MOVEMENT AND ADSORPTION OF ZINC BY A WISNER SILTY CLAY LOAM SOIL

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
BOB G. VOLK
1970

This is to certify that the

thesis entitled
MOVEMENT AND ADSORPTION OF ZINC
BY A WISNER SILTY CLAY LOAM SOIL

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Bob G. Volk

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Boyd G. Ellis
Major professor

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MOVEMENT AND ADSORPTION OF ZINC BY A WISNER SILTY CLAY LOAM SOIL

By

Bob G. Volk

AN ABSTRACT OF A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
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1970

ABSTRACT

MOVEMENT AND ADSORPTION OF ZINC BY A
WISNER SILTY CLAY LOAM SOIL

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Bob G. Volk

A Wisner silty clay loam soil was selected for study due to its extreme Zn deficiency for several field crops. Very little work has been conducted on the chemistry of Zn native to the soil or on the fate of Zn after it has been applied to the soil in fertilizers.

The first objective was to determine the relationship of pH, time of soil contact, and temperature of incubation on the relative movement of Zn carriers. The second objective was to determine the maximum amount of Zn that the Wisner soil can retain, bonding energies of the soil for Zn, and the stability of these metal soil relationships. The final objective was to study effects of CO_2 equilibrium levels on controlling the solubility of Zn in the soil solution.

Movement of Zn applied as $^{65}ZnSO_4$, $^{65}ZnEDTA$, and $^{65}ZnNTA$ under the force of leaching was examined in a soil column experiment. Variables studied were soil pH and time and temperature of incubation of Zn carrier with soil.

Results indicated that: 1) Zn from $ZnSO_4$ moved very little (less than 10 mm) in the soil columns; 2) neither temperature of incubation (5 - 35 C) nor time of incubation (0 - 28 days) produced a significant effect of movement of any Zn carrier; 3) at a soil pH of 3.65, Zn as ZnNTA was much more mobile than Zn as ZnEDTA, (ZnEDTA appeared to be almost completely dissociated at this pH); and 4) Zn as either ZnEDTA or ZnNTA was mobile at pH's of 6.3, 7.8, and 8.3 but the EDTA form was more mobile.

Stability constants and adsorption isotherms were determined for a Zn-clay and a Zn-H_2O_2 treated clay. Using an ion exchange resin method with ^{65}Zn to determine stability constants, it was found that organic matter present increased stability constant (log K) values from 2.62 to 3.06 at pH 3.5 - 4.0 and 3.22 to 3.48 at pH's 4.5 - 5.0. It was concluded from Langmuir adsorption isotherms plots that: 1) H_2O_2 treated soil has a higher bonding energy for Zn than untreated soil and; 2) adsorption maximums were 2.76 to 5.20 me/100gm for the untreated soil and 0.31 me/100gm for the H_2O_2 treated soil.

Experiments were conducted by equilibrating ZnEDTA with a Wisner silty clay loam soil with pH's adjusted from 6.88 to 8.06. Carbon dioxide concentrations of 0.03, 0.3, and 3.0% were bubbled through the soils until equilibrium was reached. Little influence of CO_2 level on Zn in solution was found. 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. No one compound has yet been found to control Zn in soil solutions.

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To SHARI

This thesis is dedicated to my wife for without her inspiration, unfailing interest, and patience, this study could not have been completed.

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INTRODUCTION

Maximum plant growth can only occur if all essential nutrients are present in ample concentrations. The role of micronutrients in plant nutrition has been increasingly emphasized over the last few years. As early as the 1920's, Zn was recommended for field crops and fruit trees; however, only since 1960 has much emphasis been placed on Zn fertilization. Higher plants such as corn, soybeans, navy or pea beans, and many vegetables have shown an absolute requirement for Zn in Michigan as well as in other states. Most studies on Zn deficiency have been devoted to determining the effectiveness of various Zn fertilizers, possible interactions of Zn with other ions, and the developing of effective methods for delineating Zn deficiencies in plants or in the soil. Very little work has been conducted on the chemistry of Zn native to the soil or on the fate of Zn after it has been applied to the soil in fertilizers.

The Wisner silty clay loam soil in Michigan has been associated with extreme Zn deficiency for several field crops. At one location in Saginaw county, pea beans (Sanilac variety) will not grow on this soil without applications of Zn. Even though total analysis show as much as 40 ppm Zn in

this soil, the addition of just 1.5 ppm Zn will eliminate Zn deficiency during a growing season. Addition of 12.5 ppm Zn in a broadcast application has been shown to eliminate Zn deficiency for at least five years. This investigation was conducted to create overall knowledge concerning possible factors affecting this lack of Zn availability on a Wisner silty clay loam soil.

The first objective was to determine the relationship of pH, time of soil contact, and temperature of incubation to the relative movement of Zn chelates in artificially prepared soil columns. The second objective was to determine the maximum amount of Zn that the Wisner soil can retain, bonding energies of the soil for Zn, and the stability of these metal soil relationships. The final objective was to study effects of CO_2 equilibrium levels on controlling the solubility of Zn in the soil solution.

LITERATURE REVIEW

Movement of Zinc

There are two basic forms of Zn applied to soils to correct Zn deficiency--inorganic Zn, which is generally applied as $ZnSO_4$ or ZnO, and organic bound Zn, which is generally applied as ZnEDTA (ethlenediamine tetraacetic acid) or ZnNTA (nitrilotriacetic acid).

Jurinak and Thorne (1955) studied the movement of various ionic forms of Zn in columns of calcareous, clay soil. Zn was applied as $ZnCl_2$, a $Zn-NH_3$ complex, and a zincate anion. After large quantities of tap water were leached through the soil columns, they found a maximum movement of 3 cm for all forms of Zn. Zn applied as $ZnCl_2$ moved a maximum of only 2 cm. They attributed these slight movement differences to: (1) a possible reaction with the $CaCO_3$; (2) neutralization of the hydroxyl ions which would bring instability to the complex; and (3) a greater sorption bond between Zn and soil than between Zn and the coordinated hydroxyl ions and water molecules, which would cause Zn adsorption by the soil. Brown, Krantz, and Martin (1962) also showed that Zn applied as ZnO or $ZnSO_4$ did not move appreciably in columns of sandy loam or silt loam soils

even when heavily leached with water. Barrows, Neff and Gammon (1960), however, found that surface applied $ZnSO_4$ was leached to a depth of 46 cm in either a Lakeland fine sand or a Red Bay fine sandy loam. Movement of applied Zn was inversely related to the soil P content and organic matter and was also affected by the type and amount of clay minerals in the soil. Vermiculites seemed to decrease mobility and kaolinite allowed more Zn movement.

Mortvedt and Giordano (1967) found that Zn movement from fertilizer granules varied from 0.5 to 2.0 cm with various fertilizer carriers. The mean movement of Zn from the fertilizer granules did not exceed 2.0 cm in any case. Other studies by Giordano and Mortvedt (1966) and Alben (1955) have also indicated that inorganic Zn is essentially immobile in soils.

On the other hand, chelated Zn is less readily inactivated in most soils. A relatively small amount of chelated metal is normally needed to supply deficient plants on most soils, Alben (1955). The effectiveness of chelates as metal carriers in soils depends on their ability to keep these metals in soluble, mobile forms. To do this, the ligand must remain in solution and continue to complex the applied metal ion, Norvell and Lindsay (1969); Hodgson (1969); and Brown (1969).

Adsorption by soil particles is the primary cause of the loss of EDTA from a soil solution. The adsorption of EDTA onto soils from ZnEDTA application is less serious

than from FeEDTA, Anderson (1964); Wallace and Lunt (1956). But in most soils the majority of EDTA remains in solution at least several weeks and probably much longer, Norvell and Lindsay (1969). Wallihan and Heymann-Herschberg (1956) found that ZnEDTA penetrated the soil and moved much faster than $ZnCl_2$.

Hodgson, Lindsay and Kemper (1967) conducted an experiment whereby Zn was allowed to diffuse from a $ZnCO_3$ precipitate through an agar-agar gel to a stream of continuously flowing water. In one treatment, part of the agar-agar was replaced by Ca-polygalacturonate to incorporate fixed negative charges in the gel in the form of carboxyl groups. In a second treatment all phases of the system were kept in equilibrium with $CaCO_3$. The transport of Zn in the system was increased more by the mobile complexing agent than it was by the fixed charges.

Soil temperature has been found to affect Zn availability to the plant. Two groups of workers have found slow growth related to Zn deficiency several weeks after emergence when the soil was wet and cold, Bauer and Lindsay (1965); Burleson et al. (1961). Decreasing soil temperature from 75° to 50° F decreased Zn content from 310 to 73 μg per pot and decreased yields of pea beans, Ellis et al. (1964). Work by Martin et al. (1965) also showed that a decrease in air temperature resulted in Zn deficiency symptoms on tomatoes. Langin et al. (1962) attributed Zn deficiency in cold, wet growing conditions to: (1) decreased

Zn availability as such, (2) decreased microbial activity, (3) restricted root growth and development. No work was found relating Zn movement in soil to temperature.

The time effects of Zn-soil contact were studied by Giordano and Mortvedt (1966) who found that movement of Zn from ZnO or $ZnSO_4$ extended to 1 cm after one day but did not move beyond this distance even after four weeks. A later study by Mortvedt and Giordano (1967) indicated that most Zn movement from P carriers occurred during the first week, except in an extremely acid soil. They also found that the amount of Zn recovered from limed soil less than 0.5 cm from the granule by extraction with 2N $MgCl_2$, varied with the carrier after one week, but was similar for all carriers after 8 weeks. In general, when granular carriers containing Zn are applied to soil, the volume of Zn-affected soil is related to the number of granules and the distance of Zn movement of the individual granules. Reactions of Zn with other components of the macronutrient carrier may result in the formation of insoluble compounds which would restrict Zn movement from the granule.

Adsorption of Zinc

The clay fraction in soils exerts an important influence on the availability of Zn. Elgabaly (1950) called the fraction of Zn that was non-exchangeable with ammonium acetate "fixed zinc" and stated that Zn can replace Mg and Al in

the octahedral position of many layer silicates. Earlier Elgabaly et al. (1943) stated that Zn-clay has a mosaic surface capable of independent cation and anion exchange, and that fixed Zn is inside empty oxygen and hydroxyl positions of the octahedral layer of montmorillonite. They also found that Zn was adsorbed partly as a monovalent complex ion after which it became part of the inner electrical double layer. De Mumbrum and Jackson (1956) determined that Zn reacted with the octahedral hydroxide in layer silicates but did not react with kaolinite. Jurinak and Thorne (1955) proposed that the unavailability of Zn was from its chemical nature because Zn forms many chemical and clay adsorption complexes.

Hibbard (1940) suggested that acid extractable Zn may be held in the crystal lattice of the clay minerals and that only the H ion would be small enough to enter and replace it. Nelson and Melstead (1955) found that with symmetry additions of Zn to a H soil system, practically all of the Zn adsorbed by the soil was replaceable with NH_4OAc. The longer the period of time of contact between the Zn and the Ca-clay, the less was the Zn removed by extraction. They also found that after Zn adsorption had occurred, the exchange capacity was not altered, showing that Zn was not occupying cation exchange positions nor being adsorbed in the double layer as a complex ion.

Mangaroo et al. (1965) found that pretreatment of clays with Ca, K, and Cu solutions resulted in Zn adsorption in the order: K-clay $>$ Ca-clay $>$ Cu-clay. Ammonium acetate

could replace Zn added to a H saturated soil system but could only partially replace Zn added to a Ca saturated soil system. Work by Nelson and Melstead (1955) indicated the amount of Zn extracted with NH_4OAc decreased with time when Zn was applied to a Ca saturated soil.

Jurinak and Bauer (1956) in studying the adsorption of $ZnCl_2$ by calcite, dolomite, and Ca substituted magnesite crystals reported that approximately ten percent of the adsorption sites available on calcite are occupied by Zn when the equilibrium Zn concentration is 9×10^{-7} M at 25° C. The Ca magnesite shows a somewhat greater affinity for Zn ions than calcite, while dolomite was intermediate. The possibility that lime minerals in the soil may constitute a potential adsorptive phase for certain cations was recognized by Leeper (1952) who postulated that, in a calcareous soil, $CaCO_3$ may be an important adsorbent of heavy metals. Canals et al. (1949) have shown that Zn is adsorbed from solution by $CaCO_3$. They found that when the temperature was raised from 20°C to 100°C the adsorption of Zn by $CaCO_3$ was greatly increased.

Considerable work has been done on the interaction of organic matter and Zn in the soil. Zn deficiencies have been reported on soils to which high levels of organic materials have been added, Thorne and Wann (1950). DeRemer et al. (1964) found that the recovery of Zn added to a soil was decreased when the soil was incubated with sugar beet tops. It was concluded that Zn is immobilized by

microorganisms during decomposition of organic materials. Ark (1936) reported that Zn deficient soils which were steam sterilized released sufficient Zn to correct the deficiency--implying microbial fixation. It should be noted here that steam sterilization will cause the reduction of organic matter to colloidal forms which might complex Zn, keeping it in an available form.

Many workers have indicated that some type of coordination compound exists between the micronutrients and soil organic matter, Bremner and Lees (1949); Lees (1950); Peech (1945). Investigations have led researchers to conclude that Zn deficiencies are caused by the formation of organic matter-Zn complexes. De Mumbrum and Jackson (1956); Miller and Ohlrogge (1958); and Hodgson et al. (1966) found that from 28 to 99 percent of the Zn in soil solution was complexed with organic matter.

Chelation in soil organic matter mainly involves the phenolic groups, Himes et al. (1963); Broadbent and Bradford (1952). According to Himes and Barber (1957) destruction of organic matter by hydrogen peroxide treatments destroyed the Zn-chelating ability of the carboxyl and phenolic groups. Infrared techniques by Randhawa and Broadbent (1965) indicated that Zn saturation of peat fractions resulted in numerous shifts in the double bond region, showing a chelation with C=O and N=O groupings. According to Bould (1963) Zn is adsorbed as a divalent cation on clays or complexed by organic matter after release from the minerals. Mortensen

(1963) concluded that soil organic matter complexes Zn by ion exchange, surface absorption, chelation, and peptidization. He also stated that hydroxyl, carboxyl, and amide groups of soil organic matter are probably responsible for chelating metals.

Soil Reaction

In considering all the factors related to Zn chemistry in the soil, pH is one of the most important, Barrows and Gammon (1960). As the pH increases due to liming, Zn availability to plants decreases, Boawn et al. (1960); Camp (1945); Lott (1938); Thorne (1957); Wear (1956). The optimum availability of Zn to plants was reported by Camp (1945) to be in the pH range of 6.0 to 6.5. Non-chelated Zn was practically unextractable at pH 7.0 to 8.5 using the dithizone extractant, Shaw and Dean (1951). Jurinak and Thorne (1955) showed Zn solubility in Na and K bentonite clay systems to be lowest between pH 5.5 and 6.7, but increased at higher pH values. Solubility of Zn in a Ca bentonite system did not increase at higher pH values and was lowest at pH 7.6. Differential solubility of alkali zincates and of Ca zincate was proposed as possible solutions to the problem. Ca ions have been reported to have no effect on Zn availability, Viets et al. (1957); Wear (1956).

Randhawa and Broadbent (1965) found that humic acid complexed very little Zn at pH values less than 3.6 but

complexing ability increased rapidly with an increasing hydroxyl ion concentration up to pH 8.5. Water-soluble chelating agents in organic material were found by Miller and Ohlrogge (1958) to complex more Zn at higher pH's. Because of the basic properties of most ligands, they are usually associated with H ions over a fairly wide range. The formation of a metal chelate compound frequently involves a displacement of H ions from the ligand according to the following scheme:

$$M^{+n} + HA \longrightarrow MA^{n-1} + H^{+}$$

$$MA^{n-1} + HA \longrightarrow MA_2^{n-2} + H^{+}$$

By decreasing the pH of a soil or solution which contains the chelate, a dissociation of the metal complex will result through the reversal of the above reactions, Chabrek and Martell (1959).

The effect of pH probably results from the differences in solubility of the various pH dependent forms of Zn occurring in the soil, De Mumbrum and Jackson (1957); Elgabaly and Jenny (1943); Nelson and Melstead (1955); and Peech (1941).

Recently, Norvell and Lindsay (1969) found that when ZnEDTA was reacted with soils, the fraction of added EDTA that remained associated with Zn was pH dependent and reached a maximum near pH 6.7. Examination of their findings suggests that $ZnSiO_3$ in equilibrium with amorphous SiO_2

could account for the level of ZnEDTA remaining in solution at each pH. Similar studies with ZnDTPA (diethlenetriamine pentaacetic acid) also showed close correspondence between the observed and predicted levels of chelated Zn in solution. However, Norvell and Lindsay (1970) published a retraction of the above findings after discovering the solubility constant for $ZnSiO_3$ was in error. Their calculations now indicate that agreement between equilibrium levels of Zn in solution and $ZnSiO_3$ is only coincidence.

Adsorption Isotherms

The process by which atoms or molecules on one material become attached to the surface of another is called adsorption. Adsorption is a means of neutralizing or satisfying the forces of attraction that exist at a surface. The unfilled forces at the surface can be satisfied by the adsorption of atoms or molecules of another species. This reduces the attraction of the surface atoms or molecules of the solid or liquid toward its neighbors of the same kind, and reduces surface tension. Thus, the process of adsorption continues until the free surface energy of the system, due to the imbalance of surface forces, has reached a minimum value. Adsorption of a gas may be a relatively weak physical adsorption or a strong interaction of a chemical nature--called chemisorption. Van der Waals forces are considered to be responsible for physical adsorption while chemisorption involves an energy of activation and heats

of adsorption on the order of chemical reactions. The forces that are responsible for adsorption from solutions have been discussed by Giles (1959). They may be classified as (a) non-polar Van der Waals attraction, (b) formation of hydrogen bonds, (c) ion exchange, and (d) covalent bond formation.

The adsorption equation developed by Langmuir (1919) and (1940) was one of the first and most important equations based on theory. Langmuir postulated that adsorption occurred as a monomolecular film. He envisioned a dynamic equilibrium such that the rate of adsorption equaled the rate of desorption. Fowler (1935) has emphasized that three important conditions are implied in the kinetic and statistical derivations of the Langmuir isotherm. These are the following:

(a) Adsorption is localized and takes place only through collisions of gas molecules with vacant sites.

(b) Each site can accommodate one and only one adsorbed particle.

(c) The energy of an adsorbed particle is the same at any site on the surface and is independent of the presence or absence of nearby adsorbed molecules.

