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PARTITIONING OF ZINC BETWEEN SOLID AND LIQUID

IN SYNTHETIC AND SOIL MATERIALS

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Boyd G Ellis

Major professor

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PARTITIONING OF ZINC BETWEEN SOLID AND LIQUID IN SYNTHETIC AND SOIL MATERIALS

By

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ABSTRACT

PARTITIONING OF ZINC BETWEEN SOLID AND LIQUID IN SYNTHETIC AND SOIL MATERIALS

By

Richard Cleveland Zielke

Metal activities in soil solutions and natural waters are primarily a function of partitioning between colloidal and aqueous phases. For Zn^{2+}, solution activity is likely controlled by adsorption-desorption rather than precipitation-dissolution reactions. Frequently adsorption is irreversible and the resulting solution activity is much lower than analytical detection limits. A batch equilibrium technique based on isotopic dilution and mass balance was developed to study adsorption and desorption of trace Zn^{2+} by Ca smectite (montmorillonite # 25, Upton, Wyoming). The method was verified analytically and hence applicable to the study of desorption in clay minerals. Desorption hysteresis commonly occurred when <1% of the CEC was occupied by Zn.

Three isotherms (Linear, Freundlich and Langmuir) were tested to determine their utility in characterizing Zn desorption. The Freundlich equation proved most useful and enabled adsorption to be viewed over several decades of Zn^{2+} activity. Comparison of model ion exchangers (Ca Dowex 50W-X8, Ca Chelex-100) with Ca smectite and Charity clay (aeric haplaquept) allowed insight to mechanisms operating in adsorption, desorption and hysteresis. For smectite, reversibility was attributed to an ion exchange mechanism while hysteresis was attributed to strong bonding at broken edge OH. Hysteresis was ubiquitous in Charity clay and was attributed to broken edge OH, Al and Fe oxides, free carbonates and organic matter.

The pH dependency of hysteresis at broken edge OH was investigated. Only at pH 3.5 was adsorption by Ca smectite completely reversible. As the pH increased, adsorption and hysteresis increased, however reversibility at high surface occupancy of Zn verified that smectites can mask precipitation in alkaline solution.

The effect of initial exchange ion on hysteresis was also investigated using homoionic Na, K, Rb and Cs smectites. Adsorption followed the lyotropic series, however adsorption and desorption by Rb and Cs smectites was sterically inhibited at interlayer exchange sites because Rb^+ and Cs^+ have a demonstrated ability to reduce swelling of smectite minerals thus reducing the rate of Zn diffusion into and out of the interlayer positions. Hysteresis in this case was merely an artifact of nonequilibrium.

DEDICATION

TO MY MOTHER, BROTHERS, THEIR WIVES AND CHILDREN

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INTRODUCTION

Zinc retention by soils and soil materials has been the subject of extensive research due to the fact that Zn is both an essential micronutrient which has been deficient in many soils and a potential environmental hazard. Several soil components have been isolated and shown to effect removal of Zn from soil solution. These include Fe, Al and Mn oxides, $CaCO_3$, humic materials and clay minerals. In order to elucidate the mechanism of adsorption, studies using synthetic and natural components ensued; however this approach has been criticized as being environmentally unrealistic owing to the complex interaction of soil colloids. Ironically, it was the comparison of single components and whole soils that revealed these interactions.

Recently, there has been a resurgence of adsorption studies utilizing whole soils and/or soils which are treated to selectively remove individual fractions associated with Zn retention. In light of the heterogenous nature of soil, it is not surprising to find conflicting evidence for adsorption and precipitation. The interrelationship between surface area, structure and reactivity of clays with metal emphasizes the importance of pure clay mineral studies. The role of organic matter in adsorption, chelation and mobilization of metals has also been demonstrated. The observation that metal retention by some soils closely resembles the behavior exhibited by amorphous Fe and Al oxides, and the subsequent role of surface hydroxyl groups in "specific adsorption" has furthered the debate over the mechanism of Zn retention in soils. Indeed, progress in this area of research can be likened to Jenny's (1961) soil acidity merry-go-round in which each turn produces a different though not unfamiliar view of what was termed the soil chemistry landscape.

