanism(s) of this association. The retention of Zn by oxides of Fe and Al (Fe₂O₃ and Al₂O₃) was studied in aqueous nonbuffered systems. Samples of finely ground Fe₂O₃ and Al₂O₃ were suspended in 80 ppm Zn solutions adjusted to pH values varying from 6.0 to 7.0. The suspension pH's were measured after 24 hours equilibration and Zn concentrations were measured in the filtrates. Adsorption of Zn by hydrated Al₂O₃ and Fe₂O₃ was highly pH dependent and increased markedly with increasing

pH. Fe_2O_3 had a higher Zn adsorption capacity at equivalent pH values than Al_2O_3 . An interesting aspect of Zn adsorption was the concomitant release of H^+ ion upon Zn adsorption. The molar ratio of H^+ release to Zn adsorbed increased with pH from 1.53 to 1.96 with an average of 1.73. In other words, an average of 1.73 moles of H^+ was released for one mole of Zn adsorbed. The fact that this value was less than two indicated that another anion was counter adsorbed. A small and uniform amount of Cl was found to be adsorbed at all the pH values. Decrease with pH of Cl to Zn molar ratio, coupled with the decrease in exchangeability of adsorbed Zn with Ba^{2+} provided evidence for postulation of two mechanisms for Zn adsorption, namely, specific and nonspecific Zn adsorption. The specific adsorption involved adsorption of Zn^{2+} species and release of two H^+ ions for each mole of Zn adsorbed. This portion was not exchangeable with Ba^{2+} and accounted for 60 to 90% of total Zn adsorption. A binding mechanism for specifically adsorbed Zn was postulated and was as follows:



The nonspecific adsorption of Zn involved adsorption of ZnCl^+ or Zn^{2+} plus Cl^- , probably onto the same site and the release of one H^+ ion for each mole of Zn adsorbed. This portion of Zn adsorption accounted for 10 to 40% of total Zn adsorbed and decreased markedly with increasing pH. The binding mechanism for nonspecifically adsorbed Zn was thought to be a monodentate type of bonding and could be represented as:



As was demonstrated above, surface aqua ($-\text{OH}_2$) and hydroxo ($-\text{OH}$) groups were believed to be involved in Zn adsorption. Lack of reversibility as well as increase in adsorption with increase in pH of the medium are both characteristics of Zn fixation in soils. Thus, it was speculated that specific adsorption of Zn may be responsible, at least to some extent, for frequently reported fixation and unavailability of added Zn to soils.

The role of Fe and Al oxides in controlling Zn solubility in soils and mechanism of adsorption or fixation of added Zn was partially investigated. However, when very large amounts of Zn are applied to soil or when microregions in soil are saturated with Zn, such as a band or point source of application, formation of new Zn solid phases, in addition to adsorption and fixation, are very likely. The identification of these new phases and studies of their chemical properties such as solubility and stability are very important in formulating agronomic practices for Zn fertilizer application. Therefore, a reaction product study using four Zn compounds and four soils was conducted. ZnSO_4 , ZnEDTA, ZnS and ZnSO_4 plus $\text{NH}_4\text{H}_2\text{PO}_4$ were banded in Stockton, Newdale, Lakeland and Plum Ridge soils and incubated for 2, 4, 8, 16 or 32 weeks. The solid-phase Zn compounds formed in soils were identified using x-ray diffraction analysis. The solubility of Zn in soil adjacent to the fertilizer band was determined by measuring the Zn concentration in soil-water extracts. The reaction product in the non-calcareous Newdale soil treated with ZnSO_4 was $\text{Zn}(\text{OH})_2$ which was metastable and persisted for only a few weeks. ZnSO_4 was precipitated as ZnCO_3 in the calcareous

Lakeland soil and as $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ in the calcareous Plum Ridge soil. Both these compounds persisted for 32 weeks or more. No solid-phase reaction products were detected in the Stockton soil treated with ZnSO_4 . This was attributed to the low pH of the fertilizer band and/or to the low concentration of the reaction product formed. No solid-phase crystalline reaction products were detected when ZnEDTA was banded in the soils. This was probably caused by Zn persisting in the soil as ZnEDTA resulting in low concentrations of ionic Zn in soil solution and therefore little or no precipitation of Zn compounds near the ZnEDTA band. ZnS, a sparingly soluble salt, dissolved very slowly such that ZnS persisted in the soils at all sampling dates. However, x-ray analysis showed the formation of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and, $\text{Ca}[\text{Zn}(\text{OH})_3]_2 \cdot 2\text{H}_2\text{O}$ in the Plum Ridge soil after 32 weeks of incubation. $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ was detected in the Newdale soil treated with ZnSO_4 plus $\text{NH}_4\text{H}_2\text{PO}_4$ at all incubation times and was the only reaction product detected. In the Lakeland soil, however, NH_4ZnPO_4 and ZnCO_3 were identified in addition to $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.

Concentrations of Zn in water-extracts of the Stockton, Newdale and Plum Ridge soils treated with ZnSO_4 decreased with time, with the largest decrease in solubility occurring during the first two to eight weeks of incubation. The concentration of Zn from applied ZnSO_4 in the calcareous soils was less than in the noncalcareous soils. Concentrations of Zn in extracts of soils treated with ZnEDTA were much higher than concentrations of Zn in extracts of soils treated with ZnSO_4 . Concentration of Zn in solution of soils treated with ZnS were very low as compared to soils treated with ZnSO_4 or ZnEDTA. Nevertheless, it was at least tenfold greater than for untreated soils. Zinc concentration in the soils treated with ZnSO_4 and ZnEDTA decreased with time whereas

Zn concentration in extracts of soils treated with ZnS increased with time. This was attributed to the partial oxidation of ZnS to less sparingly soluble compounds. It is interesting to note that the concentration of Zn in the solution of soils treated with both Zn and phosphate were much less than for soils treated only with Zn. However, although the addition of phosphate decreased Zn solubility, concentrations of Zn in solutions of soils treated with both Zn and P were still much greater than in untreated soils. The concentration of Zn in all soils treated with Zn were greater than in untreated soils indicating $ZnSO_4$, ZnS, or ZnEDTA would be good Zn fertilizers when banded in soils.

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