One form of the Langmuir equation is:

$$\theta = \frac{K_2 P}{K_1 + K_2 P} \qquad \text{or} \qquad [1]$$

$$\theta = \frac{KP}{1 + KP} \qquad [2]$$

where θ is the fraction of the surface covered, K_1 and K_2 are proportionality constants, P is the pressure of the gas, and K is equal to $\frac{K_2}{K_1}$ and is sometimes called the adsorption coefficient. The simple Langmuir isotherm gives two limiting types of behavior. At very low pressures, where $KP \ll 1$, the isotherm reduces to $\theta = KP$ which corresponds to the initial steep rise of the sorption curve, and at very high pressures, where $KP \gg 1$, θ approaches the constant maximum value of unity.

The amount of gas adsorbed (X/m) at a pressure of P and the amount of gas (b) needed for monolayer formation are related to θ by:

$$\frac{X/m}{b} = \theta \qquad [3]$$

and equation [2] becomes:

$$X/m = \frac{KbP}{1 + KP} \qquad [4]$$

upon rearrangement gives:

$$\frac{P}{X/m} = \frac{1}{Kb} + \frac{P}{b} \qquad [5]$$

If the data agrees with the Langmuir theory, plotting this equation will give a straight line with the intercept 1/Kb and the slope with the constant 1/b. This equation can apply to adsorption from a solution, but the theoretical treatment is not well developed, Boyd et al. (1947) and Graham (1953). For liquid solutions the gas pressure term

P is replaced by a concentration term (C) giving:

$$\frac{C}{X/m} = \frac{1}{Kb} + \frac{C}{b} \qquad [6]$$

Using the equation - F^{o} = RT ln K, the standard free energy of adsorption may be calculated, which constitutes a measure of the strength of the adsorption bond.

In soils, use of adsorption isotherms has been restricted to mainly P adsorption. Langmuir isotherms have been applied very successfully to P adsorption on soil by Olsen and Watanbe (1957) and Fried and Shapiro (1956). Constants calculated from Langmuir isotherms have permitted a successful theoretical approach to some of the problems of P sorption in soils.

Use of isotherms for other elements has been extremely limited. Himes and Barber (1957) suggested that Langmuir adsorption equations could be successfully used for studying the retention of Zn by soil. Udo, Bohn and Tucker (Agronomy Abstracts, 1968) reported that at low Zn concentration, the Langmuir equation was followed. They found absorption capacities varied from 0.90 to 5.1 me/100g of calcareous Arizona soil compared to cation exchange capacities of 3.3 to 17.3 me/100g. Zn adsorption capacities were related to total surface area, organic matter, and quantity of $CaCO_3$ and clay in the soil.

Stability Constants

In general, the term "stability" describes the amount of association that occurs in solutions containing two or more component species in equilibrium. The more stable the resultant complex, the greater is the probability that association will occur under a given set of conditions. Ideally, stability constants should be true thermodynamic constants expressed in terms of the activities of the species in equilibrium. In practice, since it is often difficult or impossible to determine activities, concentrations are used instead.

In this equation:

$$K = \frac{(MCh_X)}{(M)(Ch)^x} \qquad [7]$$

(K) is an expression of the stability of the complex in solution,

(M) is the concentration of the metal ion,

(Ch) is the concentration of the complexing agent, and

(**x**) is the number of moles of the complexing agent which combines with one mole of metal ion to form the metal complex.

The principle of ion exchange equilibrium can be used to determine the stability constant of the complex formed. This determination is based on the fact that the quantity of metal bound to a known weight of resin at equilibrium is proportional to the concentration of free ions in solution.

If one assumes that only a single complex species occurs in appreciable concentrations, one can solve for the partition of this species between resin and solution. In other words, a stability constant (K) may be calculated from the formula:

$$K = \frac{P_o - q_B}{(q_B - P_1)Ch} \qquad [8]$$

where

P_o = the distribution ratio of the metal in the absence of ligand,

q_B = the distribution ratio of the metal in the presence of the ligand,

P_1 = the distribution ratio of the metal-clay complex between the resin and solution,

Ch = the ligand concentration in moles.

If the formula is arranged to the form of $\frac{P_o - q_B}{Ch} = K(q_B - P_1)$ then the stability constant can be determined from the slope of a line $\frac{P_o - q_B}{Ch}$ vs. q_B.

Chapter 11 of Rossotti and Rossotti (1961) gives a very comprehensive description and development of the above theory on stability constant determination by the ion exchange method.

A second method for determination of stability constants can also be used. The stability constant of the complex or complexes can be determined from the following

relationship given by Martell and Calvin (1952).

$$\log \left(\frac{\lambda_o}{\lambda} - 1\right) = \log K + x \log (Ch) \qquad [9]$$

In this equation K, Ch, and x are the same values as defined in equations [7] and [8].

λ_o = the distribution constant of the metal in the absence of ligand.

λ = the distribution constant of the metal in the presence of ligand.

The distribution constants, λ_o and λ are the coefficients by which the concentration of free ions or free plus complex ions in solution must be multiplied to obtain the quantity of that cation bound to a definite weight of cation resin at equilibrium. The slope and intercept of a graph $\log \left(\frac{\lambda_o}{\lambda} - 1\right)$ vs. log (Ch) are the values of x and log K, respectively.

Possible sources of error in stability constant determination include: (1) analytical, (2) adsorption of the ligand or complex species by the exchange resin and (3) two or more complexing agents or complex species being present.

If more than one complex species occurs in solution, the method of Fronaeus (pages 246 and 247 of Rossotti and Rossotti, 1961) may be used to calculate the various K values.

Almost all work on stability constants has been based on the organic fraction or constituents of the organic

fraction in the soil. Miller and Ohlrogge (1958); Randhawa and Broadbent (1965); and Schnitzer and Skinner (1966) have successfully used ion exchange equilibrium to determine stability constants for Zn-organic matter, Zn-fulvic, or Zn-humic acid preparations. Values obtained for stability constants ranged from 1.7 to 7.8 depending on the pH at which the constants were determined. Log K values for Zn-fulvic acid complexes reported by Schnitzer and Skinner (1966) were considerably lower than those reported by Randhawa and Broadbent (1965).

Himes and Barber (1957) used two methods for determination of the strength of bonding of Zn by soil organic matter. By assuming that only one type of adsorption site existed, they were able to construct a Langmuir type curve which could be extrapolated to give the concentration of the complexing sites. They were able to obtain stability constants of log K = 3.4 to 5.6 for a Zn-organic matter complex. By a second method, they found that the soil-Zn log K complex values were between 5.2 and 10.4.

MATERIALS AND METHODS

Soil Preparation for Zinc Chelate Movement

Bulk samples of a Wisner silty clay loam soil, pH 7.73, were ground to pass a 2 mm plastic sieve. A pH of 8.3 was obtained by adding small increments of saturated $Ca(OH)_2$ and allowing the moist soil samples to equilibrate over a period of several months. To achieve lower pH's, small portions of 0.5 N HCl were added and the soil allowed to come to equilibrium with the acid. In this manner, stable pH's of 6.3 and 3.64 were obtained. These values of pH were constant over several cycles of drying and rewetting.

Zn chelates (0.1 M) were prepared by mixing equal molar quantities of $ZnCl_2$ with either EDTA or NTA. During this procedure ^{65}Zn as $ZnCl_2$ was added to give a ^{65}Zn concentration of 10 μc/ml of solution. The prepared Wisner soil of various pH's was next moistened to slightly less than field capacity (15% moisture on an oven-dry basis) with appropriate amounts of the prepared ^{65}Zn chelate and well mixed. Beakers of these chelate treated soils were covered with parafilm and placed under various conditions of temperature and times of incubation. These beakers were aerated daily and kept at 15% moisture by distilled water additions.

Soil Column Preparation

Columns, manufactured from plexiglass, were constructed 7 x 7 cm square with a length of 20 cm. A hole was drilled in the flat base to allow water passage. Glass wool was placed in the bottom of the column followed by about 7 cm of fine sand, and about 7 cm of prepared soil. Approximately 650 gm of air-dry soil were required for the 7 cm depth. The soil was packed as uniformly as possible using a glass stirring rod to aid in removing air spaces in the soil. The top of the soil in the column was leveled using a rubber stopper as a tamp. Water was added to the soil until the water reached about $1\frac{1}{2}$ - 2 cm from the sand and then the soil column was allowed to equilibrate. After equilibrium the percent moisture was 14% in the soil. If the soil was kept at field capacity, 18%, it became difficult to handle by becoming extremely muddy.

After appropriate incubation time and temperature, 40 gm of treated soil were weighed and very carefully placed on top of the soil column previously prepared with the same soil except lacking the ^{65}Zn chelate. Great care was taken to make sure that the soil was placed in an even layer no more than 4 mm deep. After the ^{65}Zn chelate soil was added, the columns were counted for ^{65}Zn as described later. Twenty-five ml portions of distilled water were leached through the soil column every other day until a total of 125 ml had been added. Parafilm was used to cover the

tops of the columns to limit evaporation of water from the soil surface.

A Nuclear Chicago Scintillation Counter Model 8725 with a NaI crystal was used for counting ^{65}Zn. The crystal detector was placed behind a 2.5 mm opening or slit in a column of lead bricks. The soil column was placed on the opposite side of the lead and moved up and down by means of screw type jack (Figure 1). Thus the ^{65}Zn chelate movement pattern could be determined by counting the radiation that passed through the narrow slit. The soil columns were marked with 2.5 mm gradations allowing the columns to be placed in the same position each time.

Fractionation of Soil Samples

The clay fraction ($<2\mu$) of Wisner silty clay loam was separated from the sand and silt by differential sedimentation. Dispersion was obtained by adding 2% Na_2CO_3 and shaking overnight. The clay suspension was allowed to settle 10 cm for a time interval calculated according to Stoke's Law. The settling and syphoning process was repeated ten times. Clay suspensions collected were flocculated with calcium chloride. Excess salts were removed by washing the clay three times with distilled water, three times with 75% (V/V) aqueous methanol and finally two times with methanol alone until a chloride free test was obtained using $AgNO_3$.

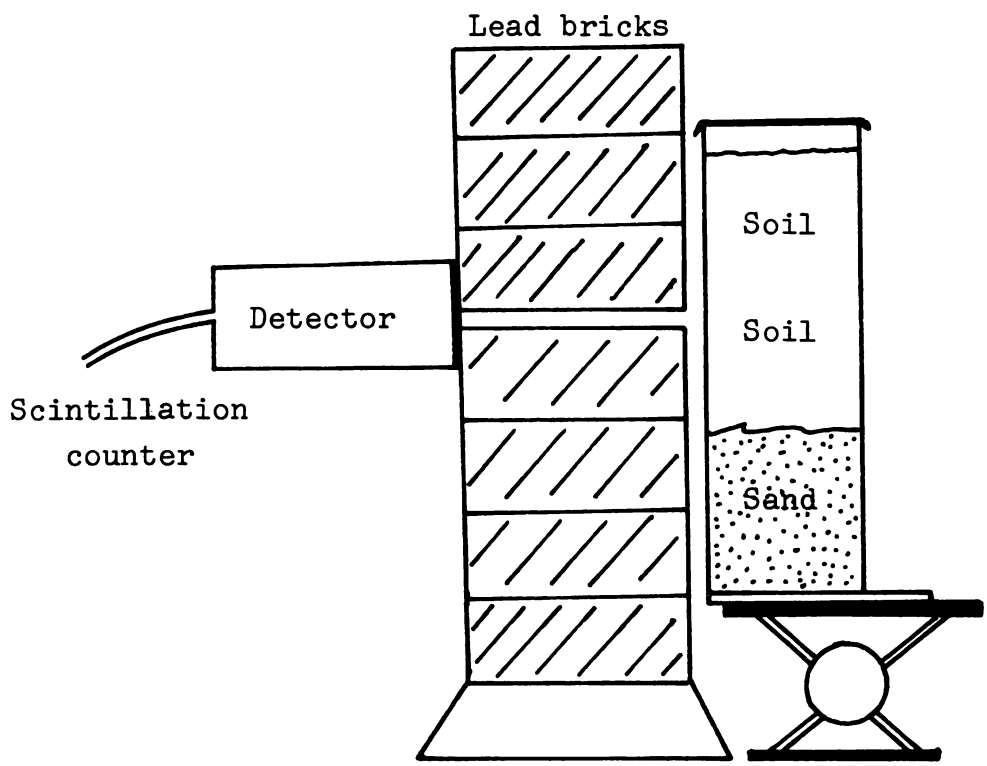

Figure 1. Schematic drawing showing equipment used for determining ^{65}Zn in soil columns.

The concentration of the Ca-clay was then determined by weighing aliquots of the clay suspensions. Clay concentration was found to be 4.92% for clay + organic matter suspensions and 4.6% for the clay suspensions with the organic matter destroyed.

Organic Matter Removal

It was necessary to first remove Ca salts, including $CaCO_3$ before treating the soil with H_2O_2 in order to avoid formation of CaC_2O_4. NaOAc buffer was used to dissolve carbonates and soluble salts in a method described by Grossman and Millet (1961).

Organic matter was oxidized with H_2O_2 by a method described by Kunze (1965).

Organic Carbon Determination

Determinations of organic carbon were performed on a Leco 70 Second Carbon Analyzer made by Laboratory Equipment Corporation in St. Joseph, Michigan.

The following data were obtained:

Table 1. Percent organic carbon - organic matter determinations on a Wisner silty clay loam soil.

Treatment	Organic Carbon	Organic Matter[a]
	%	%
H_2O_2	0.34	0.59
	0.23	0.40
None	2.15	3.71
	2.02	3.48

[a]Percent organic matter = percent organic carbon x 1.724.

Cation Exchange Capacity

Samples of soil and clay were Ca saturated by use of 1 N $CaCl_2$. Excess salt was removed by washing with 75% (V/V) aqueous ethanol until a chloride free test was obtained using $AgNO_3$. The Ca ion was displaced with Mg by washing with 1 N $MgCl_2$ four times. Ca concentration was determined by a Perkin Elmer Model 303 Atomic Adsorption Spectrophotometer. Cation exchange capacities were as follows:

Table 2. Cation exchange capacities of a Wisner silty clay loam.

Treatment	Soil Fraction	
	<2μ	Soil
	--- me/100gm ---	
None	46.2	15.2
H_2O_2	35.2	10.2

Stability Constant Determination

Quantities (0.2 - 2.0 gm) of K-saturated Dowex-50 resin, 50-100 mesh (analytical grade, AG50W purchased from Bio-Rad Laboratories) were weighed into 125 ml Erlenmeyer flasks. The K-saturated form of the resin was obtained by washing the H form with 1 N KCl and removing the excess KCl by distilled water washings. It was also necessary to neutralize the system with KOH to obtain a near neutral pH due to the low pH found when chlorides were washed free.

The swelling factor for the resin was previously determined by Dr. B. G. Ellis and found to be 0.29 ml/gm resin which is considered negligible.

Forty ml of the clay suspensions (approximately 5% by weight), 5 ml of 1 N KCl, and 5 ml ^{65}Zn (40,000 cpm) were pipetted into the Erlenmeyer flasks. The pH of the solution was adjusted to 3.5 or 5.0 using less than 10 drops of dilute HCl or KOH. A set of blanks was also prepared that contained everything but the clay suspensions. The flasks were shaken for 72 hours on a gyroscopic shaker at 24 ± 2^{o} C.

Flasks were removed from the shaker at 2 minute intervals, thus allowing the resin to settle to the bottom of the flask, and then 2 ml of clay suspension were pipetted from the top portion of the liquid. Great care was taken to avoid pipetting any resin from the flasks. The pipetted samples were placed in a Packard Auto-Gamma Spectrometer and the ^{65}Zn counted for one minute intervals.

Calculations performed on the data are described in Results and Discussion. The techniques used for stability constant determination are similar to those used and described by Rossotti and Rossotti (1961), Schnitzer and Skinner (1966), and Dr. B. G. Ellis (personal communication).

Isotherms - Zn Adsorption Maximum

Ten gram soil samples were equilibrated for 6 hours with 50 ml of 0.1 N KCl of varying Zn concentrations from 5 to

625 ppm Zn. The pH of the soil-0.1 N KCl suspension was adjusted to approximately 4.5 before Zn additions. The samples were shaken on a gyroscopic shaker, filtered, and Zn determined by atomic adsorption. The data was calculated according to the method of Langmuir (1918) as discussed by Olsen and Watanabe (1957).

$CaCO_3$, $ZnCO_3$, CO_2 Equilibrium

Samples of a Wisner silty clay loam soil were prepared in two ways. The pH of the natural soil (7.73) was adjusted with HCl or $Ca(OH)_2$ to pH's of 7.47 and 7.29. A second set of soil samples was first washed with 0.5 N HCl and the pH adjusted with $Ca(OH)_2$ to values of 6.88, 7.30, and 8.06.

A stock solution of ZnEDTA was prepared by mixing equimolar quantities of reagent grade $ZnSO_4$ with Na_2H_2EDTA. Aliquots of the ZnEDTA were adjusted to pH's approximately equal to the soil pH's. Tracer quantities of EDTA tagged with ^{14}C-labeled carboxyl groups were added, and the solutions were diluted to a final concentration of 1.5×10^{-3}M.

All chelate-soil reactions were carried out in small polyethylene bottles containing 15 g soil and 30 ml of solution. Soil suspensions were aerated continuously with air-CO_2 mixtures of 3% CO_2, 0.3% CO_2, and 0.03% CO_2. The bottles were shaken continuously at a temperature of 25 ± 2° C. Several times daily the bottles were hand shaken to resuspend adhering or settled particles. All suspensions were shaken

for two days before 2 ml of ZnEDTA chelate was added, bringing the final volume of the solution to 30 ml. Thus, the initial concentration of the ZnEDTA chelate added to the soil was 1 x 10^{-4} M or 13.1 ppm Zn expressed on a soil weight basis.

Reaction periods, following EDTA chelate additions were varied from 6 hours to 30 days. At the end of each reaction period, a set of bottles was removed and the pH of the suspensions was immediately determined. The suspensions were centrifuged and the supernatant solutions filtered to remove floating organic matter.

The concentration of ^{14}C tagged EDTA in each solution was measured by liquid scintillation using aqueous standards with a similar pH and salt content. Bray (1960) solution was used as the solvent for the aqueous samples. Solutions were analyzed for Ca, Fe, and Zn by atomic adsorption spectrophotometry.