There can be little doubt that no single component controls Zn retention and release in all environmental systems. Certainly, the often reported failure of solubility principles to characterize Zn^{2+} reactivity in soil is reason enough to pursue an adsorption approach. Reports that Zn is mainly associated with the mineral fraction in many soils and sediments, combined with the recent interest in clay minerals as sorbents for metallic and radioactive waste is the basis for selecting smectite clay as the adsorbent phase in the present study.

Although adsorption of Zn by smectite minerals has been studied and numerous fractionation and extraction schemes have been proposed, few, if any contemporary studies have focused on true desorption over a wide range of surface compositions. Many such studies have failed or neglected to control pH or ionic strength, or have attempted desorption using unrealistic concentrations of acids, competing ions or chelating agents.

The objective of this study was to characterize Zn desorption in response to pH and surface composition variables. More specifically, the objectives were to (i) verify the applicability of the principles of isotopic dilution to adsorption of trace amounts of Zn^{2+} by smectite, (ii) determine the applicability of selected adsorption isotherms in characterizing desorption phenomena for some model exchangers, (iii) determine the effect of pH on adsorption and desorption of Zn^{2+} by Ca-smectite, and (iv) determine the effect of initial exchange ion on Zn^{2+} adsorption and desorption by smectite. The results of these basic studies will hopefully have application to waste disposal engineering as well as conventional agriculture.

LITERATURE REVIEW

Mechanistically, removal of Zn^{2+} from solution by soils and clays affords extreme ambiguity. In absence of microrganisms, living plant roots and soluble organic ligands, two general processes are possible; precipitation and adsorption. For the purpose of this discussion, adsorption is the general process whereby solute adheres to the surface of a soil particle. Chemisorption is adsorption resulting from a specific chemical reaction, hence the term "specific adsorption". Ion exchange is the adsorption process by which charged solutes exchange with ions on a soil particle. Precipitation is a related process in that it is generally preceded by adsorption; the difference being that adsorption is a two dimensional process, while precipitation is a three dimensional process (Corey, 1981).

The reactivity of solutes with soils and clays is generally characterized by an adsorption isotherm. Because of their empirical nature, adsorption isotherms fail to distinguish between the totality of processes resulting in the attainment of equilibrium, and hence cannot be used to distinguish the sorption mechanism (Veith and Sposito, 1977). A detailed description of various adsorption isotherms and their use is given by Travis and Etnier (1981). Of these, three have found extensive use in describing the equilibrium between reactive solutes and soil components. These are the Linear, Freundlich and Langmuir isotherms.

The Linear adsorption isotherm is an empirical equation that relates the quantity of solute adsorbed (X) per unit mass of adsorber (m) to an equilibrium solution concentration or activity (C). Thus,

$$X/m = kC$$

where k is the distribution coefficient.

Few adsorption processes in soil obey this equation, but it has been used in conjunction with transport equations to describe radionuclide transport from geologic repositories (Burkholder, 1976) and adsorption of Na^+ and Mg^{2+} in soil columns (Lai et al., 1978). Frequently the observed isotherm is nonlinear (Frost and Griffin, 1977; Maquire et al., 1981; Brummer et al., 1983; Harter, 1983), depicting a rapid rise in adsorption followed by a bending over or tailing off to a constant value. One consequence of the asymptotic behavior at high equilibrium solute levels is that it provides first-hand observation of the adsorption capacity. Also the isotherm allows direct viewing of the relationship between solute and solid. McLaren et al. (1983) used this fact to characterize Cu^{2+} desorption hysteresis from humic acid, Fe and Mn oxides and montmorillonite.

Several researchers have described Zn adsorption using the nonlinear equation proposed by Freundlich (1926),

$$X/m = KC^{1/n}$$

where n and K are empirical constants. The equation may be linearized by taking the log of both sides:

$$\log(X/m) = 1/n \log(C) + \log(K)$$

Thus a plot of log(X/m) vs log(C) yields a straight line if the data conform to the Freundlich equation. The equation has one advantage in that it can be used to view adsorption over several orders of magnitude; however, like the Linear isotherm it fails to predict the adsorption capacity. Furthermore, log-log plots tend to minimize data variability and the two constants allow for easy curve fitting.

