

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

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Doctor of Philosophy

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by

Mahmoud Kalbasi-Ashtari

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## ABSTRACT

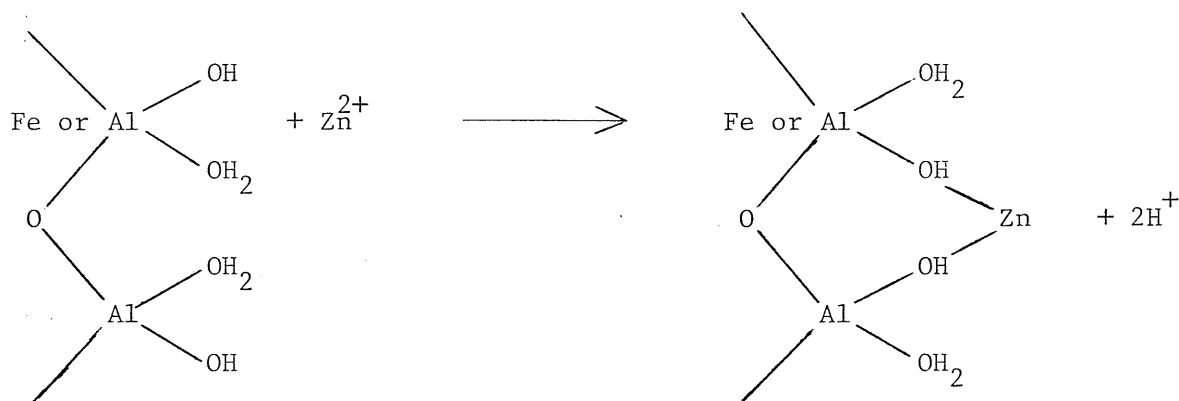
Zinc concentrations in soil solutions of four soils acidified to various pH values were compared with the concentration of Zn from sphalerite ( $\text{ZnS}$ ), hemimorphite ( $\text{Zn}_4(\text{OH})_2\text{SiO}_7 \cdot \text{H}_2\text{O}$ ) and willomite ( $\text{Zn}_2\text{SiO}_2$ ). Concentration of 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.

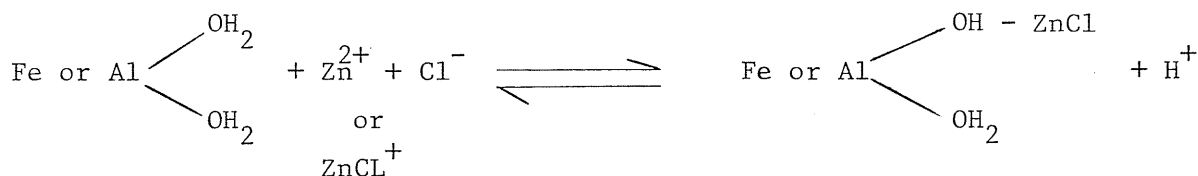
The soils used in the acidification experiment were successively extracted by an oxalate solution. Large quantities of Zn (45 to 71% of total Zn content) were extracted along with the amorphous and organic complexed Fe and Al from the soils indicating, once again, that Zn was in some manner associated 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  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  from aqueous solutions was studied. Adsorption of Zn by hydrated  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  was highly pH dependent and increased markedly with increasing pH.  $\text{Fe}_2\text{O}_3$  had a higher Zn adsorption capacity, at equivalent pH values than  $\text{Al}_2\text{O}_3$ . Hydrogen

ions were released upon adsorption of Zn on the surface of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . The molar ratio of  $\text{H}^+$  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  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  was categorized into specific and nonspecific adsorption depending upon reversibility (exchangeability with  $\text{Ba}^{2+}$ ) and two mechanisms of adsorption, one with and one without Cl adsorption were postulated. The specific adsorption involved adsorption of  $\text{Zn}^{2+}$  and release of two  $\text{H}^+$  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  $\text{ZnCl}^+$  or  $\text{Zn}^{2+}$  plus  $\text{Cl}^-$  and the release of one  $\text{H}^+$  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  $\text{H}_2\text{S}$  actually found in the atmosphere are high enough to engender control of  $\text{Zn}^{2+}$  in the soil solution of aerated soils by  $\text{ZnS}$ . However, these results contradict findings of McGregor (1972) who reported that applied  $\text{ZnS}$  maintained a higher concentration of  $\text{Zn}^{2+}$  in soil solution than found for untreated soils indicating that  $\text{ZnS}$  did not govern the concentration of  $\text{Zn}^{2+}$  in soil solution of these soils.

Weathering of Zn minerals releases  $\text{Zn}^{2+}$  into solution. Unlike  $\text{Cu}^{2+}$ , 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  $\text{ZnO}$  (Zincite), or  $\text{ZnCO}_3$ , resulting from reactions of  $\text{Zn}^{2+}$  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,  $\text{Zn}(\text{OH})_2$  may precipitate if the concentration of  $\text{Zn}^{2+}$  is high. But, such high  $\text{Zn}^{2+}$  concentrations seldom occur. The minimum solubility of  $\text{Zn}(\text{OH})_2$  occurs at pH 9.5. It dissolves at higher pH values to form zincate ions,  $\text{Zn}(\text{OH})_4^{2-}$ . The precipitated hydroxide is unstable, decomposing under both natural and laboratory conditions to zincite,  $\text{ZnO}$ . This compound is rare as a mineral, however, because usually enough carbonate or silicate is present to precipitate Zn as  $\text{ZnCO}_3$  (smithsonite),  $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$  (hemimorphite) or, at higher temperatures,  $\text{Zn}_2\text{SiO}_4$  (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,  $\text{ZnSiO}_3$ , pH and Zn concentration have to be almost as high as for precipitation of  $\text{Zn(OH)}_2$ . 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  $\text{ZnCO}_3$ ,  $\text{Zn(OH)}_2$  and  $\text{ZnSiO}_3$  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  $\text{Fe}_2\text{O}_3$ , 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  $\text{ZnSiO}_3$  phase. The absence of  $\text{ZnSiO}_3$  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  $\text{NH}_4^+$ . 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  $\text{ZnOH}^+$ ,  $\text{ZnCl}^+$ ,  $\text{Zn}(\text{CH}_3\text{Coo})_2$ ..... 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  $\text{ZnCl}^+$  nor  $\text{ZnAc}^+$  ion adsorption by bentonite. However, vermiculite expanded somewhat which was attributed to the adsorption of  $\text{ZnOH}^+$  ions. Differential thermal analysis confirmed that there was no appreciable  $\text{ZnAc}^+$  ion adsorption on bentonite and vermiculite. Also, chloride concentration data confirmed that there was no  $\text{ZnCl}^+$  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  $\text{Zn}^{2+}$  might be fixed in holes normally occupied by  $\text{Al}^{3+}$  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  $\text{NH}_4^+$ -exchange capacity, under alkaline conditions, to the precipitation of  $\text{Cu(OH)}_2$  and  $\text{Zn(OH)}_2$ . Under conditions in which the pH of the equilibrium solution was too acid for the formation of  $\text{Zn(OH)}_2$  or  $\text{Cu(OH)}_2$ , the amount of Cu and Zn retained by H-montmorillonite was similar for the  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  salts and equal to the cation exchange capacity as measured with  $\text{NH}_4^+$ . 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  $\text{NH}_4^+$ -exchange capacity was also observed by Misra and Tiwari (1966) when the