RESULTS AND DISCUSSION

Movement of Zn With Different Carriers

Little movement of ^{65}Zn from $ZnSO_4$ occurred under leaching as shown in Table 3. Approximately 1-3% of the Zn moved a maximum of 7.5 mm as illustrated in Figure 2, where counts per minute from ^{65}Zn are plotted against depth. Time or temperature of incubation had no effect on the $^{65}ZnSO_4$ movement. The applied Zn must readily be adsorbed by the organic matter and/or clay thus rendering the Zn immobile. Other workers have also found the same results--Brown, Krantz, and Martin (1962) and Barrows, Neff, and Gammon (1960).

Soil columns were marked in numbered 2.5 mm sections to insure repeatable ^{65}Zn counting measurements between water leachings. The gamma radiation counting was begun 5.0 mm above the surface of the soil in the column because after several additions of water, the soil surface became irregular, and it was difficult to determine the exact starting position of the soil surface. The gamma radiation penetrated the 10 cm. lead brick shielding to some extent and gave a tailing off effect in graphing of results when the highest radiation level was close to the counting slit.

Table 3. Influence of incubation time, temperature, and water leached on movement of ^{65}Zn from $^{65}ZnSO_4$ at pH's 3.6, 6.3, 7.7, and 8.3.

Water Leached Total	Incubation Period (days) 5° C.					
	0	7	14	21	28	Avg.
ml	%					
0[a]	4.8	4.1	5.9	6.1	6.8	5.5
25	5.2	5.9	4.8	6.7	5.4	5.6
50	4.1	6.4	5.4	6.9	6.8	5.9
75	6.8	6.2	6.4	4.1	5.4	5.8
100	5.7	5.3	6.2	5.8	6.3	5.9
125	5.5	4.3	5.0	6.3	6.5	5.5
	Incubation 15° C.					
	%					
0	3.9	7.4	3.4	6.5	3.3	4.9
25	4.8	5.9	5.4	4.1	6.3	5.3
50	5.6	4.6	4.1	7.2	5.4	5.4
75	4.1	7.2	5.7	6.9	4.2	5.6
100	6.1	6.5	4.5	5.7	3.8	5.3
125	5.2	4.4	3.2	6.5	7.2	5.3
	Incubation 25° C.					
	%					
0	4.8	5.9	6.4	6.8	3.7	5.5
25	5.6	5.9	6.1	3.2	7.4	5.6
50	7.2	8.0	3.1	5.6	4.7	5.7
75	4.9	5.2	5.3	5.8	3.7	5.0
100	3.4	5.4	5.6	6.1	6.4	5.4
125	5.3	7.1	6.4	3.2	5.8	5.6
	Incubation 35° C.					
	%					
0	3.1	7.2	6.8	4.3	5.1	5.3
25	5.7	6.4	6.2	4.1	6.8	5.8
50	4.3	5.1	5.8	4.9	4.1	4.8
75	6.1	3.8	5.1	6.2	4.7	5.2
100	5.5	7.1	4.2	5.5	5.9	5.6
125	4.5	6.2	7.1	6.3	6.1	6.0

[a]Due to some penetration of gamma rays through the lead bricks, the top 2.5 mm band of ^{65}Zn-chelate appeared to be approximately 7.5 mm deep. The values for 0 water leached are also due to this gamma ray penetration.

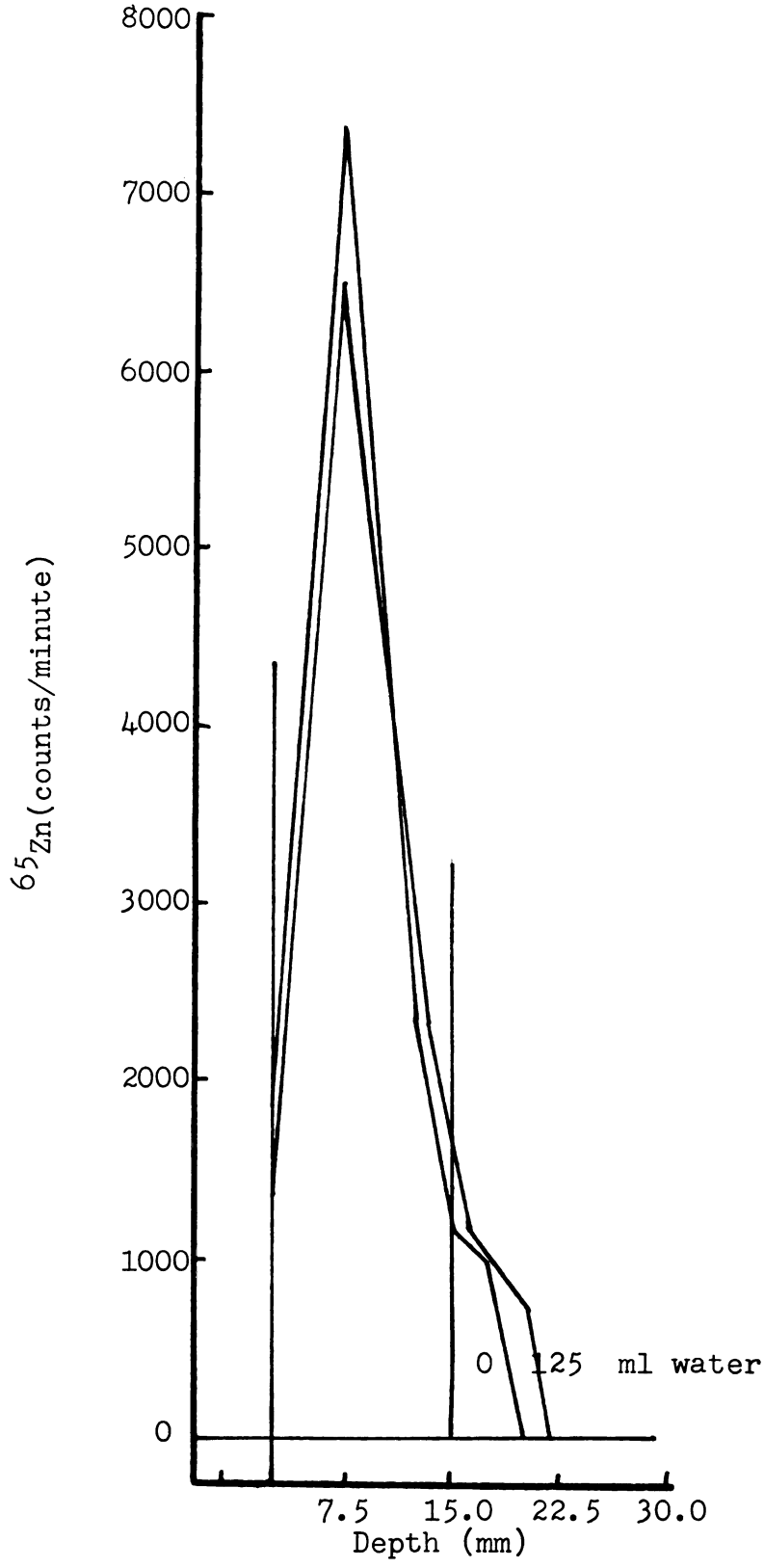

Figure 2. Distribution of ^{65}Zn as $ZnSO_4$ in a soil column.

For this reason the ^{65}Zn chelate vs. depth graphs show a peak width of around 7.5 mm with no water leaching instead of 3-4 mm, which was the depth of the ^{65}Zn chelate soil added to the column.

Several soil columns of each ^{65}Zn chelate treatment were prepared where the total soil was of the same pH under study. However, the same movement characteristics were found for the Zn if the lower 7 cm of soil was pH 7.7 for all soil pH's added to the top of this 7 cm. Therefore, it was not necessary to change the pH of the soil in the column below the added 3-4 mm of treated soil. Apparently any effect of pH on the Zn chelate soil movement took place very rapidly and movement of the soluble Zn chelate into soil of a different pH was of no consequence to the Zn solubility.

The possibility of the ^{65}Zn moving in a form other than ZnEDTA or ZnNTA was also considered. To study this possibility, EDTA and NTA were obtained from Geigy Chemical Company which was ^{14}C labeled. The radiation from the ^{65}Zn and ^{14}C could not be determined separately by means of liquid scintillation counting due to their similarity of energy spectrum (^{14}C and ^{65}Zn emitt beta energies of 0.155 and 0.32 MEV respectively, which could not be separated by pulse height analysis). Therefore, separate columns were prepared where ^{65}ZnEDTA or NTA were used on one column and ZnEDTA or NTA - ^{14}C labeled were used on the other column. Equal quantities of water were leached through each column. The ^{65}Zn radiation could easily be determined by gamma

scintillation counting. Samples of soil were taken from the ^{14}C chelate column and counted for ^{14}C by liquid scintillation. Figure 3 shows that the peak position and moving front of ^{65}Zn and ^{14}C correlate well giving a good indication that the Zn was moving in the chelated form.

After the data for the various chelate and pH treatments was plotted, an arbitrary vertical line was drawn at the 12.5 mm position (eg. Figure 4). This was the point at which the initial peak tailed off to the background counting for the zero water leaching. A planimeter was then used to measure the areas under the respective water leaching lines. The area to the left of the vertical line was that portion of ^{65}Zn chelate which did not move or was dissociated and that portion of area to the right of the vertical line was the ^{65}Zn chelate which was mobile. The percent of mobile or chelated Zn would be the area to the right of the vertical line divided by the total area under the line.

Data obtained from the Zn chelate movement is presented in Figures 4-7 and Tables 4-11. The movement characteristics of the Zn chelates was quite different depending upon the pH of the soil and the type of chelate studied.

First considering a soil pH of 3.65 for ZnNTA and ZnEDTA (Figure 4 and 5), it can be seen that the ZnNTA moved farther than the ZnEDTA. ZnNTA moved 22.5 mm for 125 ml water leaching, while ZnEDTA moved only 7.5 mm. Using area measurements, a maximum of 44.9% (39.3% if 5.6 is subtracted for 0 water leaching - Table 4) of the total ZnNTA

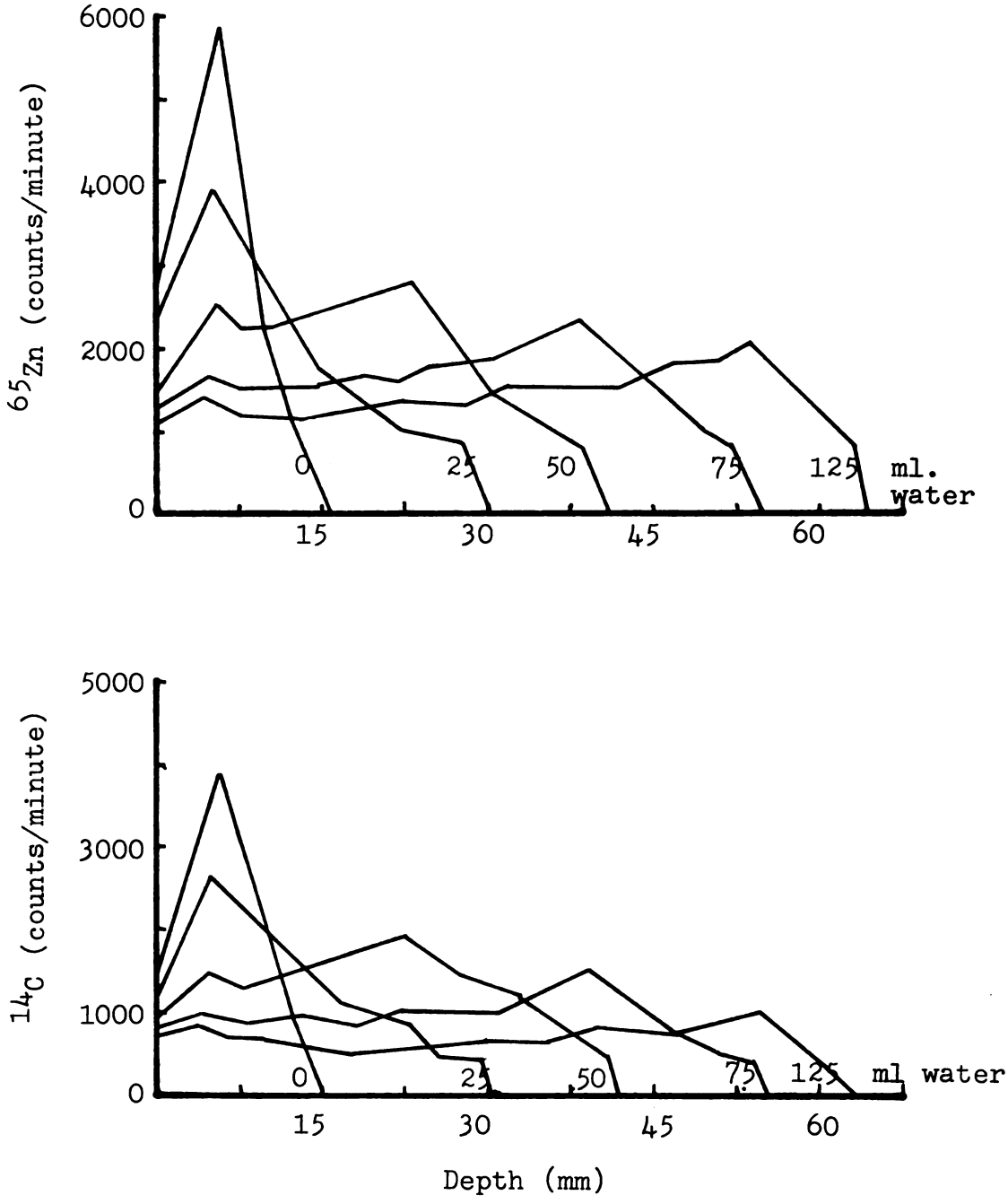

Figure 3. Distribution of ^{65}Zn and ^{14}C as Zn EDTA in a soil column at pH 6.3.

Table 4. Influence of incubation time, temperature, and water leached on movement of ^{65}Zn from $^{65}ZnNTA$ at pH 3.6.

Water Leached Total	Incubation Period (days) 5° C.					
	0	7	14	21	28	Avg.
ml	%					
0[a]	4.1	6.2	7.2	6.2	4.2	5.6
25	18.2	15.8	16.9	18.8	11.1	16.2
50	28.1	25.1	27.2	29.2	27.2	27.4
75	31.2	33.1	34.5	36.9	34.5	34.0
100	45.6	41.2	38.2	43.6	42.0	42.1
125	46.1	42.1	41.6	47.8	44.5	44.4
	Incubation 15° C.					
	%					
0	4.3	6.9	7.4	5.8	3.7	5.6
25	17.0	16.1	16.8	17.4	15.0	16.5
50	27.6	26.2	30.2	25.9	27.0	27.4
75	35.9	33.8	35.5	34.3	38.5	35.6
100	42.9	40.0	40.1	40.9	40.8	40.9
125	46.0	43.7	45.0	43.9	45.7	44.9
	Incubation 25° C.					
	%					
0	3.9	7.4	7.3	6.1	3.4	5.6
25	16.7	16.4	16.2	18.1	13.2	16.1
50	27.4	27.3	28.4	27.9	25.8	27.4
75	35.6	34.1	34.6	35.7	35.7	35.1
100	42.7	42.8	39.2	41.8	40.0	41.3
125	45.7	44.8	43.5	44.6	44.9	44.7
	Incubation 35° C.					
	%					
0	3.2	7.6	7.1	6.3	3.3	5.5
25	15.9	16.9	16.1	18.4	13.0	11.1
50	26.8	27.9	28.4	28.3	27.0	27.7
75	31.0	36.0	31.2	35.9	34.9	33.8
100	40.2	45.0	38.0	44.0	43.0	42.0
125	43.4	42.1	43.2	49.0	41.0	43.7

[a]Due to some penetration of gamma rays through the lead bricks, the top 2.5 mm band of ^{65}Zn-chelate appeared to be approximately 7.5 mm deep. The values for 0 water leached are also due to this gamma ray penetration.

Table 5. Influence of incubation time, temperature, and water leached on movement of ^{65}Zn from $^{65}ZnNTA$ at pH 6.3.

Water Leached Total	Incubation Period (days) 5° C.					
	0	7	14	21	28	Avg.
ml	%					
0[a]	5.3	6.6	6.4	5.8	6.1	6.0
25	32.8	27.1	29.9	31.2	35.8	31.4
50	47.0	49.0	45.9	48.7	50.1	48.1
75	60.4	55.1	58.5	62.6	60.2	59.4
100	61.5	69.0	61.5	64.6	60.0	63.3
125	69.5	64.3	66.5	69.2	69.1	67.7
	Incubation 15° C.					
	%					
0	5.5	6.4	6.5	5.6	6.4	6.1
25	31.6	28.0	29.5	32.5	33.9	31.1
50	49.6	46.1	47.6	49.0	50.3	48.5
75	59.2	58.2	57.7	59.9	59.5	58.9
100	63.0	65.2	62.2	65.7	62.2	63.7
125	68.3	67.3	64.7	68.1	67.7	67.2
	Incubation 25° C.					
	%					
0	5.4	6.5	6.1	6.9	6.3	6.2
25	27.3	32.2	28.3	35.0	32.0	31.0
50	48.9	47.9	45.9	49.9	50.1	48.5
75	58.9	59.3	57.6	63.0	59.4	59.6
100	62.5	65.7	61.9	66.7	61.1	63.6
125	68.6	67.9	62.0	69.1	65.9	66.7
	Incubation 35° C.					
	%					
0	5.6	6.6	5.1	5.5	6.6	5.9
25	34.0	29.0	23.2	31.5	35.0	30.5
50	52.0	47.9	45.8	48.9	51.5	49.2
75	60.5	59.5	55.3	59.0	60.6	59.0
100	64.3	65.5	60.0	65.5	62.7	63.6
125	69.1	68.2	62.3	68.0	69.3	67.4

[a]Due to some penetration of gamma rays through the lead bricks, the top 2.5 mm band of ^{65}Zn-chelate appeared to be approximately 7.5 mm deep. The values for 0 water leached are also due to this gamma ray penetration.

Table 6. Influence of incubation time, temperature, and water leached on movement of ^{65}Zn from $^{65}ZnNTA$ at pH 7.7.