The Freundlich isotherm has been used to characterize desorption hysteresis. Barney (1984) used the ratio of the Freundlich exponents N_s/N_d (where N_s and N_d are the measured exponents for sorption and desorption, respectively) as a measure of the magnitude of hysteresis in radionuclide desorption from Columbia River basalt materials. Elrashidi and O'Connor (1982) used the Freundlich equation to describe Zn sorption and desorption from nine soils of varying physical and chemical properties. Desorption of Zn from all soils was extremely hysteretic even after five desorption cycles using .01 $\underline{N}$ $CaCl_2$.

The Langmuir equation (1918), unlike the others, is derived from the kinetic theory of gases. It's adaptation to solid-liquid adsorption phenomena in soils was proposed by Boyd et al. (1947). Of the many forms derived, two have found frequent usage:

$$C/X/m = 1/Kb + C/b$$

$$X/m = KbC/(1+KC)$$

where K is a measure of the bond strength, b is the adsorption maximum and C is the ion activity.

In applying the Langmuir equation monolayer adsorption and uniform bonding energy are assumed. Based on the heterogeny of soils and clays, seldom are these assumptions met. Nonlinearity has been attributed to sites of differing bonding energy, hence two surface isotherms have been proposed (Shuman, 1975, 1977). This approach has been the subject of recent controversy (Sposito, 1982; Posner and Bowden, 1980), and it was suggested that independent evidence for sites of different bonding energy be provided before attempting to use the two surface equation. Curvilinear isotherms have also been attributed to the a lack of consideration of desorbed ions in exchange processes (Griffin and Au, 1977; and Harter and Baker, 1977). Since extreme variability can result from the division of the measured quantities (C) and X/m, no attempts to use the Langmuir equation to describe desorption have been reported.

Any discussion of Zn^{2+} adsorption by smectites should logically be preceded by a brief description of their chemical nature in relation to their properties. Smectites are layer lattice silicates formed through weathering of igneous rocks such as granite and basalt. Their behavior and abundance in soils and sediments make smectites an important class of minerals from both an agricultural and environmental standpoint. Among the most noted properties affecting ion adsorption are the tremendous surface area (8×10^5 m^2 kg^{-1}) and high CEC (80-150 cmol(+) kg^{-1}).

Smectites are comprised of a central alumina octahedra sandwiched between two silica tetrahedra. The tips of the two tetrahedra are oriented such that apical O are shared with O of the alumina octahedra. The result is a continuous two dimensional network extending in the a and b dimension with individual 2:1 units stacked in the c dimension (Grim, 1968). Depending upon the layer charge, O atoms of adjacent structural units form bonds which may be cleaved to allow lattice expansion. The magnitude of the surface charge and occurrence of exchangeable cations between structural units, in accordance with the principal of electrical neutrality, is the result of localized electron density due to substitution of Al^{3+} for Si^{4+} in the tetrahedral and Mg^{2+} and Fe^{2+} for Al^{3+} in the octahedral layers. This type of surface charge is termed permanent CEC. For the dioctahedral mineral montmorillonite #25 used in this study, the CEC (90 cmol(+) kg^{-1}) is mostly attributed to octahedral substitution while the swelling properties are attributed to the moderate surface charge and hydrated nature of exchangeable cations.

In addition to lattice substitution, cation exchange sites are thought to arise from the existence of broken bonds in the a-b dimension. Such broken O bonds and edge OH's are considered to undergo ionization and exchange under alkaline conditions and hence are termed pH dependent sites (Borchardt, 1977). Helfferich (1962) generalized ion exchange on soil colloids as being an electrostatic phenomenon which is diffusion controlled, stoichiometric and reversible.

There are several reports of non-reversible exchange of cations in pure mineral studies involving both neutral salts and transition metals. The inability to attain the same position of equilibrium when approached from either direction has been termed hysteresis or fixation. Vanselow (1932) observed hysteresis in Ca^{2+}-NH_4^+ exchange on bentonite. Wiegner (1935) attributed irreversibility to the existence of sites having different geometries and bonding energies. Based on electrostatic principles, broken edge OH's, octahedral substitution and tetrahedral substitution should provide for a range of sites with different bonding energy.

Some researchers have attributed hysteresis to the imperfect dispersion of flocculated clays and resulting inaccessibility of exchange sites (Van Bladel and Laudelout, 1967; Tabikh et al., 1960). Marshall (1964) attributed hysteresis to the possibility of attaining minimum free energy at more than one substrate composition. More recently, Maes and Cremers (1975) considered hysteresis in Zn^{2+} exchange with smectite to be composition and pH dependent. Adsorption was completely reversible at low surface occupancy and pH, but was neither stoichiometric nor reversible at high surface occupancy. The reaction could be made reversible by decreasing the pH. Due to the apparent role of OH^-, hysteresis was attributed to specific bonding. The validity of this work must be questioned since specific bonding , if it occurs, is considered a high affinity phenomenon and hence is expected at low surface occupancy.

The nonreversible sorption of Zn by bentonite was reported by Elgabaly (1950). He proposed that Zn not removed by 1 M neutral NH_4(OAC) became fixed in alumina octahedra resulting in a permanent loss of CEC. DeMumbrum and Jackson (1956) furthered this concept by proposing specific adsorption of Zn by montmorillonite. Based on perturbations of OH in IR studies, Zn retained in excess of the CEC was thought to be associated with octahedral OH groups. Tiller and Hodgson (1962) proposed that Zn^{2+} specifically adsorbed by montmorillonite in the presence of excess electrolyte (thereby eliminating nonspecific electrostatic sorption) was of two forms. One species exchangeable with Cu^{2+}, Ni^{2+}, Mn^{2+} and Fe^{2+} was considered to be associated with broken edge OH's, while the smaller nonexchangeable fraction was the result of lattice penetration.

Specific adsorption (of Cu^{2+}) on smectite has been challenged by McBride and Mortland (1974). Using IR, XRD, ESR and thermal methods, Cu^{2+} was shown to enter the hexagonal holes of the silicate structure upon dehydration. Reduction in the CEC was attributed to further penetration into the unoccupied hole in the octahedral layer. Upon rehydration, Cu^{2+} in hexagonal positions was free to move, but octahedral Cu^{2+} remained fixed, resulting in permanent loss of layer charge. Since the temperature used by DeMumbrum and Jackson (1956) was not sufficient for total dehydration of Cu^{2+}, lattice penetration could not have occurred. It was suggested that excess Cu retention was the result of incomplete removal of $Cu(OAC)_2$ while the IR shift was attributed to formation of K smectite during the preparation of a KBr pellet. As a result, specific adsorption via this mechanism at temperatures < 150 C seemed unlikely.

The reaction of silicic acid with montmorillonite is also thought to result in the formation of specific adsorption sites for transition metals (Hingston et al.,1972), although this interaction is considered to be a surface adsorbed layer rather than lattice penetration (Tiller, 1967).

Several factors have been shown to affect adsorption of Zn^{2+} and other metals by smectite. Nelson and Melsted (1955) observed that the relative adsorption of different cations in clays was $H^+ > Zn^{2+} > Ca^{2+} > Mg^{2+} > K^+$, and suggested that retention of applied Zn may be affected by ions on the sorption complex. It is likely that the H^+ was really Al^{3+} in their experiments due to clay lattice breakdown. Garcia-Miragaya and Page (1977) determined the effect of initial exchangeable ion on sorption of Cd by montmorillonite. Sorption was related to ion size and polarizability factors and decreased along the series $Na^+ > K^+ > Ca^{2+} > Al^{3+}$. Increasing ionic strength has also been shown to reduce metal sorption through complexation with inorganic ligands. In addition, solution composition was shown to affect adsorption since some ligands (eg. SO_4^{2-}) have a larger tendency to form ion pairs in solution (Garcia-Miragaya and Page, 1976; Mattigod et al., 1979). Mattigod and Sposito (1977) compiled experimental association constants for complexation of Zn^{2+} with several inorganic ligands. Such data allow prediction of solution species available for adsorption or transport based on the ionic strength and solution composition.