Water Leached Total	Incubation Period (days) 5° C.					
	0	7	14	21	28	Avg.
ml	%					
0[a]	5.5	6.8	6.6	3.2	6.2	5.7
25	32.1	28.5	27.2	33.5	31.9	30.6
50	49.5	48.0	46.5	49.1	52.0	49.0
75	59.1	52.0	59.0	60.4	58.5	57.8
100	60.4	64.3	62.2	63.7	62.9	62.7
125	68.1	66.4	64.9	69.0	68.1	67.3
	Incubation 15° C.					
	%					
0	3.2	6.6	5.5	7.9	6.8	6.0
25	32.8	29.0	28.1	31.5	35.9	31.5
50	48.6	45.3	43.1	49.9	52.0	48.0
75	60.5	57.5	57.7	58.9	60.9	59.0
100	61.2	63.0	61.0	64.5	58.4	61.6
125	69.4	65.0	67.8	69.1	69.1	68.1
	Incubation 25° C.					
	%					
0	5.9	6.3	6.8	5.6	6.3	6.2
25	31.8	27.9	29.1	31.5	34.2	30.9
50	49.8	46.0	47.8	48.9	51.2	48.7
75	58.9	59.3	57.8	58.8	59.9	58.9
100	63.2	64.3	62.1	66.2	63.8	63.9
125	67.9	67.2	63.1	68.1	66.4	66.5
	Incubation 35° C.					
	%					
0	5.6	6.3	6.3	5.6	6.9	6.1
25	31.8	27.2	34.2	32.5	34.1	32.0
50	49.5	46.5	49.5	45.0	50.3	48.2
75	59.6	58.7	58.7	60.3	57.2	58.9
100	63.8	66.2	66.2	66.1	61.4	64.7
125	68.7	65.3	68.1	68.3	67.7	67.6

[a]Due to some penetration of gamma rays through the lead bricks, the top 2.5 mm band of ^{65}Zn-chelate appeared to be approximately 7.5 mm deep. The values for 0 water leached are also due to this gamma ray penetration.

Table 7. Influence of incubation time, temperature, and water leached on movement of ^{65}Zn from $^{65}ZnNTA$ at pH 8.3.

Water Leached Total	Incubation Period (days) 5° C.					
	0	7	14	21	28	Avg.
ml	%					
0[a]	5.9	6.0	6.7	5.4	6.6	6.1
25	32.5	27.6	30.2	31.8	34.1	31.2
50	48.8	49.2	45.2	51.0	48.8	48.6
75	60.2	57.8	59.7	57.6	59.2	58.9
100	65.0	63.2	64.6	64.5	62.9	64.0
125	69.1	66.2	64.9	67.9	66.2	66.9
	Incubation 15° C.					
	%					
0	5.1	6.6	3.1	7.9	6.3	5.8
25	30.2	29.3	25.0	35.0	34.0	30.7
50	48.5	46.4	44.3	49.8	51.4	58.1
75	59.1	58.5	57.1	62.0	59.8	59.3
100	62.8	65.9	61.1	63.7	62.3	63.2
125	68.9	67.6	64.1	69.1	65.3	67.0
	Incubation 25° C.					
	%					
0	3.1	7.2	6.5	5.9	6.8	5.9
25	33.4	27.9	32.0	31.1	35.4	32.0
50	50.6	45.3	48.4	48.6	52.1	49.0
75	60.5	59.1	56.6	58.2	60.5	59.0
100	64.1	66.3	61.1	63.2	64.1	63.8
125	69.0	66.0	64.0	68.1	67.9	67.0
	Incubation 35° C.					
	%					
0	5.1	6.5	6.6	5.8	6.3	6.1
25	30.6	28.1	29.6	32.4	31.0	30.3
50	49.6	46.5	47.9	49.1	48.7	48.4
75	58.8	59.3	57.9	59.8	55.4	58.2
100	61.8	66.1	62.5	65.7	62.1	63.6
125	68.1	67.9	65.4	68.1	66.8	67.3

[a]Due to some penetration of gamma rays through the lead bricks, the top 2.5 mm band of ^{65}Zn-chelate appeared to be approximately 7.5 mm deep. The values for 0 water leached are also due to this gamma ray penetration.

Table 8. Influence of incubation time, temperature, and water leached on movement of ^{65}Zn from $^{65}ZnEDTA$ at pH 3.6.

Water Leached Total	Incubation Period (days) 5° C.					
	0	7	14	21	28	Avg.
ml	%					
0[a]	3.0	7.3	6.9	4.2	5.0	5.3
25	5.8	6.3	6.1	4.8	6.9	6.0
50	4.2	5.3	5.9	4.7	4.0	4.8
75	6.3	3.1	5.3	6.1	4.9	5.1
100	5.4	7.2	4.3	5.6	5.9	5.7
125	4.6	6.1	7.0	6.2	6.1	6.0
	Incubation 15° C.					
	%					
0	4.0	7.2	3.6	6.6	3.3	4.9
25	4.7	5.8	5.1	4.5	6.4	5.3
50	5.7	4.7	4.9	7.5	5.5	5.7
75	4.2	7.4	5.9	6.1	4.6	5.6
100	6.3	6.6	4.9	5.3	4.9	5.6
125	5.4	4.1	3.1	6.2	7.8	5.3
	Incubation 25° C.					
	%					
0	4.9	5.4	6.5	6.8	3.7	5.5
25	5.8	5.8	6.2	3.0	7.4	5.6
50	7.3	7.1	4.8	5.8	4.2	5.8
75	5.0	5.1	5.5	5.7	3.8	5.0
100	3.6	5.3	5.7	6.6	6.5	5.5
125	5.5	7.1	6.0	3.7	5.9	5.6
	Incubation 35° C.					
	%					
0	5.0	4.8	5.8	6.0	6.7	5.7
25	5.8	5.3	4.7	6.9	5.5	5.6
50	4.4	6.6	5.4	4.1	6.8	5.5
75	6.9	6.2	6.4	6.9	4.1	6.1
100	6.0	5.5	6.2	3.5	7.2	5.7
125	6.2	4.1	5.2	6.3	6.5	5.7

[a]Due to some penetration of gamma rays through the lead bricks, the top 2.5 mm band of ^{65}Zn-chelate appeared to be approximately 7.5 mm deep. The values for 0 water leached are also due to this gamma ray penetration.

Table 9. Influence of incubation time, temperature, and water leached on movement of ^{65}Zn from $^{65}ZnEDTA$ at pH 6.3.

Water Leached Total	Incubation Period (days) 5° C.					
	0	7	14	21	28	Avg.
ml	%					
0[a]	4.7	7.2	5.8	6.3	6.2	6.0
25	42.1	45.0	43.1	51.0	45.1	45.3
50	69.1	72.1	68.5	72.0	68.2	70.0
75	80.5	81.9	78.2	83.0	79.0	80.5
100	84.8	86.4	83.1	85.0	82.8	84.4
125	85.2	87.2	84.0	88.1	85.4	86.0
	Incubation 15° C.					
	%					
0	5.2	5.9	6.8	6.1	6.2	6.0
25	44.0	43.7	45.0	48.1	45.3	45.2
50	70.1	68.8	70.2	73.0	69.3	70.3
75	81.6	78.8	81.0	81.8	80.0	80.6
100	85.7	84.1	85.0	84.3	84.6	84.7
125	87.8	86.7	85.0	87.0	86.3	85.7
	Incubation 25° C.					
	%					
0	4.9	6.9	6.2	6.2	6.3	6.1
25	42.7	44.9	44.3	49.3	45.2	45.3
50	69.4	70.2	69.7	74.0	68.3	70.3
75	80.8	80.2	80.7	82.1	79.0	80.6
100	85.2	84.9	84.4	85.7	83.0	84.6
125	86.7	86.8	84.1	87.4	85.5	86.1
	Incubation 35° C.					
	%					
0	4.9	7.1	5.2	8.1	5.1	6.1
25	43.2	42.6	45.8	47.3	41.9	44.2
50	70.2	68.9	71.3	72.0	70.1	70.5
75	81.3	79.1	78.1	81.3	78.5	79.7
100	85.1	81.2	80.3	85.7	84.0	83.3
125	86.6	86.9	83.2	86.5	86.2	85.9

[a] Due to some penetration of gamma rays through the lead bricks, the top 2.5 mm band of ^{65}Zn-chelate appeared to be approximately 7.5 mm deep. The values for 0 water leached are also due to this gamma ray penetration.

Table 10. Influence of incubation time, temperature, and water leached on movement of ^{65}Zn from $^{65}ZnEDTA$ at pH 7.7.

Water Leached Total	Incubation Period (days) 5° C.					
	0	7	14	21	28	Avg.
ml	%					
0[a]	4.8	7.1	6.1	6.2	5.2	5.9
25	42.6	45.3	40.2	49.5	47.0	44.9
50	69.1	71.3	67.3	76.2	68.1	70.4
75	78.3	80.5	78.2	82.9	81.3	80.2
100	84.1	86.3	81.3	86.3	79.6	83.5
125	84.5	87.7	81.3	87.6	87.1	85.6
	Incubation 15° C.					
	%					
0	5.2	7.3	6.1	6.9	6.1	6.3
25	44.9	42.7	49.1	44.5	46.3	45.5
50	70.1	71.2	69.3	74.2	68.2	70.6
75	82.1	79.0	80.1	81.2	80.0	80.5
100	84.8	85.9	84.1	83.2	84.1	84.4
125	87.4	86.9	84.0	86.5	85.3	86.0
	Incubation 25° C.					
	%					
0	6.2	6.3	6.8	5.1	3.2	5.5
25	42.8	44.1	47.3	45.1	46.4	45.1
50	68.1	76.3	68.1	68.3	69.5	70.1
75	79.2	80.7	80.1	82.1	83.0	81.0
100	84.9	83.6	84.6	85.7	85.6	84.9
125	86.1	87.9	86.8	86.7	85.7	86.6
	Incubation 35° C.					
	%					
0	6.3	6.1	6.9	3.1	6.6	5.8
25	49.3	44.3	43.2	42.1	45.0	44.8
50	73.1	69.2	71.4	69.4	68.3	70.3
75	82.3	79.8	82.3	79.8	74.3	79.7
100	85.7	84.4	84.9	84.7	83.2	84.6
125	87.9	84.6	85.3	85.8	86.9	86.1

[a]Due to some penetration of gamma rays through the lead bricks, the top 2.5 mm band of ^{65}Zn-chelate appeared to be approximately 7.5 mm deep. The values for 0 water leached are also due to this gamma ray penetration.

Table 11. Influence of incubation time, temperature, and water leached on movement of ^{65}Zn from $^{65}ZnEDTA$ at pH 8.3.

Water Leached Total	Incubation Period (days) 5° C.					
	0	7	14	21	28	Avg.
ml	%					
0[a]	6.4	6.1	6.5	5.8	4.2	5.8
25	45.3	48.7	45.7	41.7	41.7	44.6
50	69.9	73.2	70.2	68.2	69.3	70.2
75	79.2	81.9	82.7	78.3	80.8	80.6
100	84.1	83.6	85.9	83.1	85.1	84.4
125	85.9	86.5	89.1	80.2	85.3	85.4
	Incubation 15° C.					
	%					
0	6.9	4.2	6.2	6.5	6.1	6.0
25	42.9	43.2	40.5	50.2	45.3	44.4
50	70.3	68.9	68.3	75.3	69.6	70.5
75	81.0	79.1	80.7	83.6	79.3	80.7
100	86.3	83.2	84.4	85.6	84.2	84.7
125	86.9	85.7	84.1	88.2	88.7	86.7
	Incubation 25° C.					
	%					
0	4.3	4.2	6.9	6.4	6.6	5.7
25	38.7	39.7	46.2	50.5	49.0	44.8
50	65.0	70.1	70.3	73.2	66.2	69.0
75	78.2	79.8	83.0	85.5	74.3	80.2
100	83.6	84.8	86.0	87.1	85.4	85.4
125	86.5	85.8	89.0	88.0	85.5	87.0
	Incubation 35° C.					
	%					
0	6.1	6.5	6.9	4.2	6.9	6.1
25	45.3	45.7	41.7	45.1	50.9	45.7
50	69.8	70.2	68.9	75.3	70.3	70.9
75	79.3	81.8	78.3	82.7	80.8	80.6
100	86.3	85.5	83.3	84.5	85.3	85.0
125	85.3	80.2	89.1	89.5	88.6	86.5

[a]Due to some penetration of gamma rays through the lead bricks, the top 2.5 mm band of ^{65}Zn-chelate appeared to be approximately 7.5 mm deep. The values for 0 water leached are also due to this gamma ray penetration.

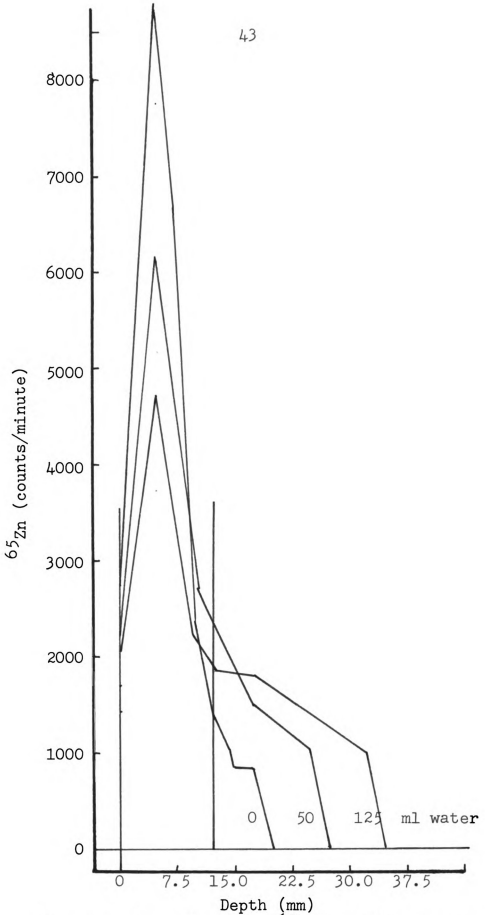

Figure 4. Distribution of ^{65}Zn as ZnNTA in a soil column at pH 3.65.

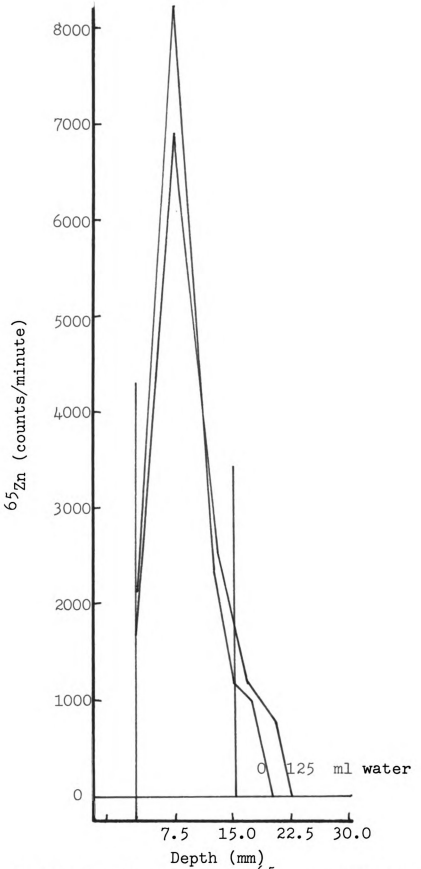

Figure 5. Distribution of ^{65}Zn as ZnEDTA in a soil column at pH 3.65.

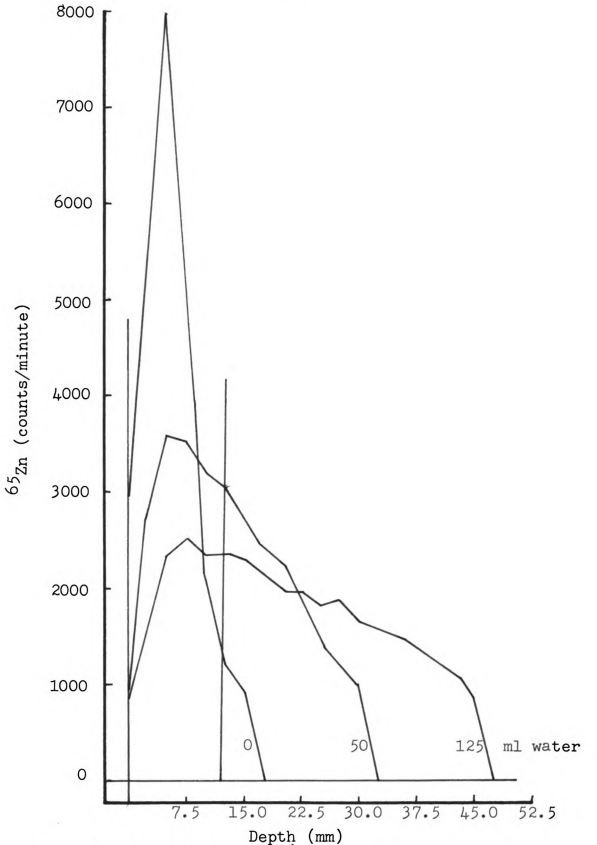

Figure 6. Distribution of ^{65}Zn as ZnNTA in a soil column at pH 6.30.

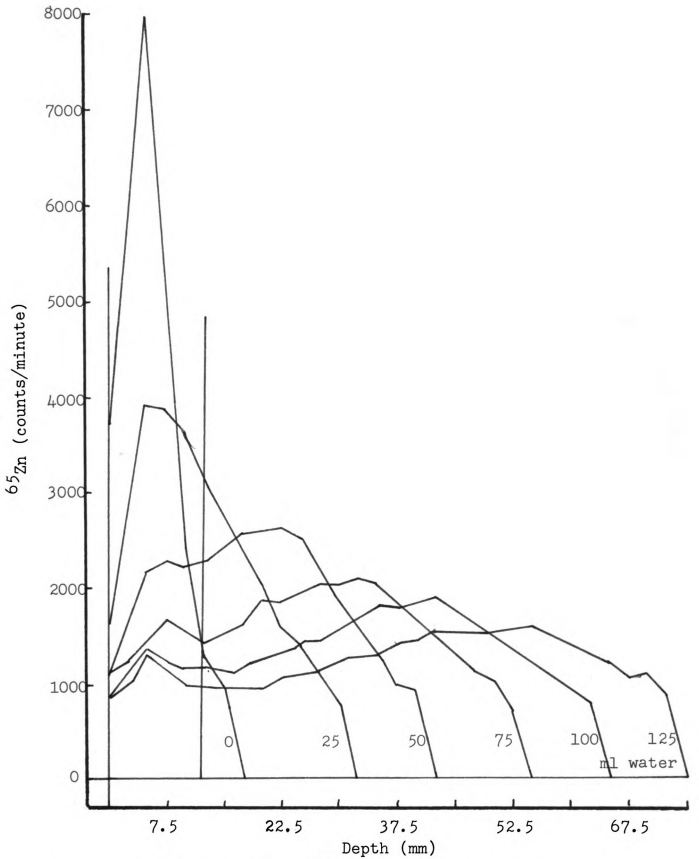

Figure 7. Distribution of ^{65}Zn as ZnEDTA in a soil column at pH 6.30.

moved into a region of the soil below the top 7.5 mm, while only 6.0% (0.7% if 5.6 is subtracted for 0 water leaching - Table 8) of the ZnEDTA moved into new soil. Because the only mobile form of Zn is in the chelated form, the Zn must have dissociated almost immediately from the EDTA at this low pH and thus remained in the top portion of the column. For the ZnNTA, almost half of the Zn remained in the chelated or mobile form with 125 ml of water leaching. Incubation times as well as incubation temperatures had essentially no effect on the solubility of these Zn chelates (Tables 4 and 8).