Since the mechanism of adsorption cannot be determined from adsorption isotherms, indirect methods have been used. The fact that Zn^{2+} adsorption was complete in 15 minutes suggested a ion exchange mechanism (Bourg and Filby, 1974). In a later study this hypothesis was confirmed by demonstrating that Zn^{2+} in solution was in kinetic equilibrium with Zn adsorbed on the surface of montmorillonite (Bourg and Filby, 1976). Bingham et al. (1964) also suggested an ion exchange mechanism since Zn retained by H-montmorillonite did not exceed the CEC if the solution pH was low enough to prevent $Zn(OH)_2$ formation.

Singhal and Kumar (1977) used the exchange isotherm approach of Gaines and Thomas (1953) to calculate thermodynamic parameters for Zn^{2+} exchange on Mg-bentonite. Zinc exchange was found to be endothermic, however the use of thermodynamic approaches has been questioned since exchange is not always stoichiometric or reversible for metals which form hydroxy salts (Maes and Cremers, 1975).

Farrah and Pickering (1978) used selective extraction procedures to characterize nonexchangeable Zn on montmorillonite, illite and kaolinite. Solvents were classified as acid, protonated, ligand and competing species, and their efficiency at removing Zn^{2+} previously sorbed at pH 5 and 7 was evaluated. While EDTA could completely remove sorbed Zn at both pH's, competing species exhibited a pH dependence. At pH 5 where exchange mechanisms have been proposed, sorbed Zn could be removed completely with 0.1 $\underline{M}$ $NaNO_3$ or 0.05 $\underline{M}$ $CaCl_2$. At more dilute concentrations extraction was incomplete, but the fact that some reagents resulted in total recovery is evidence of minimum irreversibility. The pH dependence of extraction suggests that clays are polyfunctional, containing mostly traditional exchange sites with some sites exhibiting affinities for protons and metal ions.

The pH dependency of Zn^{2+} reactions in clays has received considerable attention. While clays appear to act as nucleation centers for Zn-hydroxy species (Farrah and Pickering,1976), there is no known physical evidence for a precipitated solid phase. Much of the evidence is based on solubility principles wherein thermodynamic data is either unavailable or inaccurate due to analytical limitations.

In pure clay studies marked uptake of Zn^{2+} increased when the pH exceeded the formation constant of $Zn(OH)_2$ (Farrah and Pickering, 1977. In other studies adsorption in excess of the CEC has been attributed to the formation of $ZnOH^+$ in bulk solution (Hodgson et al., 1964), but based on calculations of the $Zn^{2+}/ZnOH^+$ ratio, this explanation assumes preference for the hydrolyzed species which seems unlikely from an electrostatic viewpoint (Bingham et al., 1964).

Frost and Griffin (1977) suggested that Zn^{2+} adsorption from landfill leachate occurred by ion exchange at pH's < 6, while precipitation as $Zn(OH)_2$ resulted at higher pH's. Farrah and Pickering (1976) observed precipitation of $Zn(OH)_2$ in pure solution at pH's > 6.5 followed by dissolution and formation of the zincate anion at pH's > 10.5. In the presence of montmorillonite the pH required for precipitation was reduced by 0.5 units. Furthermore, since deprotonation and dissociation did not occur at high pH, chemisorption, not simple precipitation was implied. It should be noted that the conclusions in both these studies were based solely on comparisons of isotherms obtained in the presence and absence of clays in solution.

Up to this point the discussion has focused on reactions of Zn^{2+} involving pure clay minerals. Even in such homogeneous materials there is a general lack of distinction between adsorption and precipitation processes. Furthermore the occurrence of hysteresis, specific bonding and the debate over the role of surface OH's in Zn retention has not been fully resolved. The behavior of Zn^{2+} in the presence of whole soils and soil clays, though not completely different, is unique enough to present a brief review for contrast and comparison. More extensive reviews are given by Lindsay (1972), Nicholas and Egan (1975) and Shuman (1980).