The log K value for H_2EDTA is 6.16 while for H_2NTA it is 2.49. The dihydrogen form (which is expected when divalent ions dissociate from a chelate) of the EDTA is considerably more stable and would be formed more readily than H_2NTA. Calculations show that approximately 5×10^3 as much NTA is available to chelate with Zn than EDTA at a pH of 3.65. This fact would account for the immediate dissociation of Zn from EDTA at low pH's. It also should be noted here that at low pH's FeEDTA and FeNTA have stability constants of 25.1 and 15.9 respectively. These log K values are very high and would thus compete very favorably with the H for the chelate. The FeEDTA would be expected to form before the FeNTA due to its higher stability constant, (approximately 10^8 times higher).

The pH effect on chelate solubility brings another important aspect to correcting Zn deficiency on acid soils.

Even though the pH of the soil studied was extremely low, the dissociation of ZnEDTA must be considered when applied to acid soils which are Zn deficient.

Figures 6 and 7 with Tables 5 and 9 show the data for the chelate movement at soil pH 6.3. No differences in movement were found for either Zn chelate at all temperatures of incubation and for pH's of 6.3, 7.7, or 8.3 (Tables 5-7 and 9-11). Incubation times had no effect on movement of the Zn chelate with the possible exception of 28 days incubation time where 1-2% less movement was noted for a few isolated cases.

At pH 6.3 ZnNTA moved a maximum of 35 mm with 125 ml of water leaching while ZnEDTA moved by far the most of all treatments--62.5 mm. It is obvious that at the higher pH's the Zn remained chelated and thus soluble, allowing a much greater movement. In addition to moving farther, approximately 80 - 85% of the ZnEDTA moved into lower regions of the soil column vs. 60 - 65% of the ZnNTA. This data can also be explained by differences in stability constants for the two chelates. ZnNTA and ZnEDTA have log K values of 10.45 and 16.50 respectively. The much larger value for ZnEDTA would allow for greater stability under conditions of neutral soil pH and thus greater movement under leaching.

Quite different patterns of movement are also noted for the chelates at the higher pH's (Figure 6 vs. 7). The ZnNTA showed a tailing off effect when the various amounts of water were leached. Some of the Zn must have immediately

dissociated from the NTA upon addition of the chelate to the soil, and some is slowly dissociating over a period of time. For the same pH's, however, ZnEDTA shows only a very small portion of the Zn fixed upon addition of the chelate to the soil as illustrated by the small peak at 2.5 mm (Figure 7). Most of the Zn is mobile or in the chelated form throughout the period of study causing an actual broad moving peak (Figure 7).

Stability Constant Determinations

Data just presented showed that either ZnNTA or ZnEDTA were stable in the calcareous Wisner silty clay loam soil for at least one month. Yet the extreme deficiency observed in the field on pea beans grown on this soil even though total Zn is moderate in concentration suggests that the soil binds Zn strongly and might have been expected to compete with the chelate for Zn. For this reason, studies were conducted to determine the stability of Zn with the soil.

Several factors complicate the determination of a stability constant with soil, namely:

(1) A value for the concentration of soil is needed.

(2) Many methods for determination of a stability constant can not be used in a soil system.

(3) Only one complex species should be formed in appreciable concentrations.

(4) A scarcity of values in the literature makes comparison difficult.

An ion exchange method was employed in this study for determination of stability constants.

If resins are equilibrated with a solution containing metal ions, they may take part in an exchange reaction of the following nature:

$$Na_r^+ + BA_n \rightleftharpoons (BA_n)_r + Na^+ \qquad [10]$$

where

r = resin phase,

Na = sodium,

B = central group (Zn),

A_n = ligand (clay or clay + organic matter).

From the above equilibrium, the distribution of B between the ion exchange resin and ligand phase can supply information concerning the species present in the solution.

The partition coefficient of BA_n can be given as

$$P = E_c \left(\frac{Na^+r}{Na^+}\right) \qquad [11]$$

and will be constant provided that the equilibrium or exchange constant (E_c) and the ratio of the Na ion concentration in the two phases is kept constant. The latter condition was easily met in this study by using a K-saturated resin and a high constant concentration of K in the aqueous phase.

Most early workers found that the exchange constant E_c was dependent on the load on the resin; however, E_c can be constant over a small range of $(BA_n)_r$ concentration, if the load on the resin is very small (Rossotti and Rossotti, 1961). In the present study, tracer quantities of ^{65}Zn were used to keep the load on the resin as small as possible.

A strong acidic monofunctional resin (Dowex-50) was also employed to insure that the constant (E_c) is as independent of H ion concentration as possible.

Data obtained from the stability constant-ion exchange study is listed in Tables 12-15. The values listed for water and clay suspensions are in counts per minute of ^{65}Zn in the solution which was in equilibrium with the amount of resin listed. The method of Rossotti and Rossotti (1961) was used for data calculation. Using their method, the equation:

$$\frac{P_o - q_B}{Ch} = K(q_B - P_1) \qquad [12]$$

was plotted with $\frac{P_o - q_B}{Ch}$ as the vertical exis and q_B as the horizontal axis (Figures 8 and 9). In this equation:

P_o = the distribution constant of metal in the absence of ligand,

q_B = the distribution constant of metal in the presence of ligand,

P_1 = the distribution ratio of the metal-clay complex between resin and solution (partition coefficient),

K = stability constant,

Ch = ligand concentration in moles.

The values of K and P_1 can be obtained from the slope and intercept on the graph. Calculated values for P_o, q_B, and $P_o - q_B$ are given in Tables 12-15.

The graphs (Figures 8 and 9) show that the data follows a linear relationship, enabling slopes to be easily evaluated. There is a deviation from linearity on Figure 9 for the larger weights of resin. Errors at these larger weights might be due to equilibrium not being attained or from not enough reactive sites on the clay to obtain the linear relationship.

In order to make meaningful determination of stability constants, a value for the concentration of clay is needed (Ch). All stability constants reported in the literature are in terms of moles; however, as long as the units of the stability constants are given, the constants could be stated in terms of cation exchange or grams of soil. Conversion could then be made between the units given. Since cation exchange capacity is an important factor in determining clay reactivity, an equation may be set up where:

$$\frac{(\text{C.E.C.})(\text{clay concentration -gms/l})}{2 \times 10^5} = \frac{\text{moles of divalent ion}}{\text{l of suspension}} \quad [13]$$

Table 12. Data for stability constant determination of a Wisner silty clay loam soil at pH 3.5 - 4.0, clay + organic matter.

Resin Weight	Medium		P_o [b]	q_B [c]	$P_o - q_B$	$\frac{P_o - q_B}{Ch}$ [d]
	H_2O	Suspension				
g	counts/minute/2 ml					$\times 10^{-2}$
0.2	4890 [a]	25,187	4.614	0.090	4.524	4.113
0.4	3300	22,282	7.318	0.232	7.086	6.442
0.8	2163	16,800	11.691	0.634	11.057	10.052
1.2	1550	13,579	16.691	1.022	15.688	14.262
1.6	1142	11,502	23.037	1.387	21.650	19.682
2.0	990	10,259	26.720	1.676	25.044	22.767
0	27,451	27,451				

[a] Average of three replications

[b] $\frac{27,451 - H_2O \text{ media}}{H_2O \text{ media}}$

[c] $\frac{27,451 - \text{suspension (clay) media}}{\text{suspension (clay) media}}$

[d] $Ch = 1.1 \times 10^{-2}$ M

Table 13. Data for stability constant determination of a Wisner silty clay loam soil at pH 4.5 - 5.0, clay + organic matter.

Resin Weight	Medium		P_o[b]	q_B[c]	$P_o - q_B$	$\frac{P_o - q_B}{Ch}$[d]
	H_2O	Suspension				
g	counts/minute/2 ml					X 10^{-2}
0.2	6784[a]	27,300	3.046	0.006	3.040	2.764
0.4	5400	27,007	4.084	0.016	4.068	3.698
0.8	4041	25,500	5.793	0.077	5.716	5.196
1.2	3000	24,271	8.150	0.131	8.019	7.290
1.6	2450	22,725	10.204	0.208	9.996	9.087
2.0	1950	21,517	13.077	0.276	12.801	11.637
0	27,451	27,451				

(a) Average of three replications

(b) $\frac{27,451 - H_2O \text{ media}}{H_2O \text{ media}}$

(c) $\frac{27,451 - \text{suspension (clay) media}}{\text{suspension (clay) media}}$

(d) $Ch = 1.1 \times 10^{-2}$ M

Table 14. Data for stability constant determination of a Wisner silty clay loam soil at pH 3.5 - 4.0, clay - H_2O_2 treated.

Resin Weight	Medium		P_o[b]	q_B[c]	$P_o - q_B$	$\frac{P_o - q_B}{Ch}$[d]
	H_2O	Suspension				
g	counts/minute/2 ml					X 10^{-2}
0.1	9035[a]	25,079	2.01	0.085	1.93	2.383
0.3	4884	18,598	4.57	0.46	4.11	5.074
0.5	3241	12,932	7.39	1.10	6.29	7.765
0.7	2420	9,531	10.24	1.85	8.39	10.358
1.0	1805	7,648	14.07	2.77	11.30	13.951
1.5	1246	6,425	20.83	3.23	17.61	21.741
2.0	979	6,031	26.78	3.80	22.98	38.270
0	27,204	27,204				

[a] Average of three replications

[b] $\frac{27,204 - H_2O \text{ media}}{H_2O \text{ media}}$

[c] $\frac{27,204 - \text{suspension (clay) media}}{\text{suspension (clay) media}}$

[d] $Ch = 8.1 \times 10^{-3}$ M

Table 15. Data for stability constant determination of a Wisner silty clay loam soil at pH 4.5 - 5.0, clay - H_2O_2 treated.

Resin Weight	Medium		P_o[b]	q_B[c]	$P_o - q_B$	$\frac{P_o - q_B}{Ch}$[d]
	H_2O	Suspension				
g	counts/minute/2 ml					X 10^{-2}
0.1	10,389[a]	27,500	1.62	0	1.62	2.00
0.3	6350	25,300	3.28	0.075	3.21	3.963
0.5	4900	23,375	4.55	0.16	4.39	5.420
0.7	4281	22,522	5.35	0.21	5.14	6.346
1.0	3525	20,700	6.72	0.31	6.41	7.914
1.5	2550	17,770	9.67	0.53	9.14	11.284
2.0	1984	13,808	12,71	0.97	11.74	14.494
0	27,204	27,204				

[a] Average of three replications

[b] $\frac{27,204 - H_2O \text{ media}}{H_2O \text{ media}}$

[c] $\frac{27,204 - \text{suspension (clay) media}}{\text{suspension (clay) media}}$

[d] $Ch = 8.1 \times 10^{-3}$ M

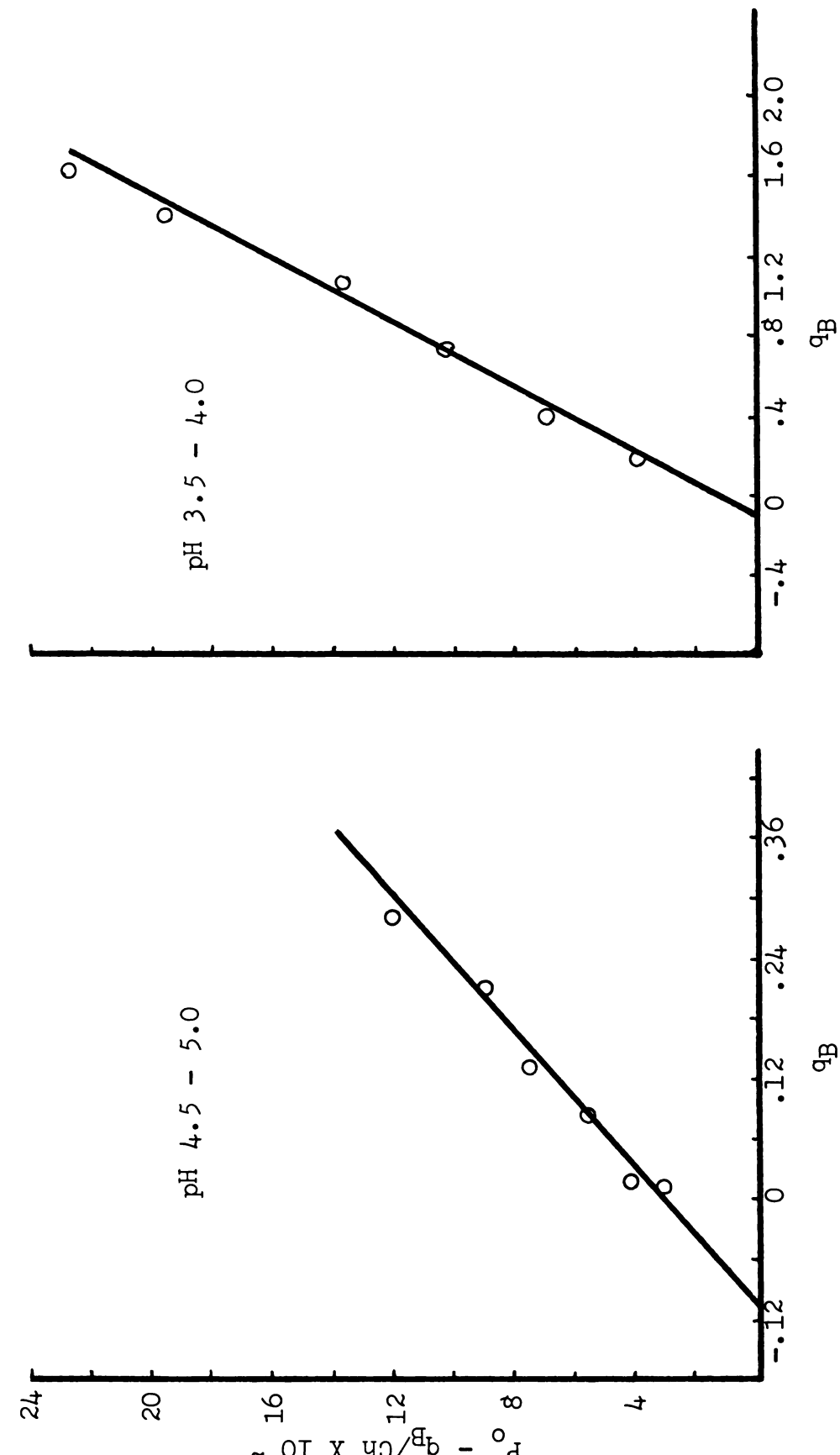

Figure 8. Partition of Zn between resin and clay + organic matter suspension.

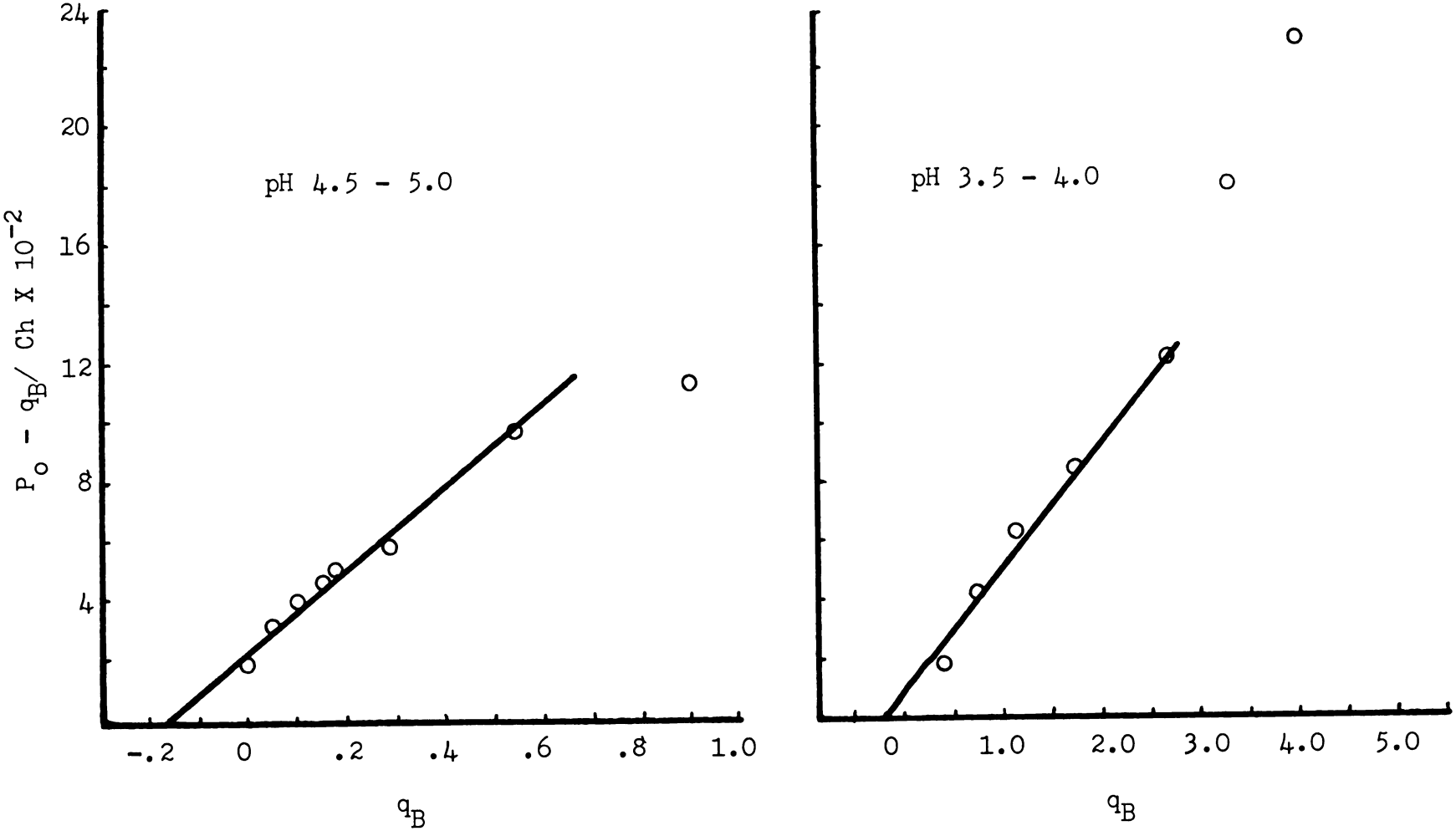

Figure 9. Partition of Zn between resin and clay - H_2O_2 treated suspension.

Using this relationship, the following table is given:

Table 16. Concentration of a Wisner silty clay loam soil.

	Clay Concentration (gms/l)	C.E.C. me/100g	Moles M/l
Clay + organic matter	49.2	46.2	1.1×10^{-2}
Clay - H_2O_2 treatment	46.2	35.2	8.1×10^{-3}

The value of moles of clay was then divided into the $(P_o - q_B)$ values giving the stability constants listed in Table 17.

Table 17. Stability constants for a Wisner silty clay loam soil in moles.

	pH	Slope[a] $\times 10^{-2}$	Log K
Clay + organic matter	3.5 - 4.0	11.429	3.06
	4.5 - 5.0	30.435	3.48
Clay - H_2O_2 treatment	3.5 - 4.0	4.127	2.62
	4.5 - 5.0	16.552	3.22

[a]Slope from Figures 8 and 9.

Another method for expressing stability constants is in terms of a weight unit of soil or clay. The following table is a recalculation of K on this basis.

Table 18. Stability constants for a Wisner silty clay loam soil in grams.

	pH	Clay Concentration (gm/40 ml)	Slope	Log K
Clay + organic matter	3.5 - 4.0	1.97	6.38	0.81
	4.5 - 5.0	1.97	16.99	1.23
Clay - H_2O_2 treatment	3.5 - 4.0	1.84	1.82	0.26
	4.5 - 5.0	1.84	7.29	0.86

It is readily obvious from Tables 16 and 17 that the value placed on (Ch) determines the stability constant obtained. Very few values have been found in the literature expressing stability constants in terms of grams of clay or soil, so comparison of the accuracy of these values is difficult. Himes and Barber (1957) determined the stability constant of Maumee soil to be 5.6 at pH 7 and 3.4 at pH 4.5.

Effects of pH on the determination of stability constants is similar to that found by Randhawa and Broadbent (1965) who reported log K values for Zn-humic acids at pH values 3.6, 5.6, and 7.0 to be 4.42, 6.18, and 6.80, respectively. However, Schnitzer and Skinner (1966) stated that pH had relatively little effect on the stability constants of Zn-fulvic acid fractions of organic matter. Their calculated log K values were 1.73 at pH 3.5 and 2.34 at pH 5.0. In the present study, relatively small differences (0.42 - 0.60, Table 17) were obtained in log K values for

the equilibrium pH of 3.5 - 4.0 and 4.5 - 5.0. The slight increase in stability due to pH is readily explainable in terms of H competition. Hydrogen ions compete with the metal ion for the ligand so that a decrease in pH results in a reduction of the free ligand concentration and a resulting decrease in the amount of metal complexed. In other words, at a higher pH more complexing sites on the complexing material were available for combination with Zn and thus gave an increase in the stability constant value.

There is wide variability of data for stability constants reported in the literature, depending upon the pH at which the constants were determined and the type of organic material used. Log K constants ranged from 1.7 to 7.8. No constants were found using a soil clay as the ligand, so the accuracy and validity of the determined values is difficult to substantiate. With the organic matter destroyed, the equilibrium would be of the form:

$$\text{clay} + \text{Zn} \rightleftharpoons \text{Zn} - \text{clay}$$

If the organic matter is present, the equilibrium would approximate:

$$\text{clay} + \text{organic matter} + \text{Zn} \rightleftharpoons \text{Zn-clay} + \text{Zn-organic matter} + \text{Zn-clay-organic matter}$$

All previous work on stability constants has dealt directly with only the organic constituents of the soil. While the organic complexing fraction of the soil is very

important, it comprises only a small portion of the total Zn present in a soil system. Of the available or 0.1 N HCl extractable Zn present, organic matter has been found to complex anywhere from 25 to 95%. In the present study, organic matter was found to increase the log K stability constant value from 2.62 to 3.06 at pH 3.5 - 4.0 and from 3.22 to 3.48 for pH 4.5 - 5.0 (Table 17). The values represent a very small increase due to organic matter.

The percent organic matter found (3.65) was that which was associated with the clay after clay separation from the soil by differential sedimentation. After H_2O_2 treatments, approximately 0.5% organic matter remained associated with the clay fraction. Even though the organic matter content was decreased around seven fold, the contribution to the log K value of the remaining organic fraction held by the clay could have been considerable. If the organic fraction--humic or fulvic acid--is extracted from the soil, as most other investigators on stability constants have done, the extraction procedure is certain to change some of the properties of the organic matter and thus change some of the stability constant values. Therefore, differences in stability constants, for the organic fraction of soils are easily realized.

Due to the lack of values to which the calculated stability constants can be compared, a general discussion on the limitation of the accuracy of these values would be appropriate. Several major problems are encountered when

the determination of stability constants is carried out by the ion exchange method. First of all, in the calculations it is assumed that only one complex (Zn-ligand) is formed in appreciable concentrations. The possibility of only this one species being present in a soil clay is quite remote. In the soil, Zn has been found to adsorb onto calcareous materials (Jurinak and Bauer, 1956), form $Zn(OH)_2$ (Jurinak and Thorne, 1955), and found in crystal lattices (De Mumbrum and Jackson, 1956).

The second major difficulty is in the adsorption of clay onto the resin. According to Rossotti and Rossotti (1961), the value of the partition coefficient (P_1) can be determined from the (x-axis) intercept on Figures 8 and 9. In order to accomplish this, a value for (Ch) in the term $\frac{P_o - q_B}{Ch}$ needs to be given. The uncertainty of exactly what value should be used for (Ch)--such as moles or grams of clay--makes the partition coefficient determination very difficult. If the value is given for (Ch) in terms of moles of clay as in Table 17, the partition coefficient ranges from 5 to 16%, indicating a large amount of the Zn-clay species has been adsorbed by the resin. If this is in fact true, the value calculated for the stability constant would be in error. However, if two or more complexing species are present, the simple intercept method for determining P_1 can not be used. Work by Dr. B. G. Ellis on the partition coefficient of a Cu-gluconate, ion exchange equilibrium

substantiated the fact that if two complex species are present, P_1 values can not be determined from the x axis intercept.

The large adsorption values--5 to 16%--calculated in this study, indicate that either two or more complex species of Zn-ligand are present or that the equation for determining P_1 does not hold true for very low resin weights.

In summary, all investigations to date, have primarily considered organic matter as being one of the most important sources of Zn to the plant, and thusly have only calculated stability constants for the organic fraction of soils. The plant undoubtedly can utilize Zn from more than one source in the soil. With this view, the author contends that an overall stability constant for a Zn-clay organic matter complex would help soil scientists to predict the behavior of Zn in the soil system.

Zn Adsorption

According to the Langmuir isotherm, the fraction of Zn adsorbed to the soil is related to the equilibrium Zn concentration. The main advantage of applying the Zn adsorption isotherm to soils is that it provides a method to describe the behavior of the adsorbed Zn. If data follows the Langmuir equation, two facts are known concerning Zn adsorption: (1) the adsorption maximum; (2) a constant related to the energy of adsorption. It may be

possible to relate adsorption maximum to various soil parameters eg. surface area, organic matter content, or C.E.C. The constant related to the energy of adsorption would be important in determining what fractions of the soil might be most important in Zn adsorption.

Tables 19 and 20 give the data for the Langmuir adsorption plots shown in Figures 10 and 11. Table 21 gives the adsorption maximum for the Wisner silty clay loam soil as well as (K), the constant proportional to the free energy of adsorption. Figure 11 is a typical Langmuir plot showing a straight line relationship, while Figure 10 deviates slightly from the normal plot in that the data follows two straight line relationships--one at low equilibrium and one at high equilibrium Zn concentrations. Adsorption maximum for the peroxide treated soil was 0.31 me/100g soil. Values of 2.76 or 5.20 me/100gm soil were obtained for the untreated soil for low and high Zn equilibrium concentrations respectively.

This data agrees well with previously determined adsorption maximums. Udo et al. (1968) found that adsorption capacities varied from 0.90 to 5.1 me/100gm soil compared to C.E.C.'s of 3.3 to 17.3 me/100gm respectively.

Soil factors affecting the adsorption maximum of Zn have been investigated by many workers. The most important ones include surface area, percent organic matter, $CaCO_3$ content, pH, and percent clay in the soil. In determination of adsorption capacities the ionic strength of the

Table 19. Langmuir adsorption parameters for a Wisner silty clay loam soil.

Zn Added	(C) Equilibrium Zn in Solution	(X/m) Fixed Zn	$\frac{C}{X/m}$
(ppm) or (M/l) X 10^4	(M/l) X 10^4	(mg/100gm)	
5	0.769	0.051[a]	2.34	0.022
10	1.538	0.103	4.67	0.022
20	3.076	0.162	9.48	0.017
40	6.15	0.38	18.77	0.020
80	12.31	1.031	36.7	0.028
120	18.46	2.06	53.3	0.039
200	30.77	6.09	80.2	0.076
250	38.46	8.69	96.8	0.090
300	46.15	11.62	112.3	0.103
350	53.85	16.00	123.0	0.130
400	61.54	19.85	135.5	0.146
450	69.23	24.98	143.8	0.174
500	76.92	30.12	152.1	0.198
625	96.15	40.00	183.0	0.219

[a]Values are the average of three replications.

Table 20. Langmuir adsorption parameters for a Wisner silty clay loam soil treated with H_2O_2.

Zn Added	(C) Equilibrium Zn in Solution	(X/m) Fixed Zn	$\frac{C}{X/m}$
(ppm) or (M/l) X 10^4	(M/l) X 10^4	(mg/100gm)	
5	0.769	0.24[a]	3.43	0.140
10	1.538	0.46	7.04	0.131
20	3.076	1.18	12.3	0.190
40	6.15	3.29	18.6	0.354
80	12.31	9.11	20.8	0.876
120	18.46	14.46	26.0	1.11
160	24.62	19.38	34.0	1.14

[a]Values are the average of three replications.

Table 21. Calculated adsorption maximum and E values.

	Slope	Adsorption Maximum (b)		Intercept	K
		(mg/100g)	(me/100g)	(M/l) X 10^4	(X 10^{-4})
Untreated Soil					
Part B	0.0051	195.0	5.20	0.044	0.12
Part A	0.0097	103.4	2.76	0.016	0.60
H_2O_2 Treated Soil	0.0867	11.54	0.31	0.090	0.96

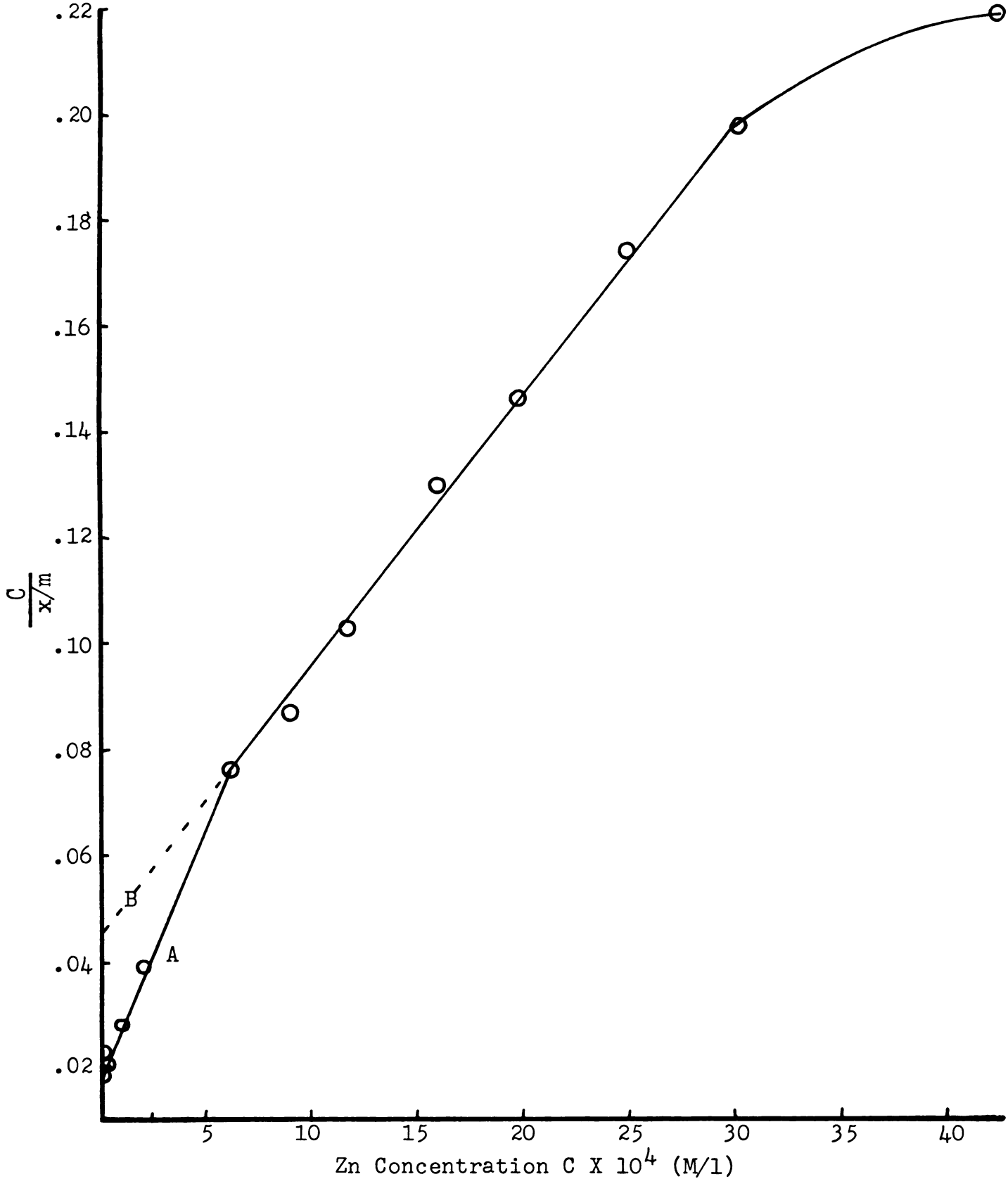

Figure 10. Langmuir plot of Zn adsorption data for a Wisner silty clay loam soil.

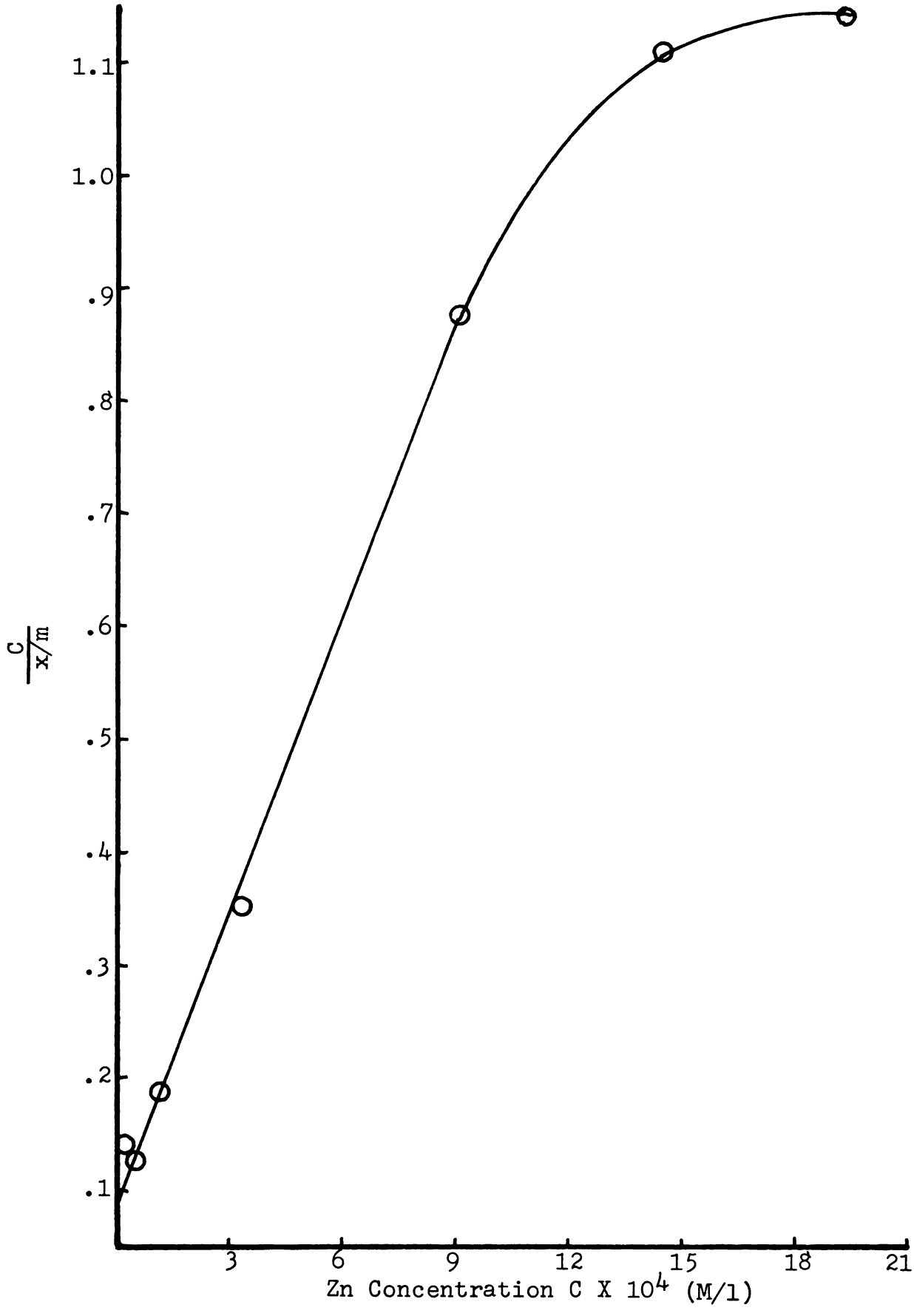

Figure 11. Langmuir plot of Zn adsorption data for a H_2O_2 treated Wisner silty clay loam soil.

equilibrium solution (0.1 N KCl in the present study) is also important. Himes and Barber (1957) developed a regression equation where Zn adsorbed was related to Zn added, pH, and the ionic strength of the solution. In investigating the chelating ability of the soil, they also found that removal of organic matter by oxidation with H_2O_2 destroyed the ability of the soil to chelate Zn; whereby, removal of hydrous silicates did not influence the retention of Zn by the soil.

Another factor that should be considered is the possible precipitation of $Zn(OH)_2$ in determination of adsorption isotherms. The initial pH of the soil suspensions was adjusted to 4.5 and after equilibrium was reached, pH's of the suspensions ranged from 3.0 to 3.9. At these low pH's, it is highly doubtful that precipitation of $Zn(OH)_2$ will occur. Bingham et al. (1964) found in studies of metal retention in relation to pH of equilibrium solution that no retention of Zn occurred in excess of the C.E.C. provided the pH of the system was below 5.5 to 6.5. Solubility product calculations indicate that Zn additions (0.7 to 96.2 x 10^{-4} M) to these soils are far below the Zn concentrations required for $Zn(OH)_2$ precipitation (approximately 1 M at pH 5). Other work by Udo et al. (1968) showed that below the Langmuir adsorption capacity, the $Zn(OH)_2$ ion product in the solution phase increased with Zn additions, while above this point the $Zn(OH)_2$ product remained relatively constant.

The values of the bonding term (K), Table 21, calculated from the Langmuir equations, provides an estimate of the average bonding energy of Zn on the major adsorbing surfaces. These energies have a large error term inherent in the method of calculation. The H_2O_2 treated soil has a higher energy of adsorption indicating that the Zn adsorbed to the surface of the clay is held very tightly in comparison to that Zn held or chelated by the organic matter in the soil. The linear fit of the data with the Langmuir isotherm suggests near uniformity in bonding energy of Zn for the concentrations of Zn used.

The difference in adsorption maximums for the H_2O_2 treated and untreated soils is quite striking (Table 21). The untreated soil has adsorption maximums approximately 10 to 20 times that of the soil with the organic matter destroyed. This information would show the importance of organic matter on Zn adsorption and would support the findings of Himes and Barber (1957) in that retention of Zn by soils is largely a function of the amount of organic matter present.

It is interesting to note that the adsorption maximum for the H_2O_2 treated soil (0.31me/100gm) is much less than the C.E.C. for the Wisner soil. This fact might indicate that the isotherm plotted would only represent a small fraction of the Zn that is capable of adsorption onto the clay. Perhaps if a wide enough equilibrium concentration of Zn could be used, a series of lines could be drawn whose adsorption maximum sum would approximate the C.E.C. The Langmuir

plot drawn in this work may only be the first very small fraction of Zn that is most strongly bound to the clay.

The untreated soil may show two of these possible adsorption maximum lines (Figure 10). Line (A) would approximate a small fraction of Zn that is tightly bound to the clay or clay-organic matter complex, while line (B) would represent a less strongly held Zn fraction eg. organic matter. Because the H_2O_2 treated soil gave a much higher bonding energy for Zn, it seems plausible to suggest that this Zn may not be as available for plant use as the more weakly held Zn in the untreated soil. This suggests that Zn-organic complexes may be very important in Zn fertility.

The Langmuir surface adsorption equation can be used as a means for characterizing Zn as a solid-phase supply in relation to solution characteristics. While this characterization does not necessarily identify the soil phase, it does have the advantage of describing the system with a set of constants which, when known, can be used to predict the effect of placing a stress on the soil system.

Equilibrium Relationships of Zn With EDTA in Soils

EDTA is involved in equilibria with a variety of cations in the soil solution, each of which is concurrently involved in equilibria with one or more soil phases. The relative importance of each EDTA complex present could, in principle, be calculated from formation constants, solubility products,

and other appropriate equilibrium constants. This is not possible, in general, because of the heterogeneous, poorly defined nature of participating soil phases. For this reason, most investigators of EDTA reactions in soil have been primarily empirical, Lindsay and Norvell (1969) and Lindsay, Hodgson, and Norvell (1967).

An equilibrium expression can be derived which will relate the amount of free Zn in solution with the amount of Zn complexed with the EDTA. In this manner, it was hoped that free Zn could be related to variables such as pH, Ca concentration, and CO_2 levels in the soil solution. The hypothesis that $ZnSiO_3$ controls the solubility of Zn in soils was also to be investigated. However, just prior to writing of this thesis, the original authors of the paper proposing the $ZnSiO_3$ hypothesis, Lindsay and Norvell (1969), published a retraction showing the impossibility of formation of this compound in soils.

A small percentage of the EDTA, as determined by ^{14}C analysis, was lost from the solution by adsorption onto the soil. The total loss ranged from 0 to 21%. This agrees well with that found by other workers, Hill-Cottingham and Loyd-Jones (1957). Due to this loss, the results are expressed as the percentage of EDTA remaining in solution that was complexed with Zn.

The Zn measured in solution was assumed to be present as an EDTA complex because Zn could not be detected when a

1×10^{-4} M $ZnCl_2$ solution was reacted with the soil suspension for several hours in the absence of EDTA.

In interpretation of ZnEDTA reactions, the Ca competition must be considered. The importance of Ca competition would be much easier to evaluate if CaEDTA could be measured directly. However, it is difficult to determine the concentration of the EDTA in the presence of excess Ca and various other EDTA complexes. In this work, any EDTA in solution which is not present as a ZnEDTA ligand will be assumed to complex Ca, due to the stable complex which Ca forms with EDTA (log K of 11.41) and due to the relative abundance of Ca in the soil solution (Tables 22 and 23).

The reactions of ZnEDTA are summarized in Figures 12-15 and Tables 22-23. The difference in soils used for the experiments was in the manner of pH adjustment. Soil (A), Table 22, was adjusted to various pH's by adding small amounts of dilute HCl or saturated $Ca(OH)_2$ thus leaving solid $CaCO_3$ in the soil. Soil (B), Table 23, was first washed with dilute HCl and then small increments of $Ca(OH)_2$ were added to effect a pH change. By washing with acid, soil (B) had no native or solid $CaCO_3$ present.

Figures 12 and 13, show major differences for the two soils with respect to percent EDTA complexed with Zn at 30 days equilibrium. Percentages ranged from 31 to 55 and 13 to 32 for soils (A) and (B) respectively. Reasons for these large differences can be attributed to the amounts of Ca present in the two soils. From Tables 22 and 23 at 30 days

Table 22. Effect of CO_2 level and time on pH, ZnEDTA, and Ca concentration for soil A.

	3% CO_2			0.3% CO_2			0.03% CO_2		
6 HOURS									
Initial pH	7.29	7.47	7.71	7.29	7.47	7.71	7.29	7.47	7.71
ZnEDTA X 10^{+5} M	7.34	7.23	7.78	7.34	7.25	8.20	7.15	7.55	8.66
Ca X 10^{+3} M	3.54	3.10	1.48	2.89	2.28	0.98	2.88	2.20	0.96
$\frac{[ZnEDTA]}{[EDTA]}$ X 100	83.3	77.7	80.6	77.8	75.1	80.2	75.5	80.8	85.3
Actual pH	7.20	7.34	7.47	7.41	7.54	7.76	7.44	7.65	7.88
18 HOURS									
ZnEDTA X 10^{+5} M	5.23	5.18	6.52	4.80	4.72	6.35	5.31	4.89	6.75
Ca X 10^{+3} M	2.82	2.47	1.14	2.81	2.23	1.10	2.82	2.07	0.89
$\frac{[ZnEDTA]}{[EDTA]}$ X 100	59.4	64.1	77.8	59.0	59.7	70.2	62.0	60.8	74.8
Actual pH	7.51	7.61	7.79	7.53	7.65	7.83	7.62	7.70	7.86
2 DAYS									
ZnEDTA X 10^{+5} M	4.60	4.68	5.83	4.14	3.89	5.57	3.65	3.85	5.57
Ca X 10^{+3} M	3.36	2.83	1.23	3.25	2.59	1.12	2.84	2.13	0.88

Table 22, cont'd

	3% CO_2			0.3% CO_2			0.03% CO_2		
$\frac{[ZnEDTA]}{[EDTA]}$ X 100	49.1	50.7	62.8	43.9	42.1	57.2	39.8	41.5	60.4
Actual pH	7.45	7.49	7.55	7.33	7.59	7.61	7.61	7.79	7.78
10 DAYS									
Initial pH	7.29	7.47	7.71	7.29	7.47	7.71	7.29	7.47	7.71
ZnEDTA X 10^{+5} M	4.20	4.12	5.05	3.79	3.29	4.97	3.63	3.38	3.78
Ca X 10^{+3} M	3.39	3.05	1.26	2.89	1.71	1.32	2.95	2.27	1.02
$\frac{[ZnEDTA]}{[EDTA]}$ X 100	46.4	46.1	56.2	43.3	36.0	55.7	38.2	37.7	41.0
Actual pH	7.25	7.45	7.70	7.36	7.67	7.64	7.55	7.65	7.80
Theoretical pH	7.00	7.02	7.21	7.53	7.64	7.70	8.03	8.08	8.26
$[Zn^{++}]$ - log	8.21	8.26	8.48	8.33	8.70	8.46	8.42	8.54	8.84
30 DAYS									
ZnEDTA X 10^{+5} M	3.49	4.25	4.09	3.78	2.89	4.40	2.82	4.17	3.71
Ca X 10^{+3} M	2.33	2.69	1.56	2.39	1.70	1.25	2.19	2.96	1.01

Table 22, cont'd

	3% CO_2			0.3% CO_2			0.03% CO_2		
$\frac{[ZnEDTA]}{[EDTA]}$ X 100	37.9	52.0	54.7	42.1	33.6	48.6	30.7	47.9	40.1
Actual pH	7.49	7.15	7.53	7.28	7.57	7.55	7.65	7.22	7.65
Theoretical pH	7.08	7.05	7.16	7.57	7.64	7.71	8.09	8.02	8.26
$[Zn^{++}]$ - log	8.53	8.21	8.40	8.44	8.75	8.61	8.70	8.24	8.86

Table 23. Effect of CO_2 level and time on pH, ZnEDTA, and Ca concentration for soil B.

	3% CO_2			0.3% CO_2			0.03% CO_2		
6 HOURS									
Initial pH	6.91	7.33	8.04	6.91	7.33	8.04	6.91	7.33	8.04
ZnEDTA X 10^{+5} M	8.35	7.95	7.65	8.35	7.95	8.28	8.20	7.57	7.72
Ca X 10^{+3} M	6.10	5.85	3.93	5.18	5.23	2.45	5.95	5.90	2.30
$\frac{[ZnEDTA]}{[EDTA]}$ X 100	98.1	86.0	85.0	98.8	83.7	87.0	100.0	80.2	82.9
Actual pH	6.63	6.75	7.01	6.98	7.30	7.70	6.90	7.40	7.95
18 HOURS									
ZnEDTA X 10^{+5} M	7.40	6.86	6.46	6.86	7.32	6.00	7.02	5.62	5.84
Ca X 10^{+3} M	6.15	6.78	4.46	6.30	5.69	3.15	6.35	5.76	2.92
$\frac{[ZnEDTA]}{[EDTA]}$ X 100	90.1	78.6	75.5	88.9	82.5	67.6	93.9	64.4	68.5
Actual pH	7.15	6.93	7.03	7.39	7.53	7.73	7.25	7.55	7.91
2 DAYS									
ZnEDTA X 10^{+5} M	6.15	4.54	4.32	4.92	3.94	4.46	4.25	4.54	3.26
Ca X 10^{+3} M	7.05	7.84	5.09	6.05	6.33	3.64	6.18	6.40	2.93

Table 23, cont'd

	3% CO_2			0.3% CO_2			0.03% CO_2		
$\frac{[ZnEDTA]}{[EDTA]}$ X 100	72.1	50.5	48.8	58.4	44.4	48.7	50.0	52.5	37.8
Actual pH	6.96	7.15	7.37	7.45	7.55	7.57	7.58	7.39	7.96
10 DAYS									
Initial pH	6.91	7.33	8.04	6.91	7.33	8.04	6.91	7.33	8.04
ZnEDTA X 10^{+5} M	2.29	2.40	1.74	2.11	1.74	1.74	2.35	2.11	1.49
Ca X 10^{+3} M	5.85	6.83	5.85	5.55	5.97	4.65	5.60	5.85	4.28
$\frac{[ZnEDTA]}{[EDTA]}$ X 100	28.1	29.5	19.0	24.8	19.7	18.7	28.4	24.2	16.5
Actual pH	7.32	7.13	7.80	7.66	7.60	7.80	7.64	7.70	8.10
Theoretical pH	6.88	6.84	6.88	7.38	7.37	7.43	7.89	7.88	7.94
$[Zn^{++}]$ - log	8.31	8.22	8.54	8.41	8.51	8.65	8.33	8.40	8.75
30 DAYS									
ZnEDTA X 10^{+5} M	2.48	2.05	2.72	1.49	1.19	1.31	2.54	1.25	1.27
Ca X 10^{+3} M	6.83	5.48	6.33	5.85	6.46	4.30	5.25	6.20	4.20

Table 23, cont'd

	3% CO_2			0.3% CO_2			0.03% CO_2		
$\frac{[ZnEDTA]}{[EDTA]}$ X 100	30.4	22.7	31.9	17.8	13.1	14.5	30.2	13.9	13.9
Actual pH	6.91	7.78	7.11	7.48	7.59	8.01	7.37	7.83	7.91
Theoretical pH	6.84	6.89	6.86	7.38	7.35	7.44	7.90	7.86	7.95
$[Zn^{++}]$ - log	8.20	8.47	8.20	8.57	8.69	8.82	8.32	8.67	8.85

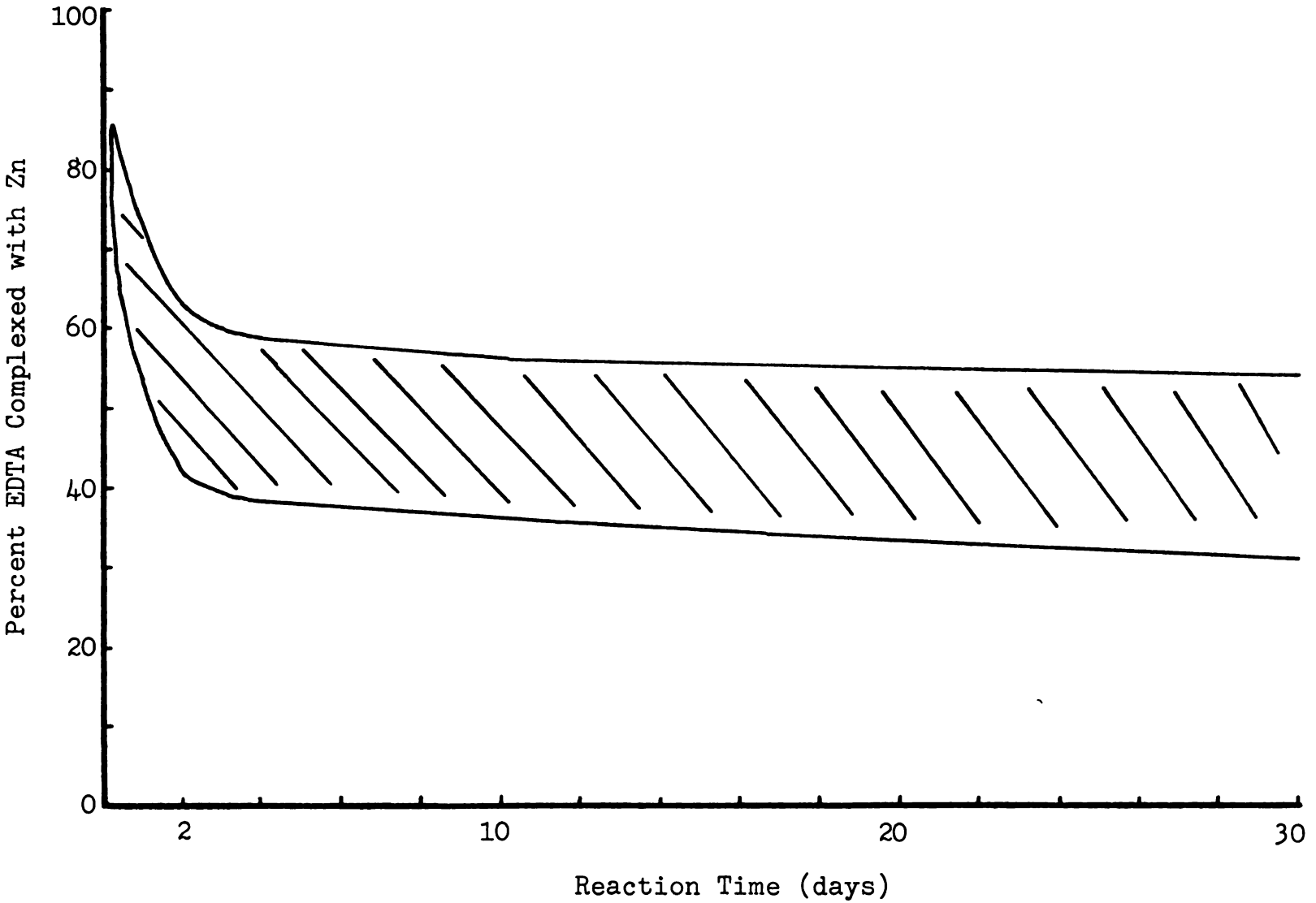

Figure 12. Loss of Zn from ZnEDTA on soil A at pH's 7.29, 7.47, 7.71.

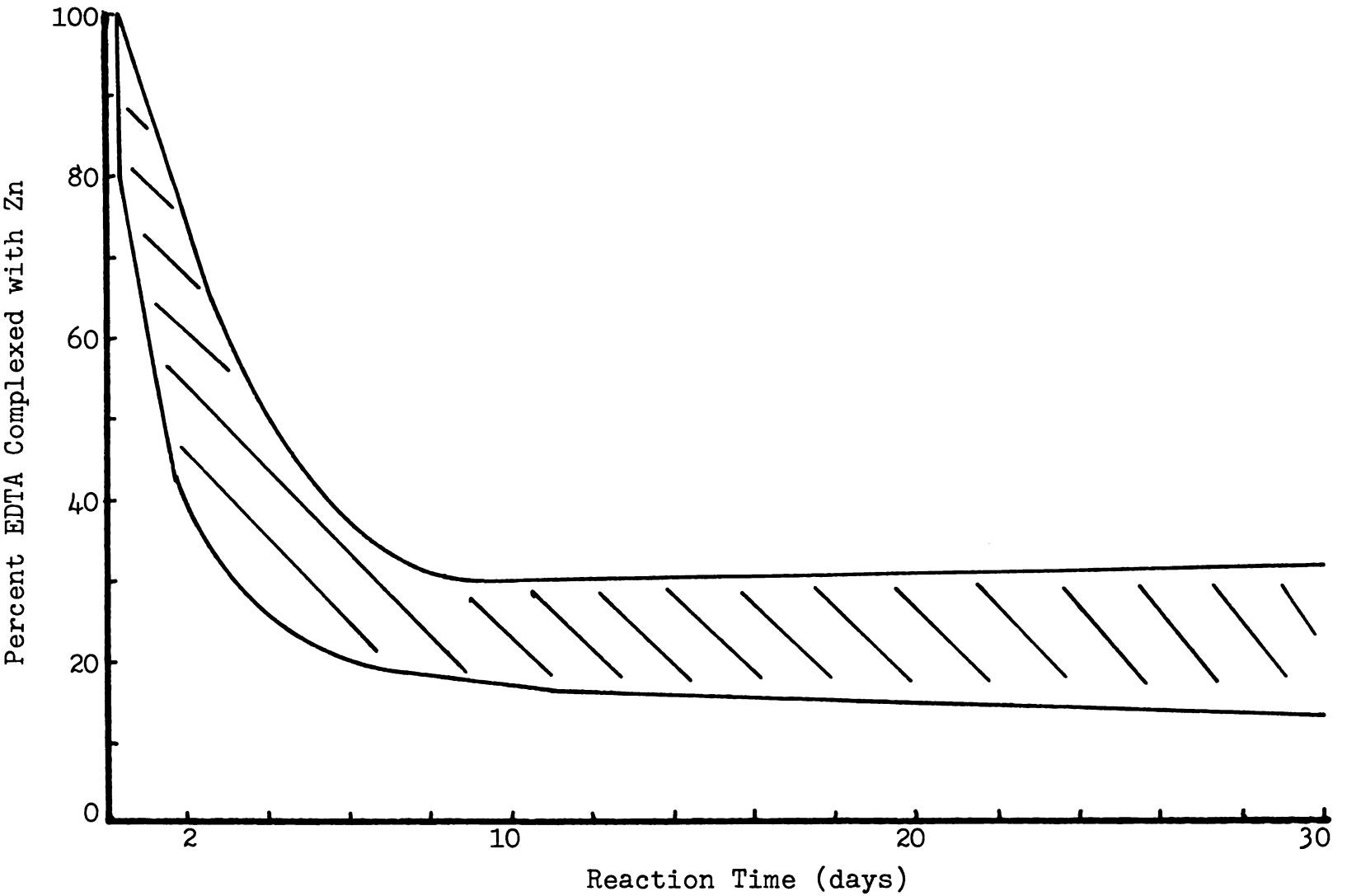

Figure 13. Loss of Zn from ZnEDTA on soil B at pH's 6.91, 7.33, 8.04.

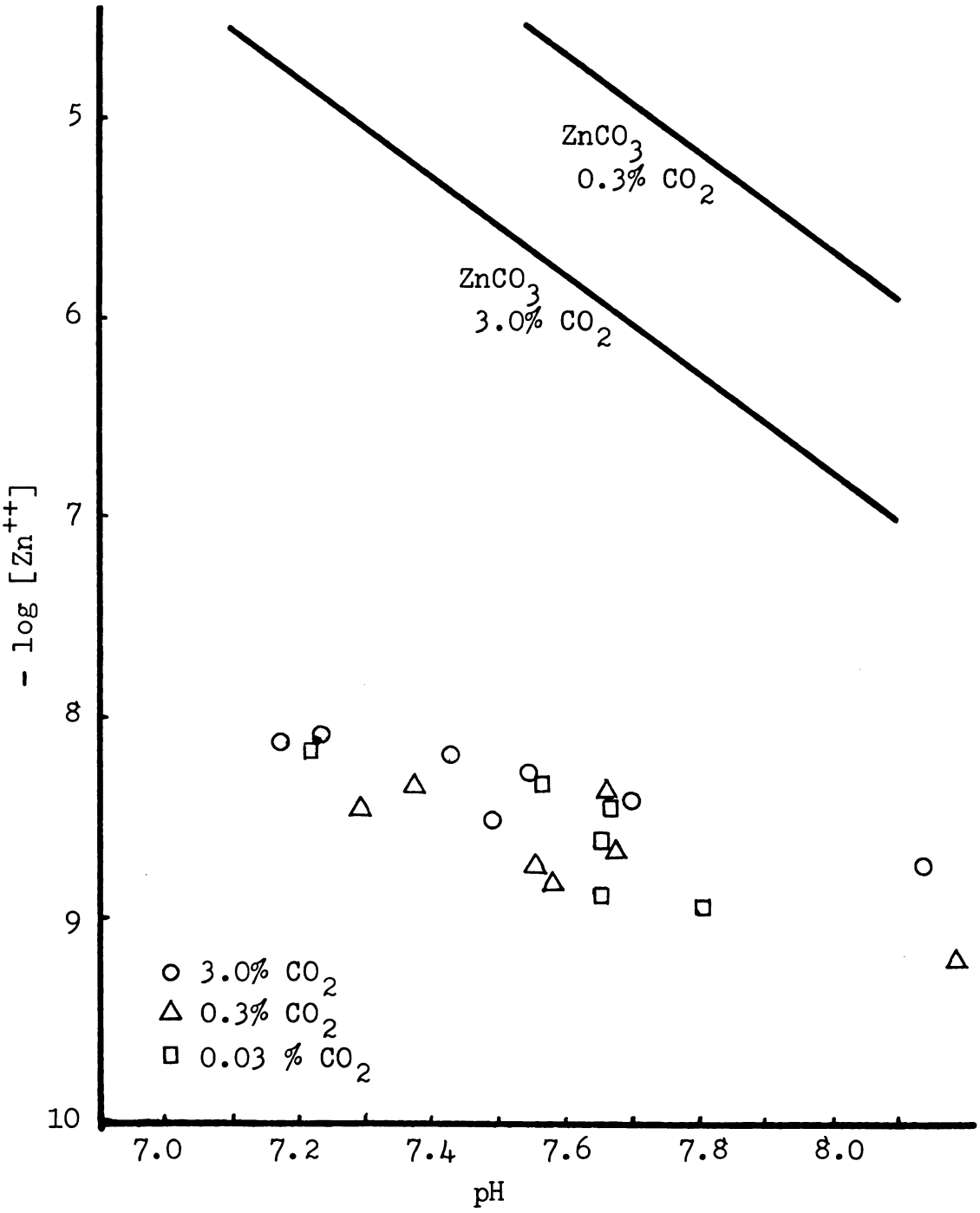

Figure 14. Reaction of ZnEDTA with soil A at different pH's.

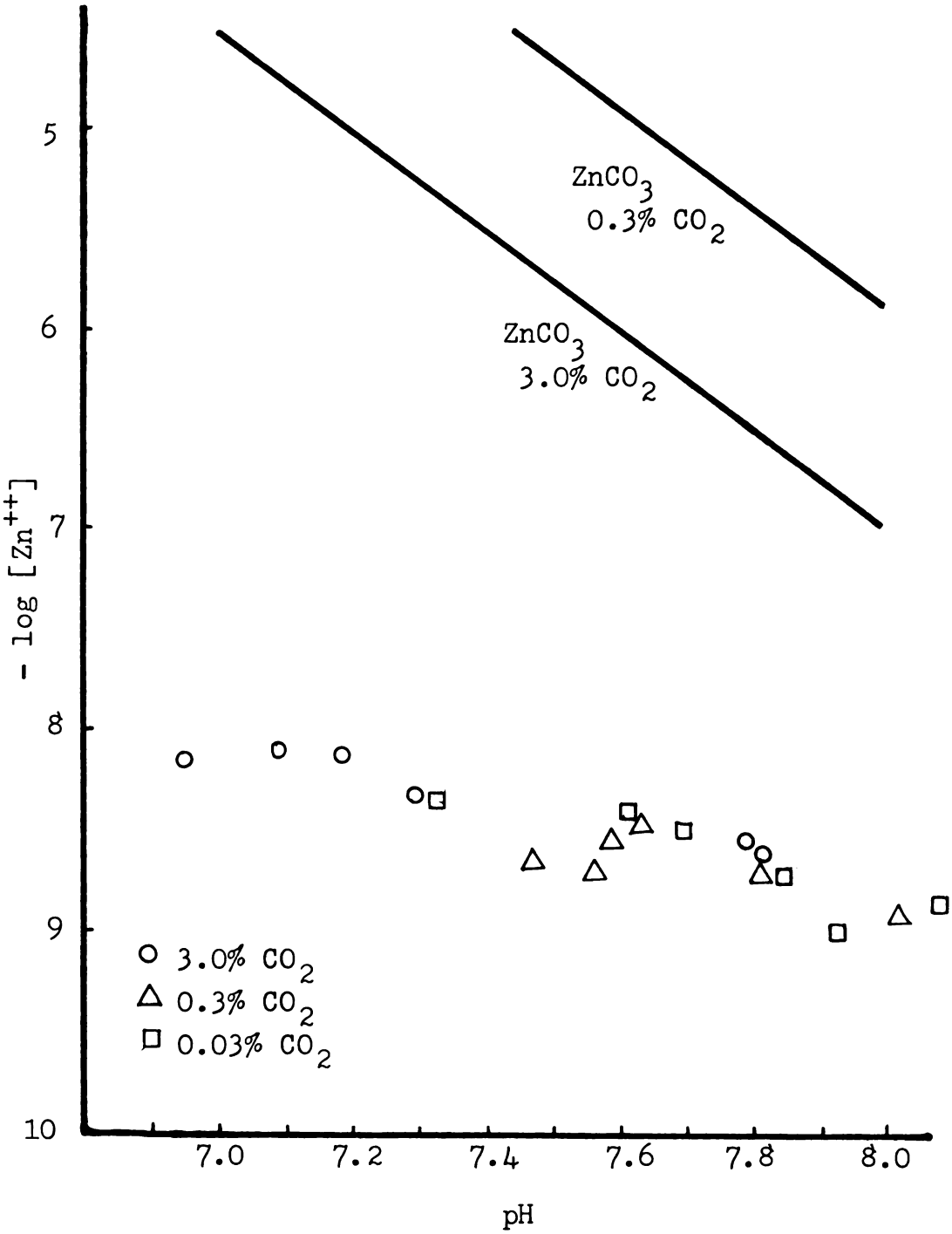

Figure 15. Reaction of ZnEDTA with soil B at different pH's.

equilibrium, approximately $2\frac{1}{2}$ to 6 times as much Ca was found in soil (B) as soil (A). Even though the stability constant for CaEDTA is smaller than that of ZnEDTA (11.41 vs. 17.08), the larger quantity of Ca present would be mass action cause the ZnEDTA to dissociate and thus give smaller amounts of Zn complexed with EDTA.

In these suspensions the loss of Zn from solution was very rapid initially. Further losses occurred quite slowly and in most cases the percentages of ZnEDTA became nearly constant with time. The large majority of Zn lost from the EDTA must have been displaced by Ca because no other metals other than the applied metal and Ca could be found by atomic adsorption techniques. Competition from Ca was also suggested by the very rapid initial displacement of Zn from EDTA which indicated that the displacing cation was present in abundance.

Lindsay and Norvell (1969) in studies of EDTA chelates found that ZnEDTA reached a maximum stability at pH 6.75 and tapered off at pH's on either side of this value. They stated that this maximum stability resulted primarily from decreased competition by Fe for the EDTA ligand as the pH increased to 6.75 and a more rapid decrease in the concentration of Zn than in that of Ca for pH's above 6.75. Therefore, this maximum stability pH represented a balance between the two opposing trends. In the present work, no Fe was found in the soil solution so less than one percent of the EDTA could have been complexed by Fe. Also, the pH

range considered was very narrow (6.9 - 8.1) compared to the pH range of Lindsay and Norvell (1969).

Large differences were also found for the time it takes to reach equilibrium or a constant percent of ZnEDTA ligand. Soil (A) required around 2-4 days for equilibrium while soil (B) required 8-10 days. This difference can be explained by two factors. First, since no $CaCO_3$ was present initially in soil (B), much more Ca was available to react with the EDTA for the first few days or until equilibrium was obtained between Ca, CO_2, and $CaCO_3$. The formation of $CaCO_3$ would remove some of the Ca from solution. The second explanation is that the larger drop soil (B) must undergo to reach the lower percentage of ZnEDTA would normally take a longer period of time.

Using the CO_2 and Ca concentrations as controlling the solubility of $CaCO_3$ and thus the pH of the soil, theoretical pH values for 10 and 30 day equilibrium times are given in Tables 22 and 23. Correlation between the actual pH and theoretical pH is very poor; however, the trend of increasing Ca concentration along with decreasing pH is generally true for the actual pH values determined. A discussion of the analytical problems will follow later.

The range for percentages of ZnEDTA ligand formed for each time period is quite variable but follows the trend of higher Ca concentrations causing lower amounts of Zn to be complexed with EDTA. Data from the experiment indicates that

the amount of Ca present in a soil system is very important in determining the amount of ZnEDTA in solution.

The fraction of EDTA occupied by Zn approaches equilibrium after 10 to 30 days. This indicates that the Zn concentration approaches a constant level and that a temporary equilibrium has been established between the Zn in solution and compounds or other phases in the soil.

In order to calculate the amount of free Zn in solution, the stability constants of Zn and Ca need to be known. From these relationships:

$$Zn^{2+} + EDTA \rightleftharpoons ZnEDTA \qquad K = 10^{17.08} \qquad [14]$$

$$Ca^{2+} + EDTA \rightleftharpoons CaEDTA \qquad K = 10^{11.41} \qquad [15]$$

the following can be written:

$$Zn^{2+} = \frac{(ZnEDTA)(10^{-5.67})(Ca^{2+})}{(CaEDTA)} \qquad [16]$$

Figures 14 and 15 show a plot of soil pH vs. - log (Zn^{2+}) for free Zn values calculated from equation (16) at 10 or 30 days equilibrium as well as theoretical lines for $ZnCO_3$ in equilibrium with 3 and 0.3% CO_2. The equilibrium reactions for the theoretical equilibriums are given below:

$$ZnCO_{3(s)} + 2H^{+} \rightleftharpoons Zn^{2+} + CO_2 + H_2O \qquad [17]$$

$$K = 10^{+7.54}$$

therefore

$$[Zn^{2+}] = \frac{10^{7.54}\ (H^+)^2}{[CO_2]} \qquad [18]$$

At $[CO_2]$ = 0.0003 atmospheres

$$[Zn^{2+}] = 10^{11.06}\ (H^+)^2 \qquad [19]$$

At $[CO_2]$ = 0.003 atmospheres

$$[Zn^{2+}] = 10^{10.06}\ (H^+)^2 \qquad [20]$$

At $[CO_2]$ = 0.03 atmospheres

$$[Zn^{2+}] = 10^{9.06}\ (H^+)^2 \qquad [21]$$

All points for both soils fall below the theoretical lines for the $ZnCO_3$. This compound is far too soluble to account for the free Zn concentrations reported in this paper. Other Zn compounds, such as $Zn(OH)_2$ and $ZnSiO_3$, also would fall in the same general region of the graph as the $ZnCO_3$, thus making these compounds too soluble to control the level of Zn in solution. In addition, the points of the graph seem to follow a trend that indicates a line of a different slope than postulated compounds. This fact would possibly mean that the Zn solubility is not controlled by a divalent form of the ion. No trend for CO_2 levels and Zn solubility was found. It is possible that the postulated compounds for controlling Zn solubility could form as initial reaction

products from Zn fertilizer, and then a more insoluble compound would form at a later time.

Several problems were encountered in determining the equilibrium relationship of Zn with EDTA in soils.

(1) It was very difficult to obtain precise pH measurements in the soil system. As soon as the soils were removed from the CO_2 bubbling apparatus, the pH would slowly begin to change.

(2) It was impossible to obtain uniform CO_2 bubbling rates through the soil suspensions.

(3) Changing the pH of the native soil may have altered chemical as well as physical properties which may be important in Zn solubility.

CONCLUSIONS

(1) Very little movement of $ZnSO_4$ occurred in a soil column after water leachings at all pH's.

(2) At a soil pH of 3.65, 44.9% of the ZnNTA moved 22.5 mm while ZnEDTA immediately dissociated and was essentially immobile.

(3) At soil pH's of 6.3, 7.7, and 8.3, 60 to 65% of the ZnNTA moved 35 mm while 80 - 85% of the ZnEDTA moved 62.5 mm with 125 ml of water leached. ZnEDTA at these higher pH's was the most soluble form of Zn applied to the soil columns.

(4) Different patterns of movement were noted for the chelates at pH's of 6.3, 7.7, and 8.3. ZnNTA showed a tailing off effect for its movement while ZnEDTA moved in a broad peak. This indicates that more ZnEDTA must have remained in a chelated or more soluble form than ZnNTA.

(5) Time or temperature of incubation had no noticeable effect on the movement of the Zn carriers studied.

(6) Organic matter increased stability constant (log K) values for the Zn-clay from 2.62 to 3.06 at pH 3.5 - 4.0 and from 3.22 to 3.48 at pH's 4.5 - 5.0.

(7) As the pH of the clay was increased, the stability constants increased due to more availability of complexing sites.

(8) Adsorption maximums for Zn were much greater in the untreated soil (2.76 to 5.20 me/100gm) than for the H_2O_2 treated soil (0.31 me/100gm). This information indicates the importance of organic matter on Zn adsorption by the soil.

(9) The H_2O_2 treated soil has a higher bonding energy for Zn than the untreated soil.

(10) CO_2 equilibrium studies show no effect on the solubility of Zn compounds in the soil.

(11) $ZnCO_3$, $Zn(OH)_2$, and $ZnSiO_3$ are too soluble to account for the low levels of Zn in the soil solution.

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