Zinc retention in soils has been attributed to a variety of components besides clay minerals. Some studies have reported significant correlations with the CEC (Shuman, 1975), while others have not (Harter, 1983). Many researchers have emphasized the importance of organic matter (Tyler and McBride, 1982; Kuo and Baker, 1980). Retention of Zn^{2+} by acid subsoils indicates that Al, Fe and Mn oxides may control Zn adsorption (Kalbasi et al., 1979; Shuman, 1976, 1977; Kinniburg and Jackson, 1982; McBride and Blasiac, 1979). Adsorption of Zn on Ca and Mg-carbonates has also been reported (Jurniak and Bauer, 1956). Tiller et al. (1984) fractionated several soils and identified different magnitudes of influence for Zn adsorption by organic matter, Al and Fe oxides and clays. All these materials are presumed to sorb Zn^{2+} through different mechanisms (Cavallaro and McBride, 1984). Regardless of the mechanism of adsorption, soils exhibit a definite pH effect (Kurdi and Donner, 1983; Bar-Yosef, 1979; Harter, 1983).

There is general agreement among researchers that Zn retention in acid soils occurs on a variety of soil components and that Zn^{2+} in the soil solution is controlled by adsorption-desorption reactions. Conversely, there is sufficient evidence for Zn precipitation in alkaline soils. Among the various Zn^{2+} controlling solid phases suggested are Zn-carbonate (Udo et al., 1970), Zn-phosphate (Kalbasi et al., 1978), Zn-silicate (Tiller and Pickering, 1974), ZnS (Kittrick, 1976) and $Zn(OH)_2$ (Saeed and Fox, 1977). Lindsay (1979) reported that many of these compounds were too soluble to control Zn^{2+} activity, and proposed the existence of the unknown compound "soil Zn".

While precipitation of Zn undoubtedly occurs in some soils, distinction between the adsorption-precipitation boundary is difficult. Recently Brummer et al. (1983) investigated this problem, and concluded that Zn^{2+} in equilibrium with whole soils below pH 7 was controlled exclusively by adsorption-desorption processes. In neutral to alkaline soils precipitation is likely only if sufficient Zn^{2+} is added to ensure complete saturation of the adsorption complex. Such observations emphasize the importance of clays, Al and Fe oxides, carbonates, humus and soluble ligands in masking precipitation reactions in soils, and further imputes a need to understand adsorption and particularly desorption phenomenon in soils and clays.

CHAPTER II

ADSORPTION AND DESORPTION OF ZINC BY SMECTITE: COMPARISON OF RADIOTRACER AND ANALYTICAL METHODS

Introduction

Much of the evidence for removal of Zn^{2+} and other heavy metals from solutions by soils and clay is expressed in the form of an equilibrium adsorption isotherm. Failure to attain the same position of equilibrium when approached from the opposite direction is termed hysteresis, and there is extensive chemical evidence for hysteresis when heavy metals are adsorbed by soils (Kuo and Mikkelsen, 1979; Elrashidi and O'Connor, 1982) and pure clay minerals (Tabikh et al., 1960; Van Bladel and Laudelout, 1967; McLaren et al., 1973: Maes and Cremers, 1975).

Because of the large surface area and high CEC, smectite clays are considered to contribute to Zn retention in many soils. Among the mechanisms proposed for Zn retention by smectites are ion exchange (Bourg and Filby, 1976; Bingham et al., 1964), specific adsorption (Brummer et al., 1983), and precipitation (Frost and Griffin, 1977). Generally, cation exchange is suggested if the reaction is rapid, stoichiometric and most importantly, reversible (Helfferich, 1962). Hysteresis is usually associated with non-reversibility in the low end of the adsorption isotherm where precipitation seems unlikely (Tiller and Hodgson, 1960; Tiller et al., 1984). As a result such hysteresis has been termed "specific adsorption".

Demumbrum and Jackson (1956) proposed that specific adsorption of Cu^{2+} and Zn^{2+} was the result of lattice penetration, but McBride and Mortland (1974) have demonstrated using IR, ESR and thermal methods that temperatures exceeding 150 C were required for this process. While these physical methods have proven useful in studying the surface chemistry of clays, they are not sensitive enough or not applicable to the study of Zn^{2+} at low surface occupancy where hysteresis is often observed. Similarly, the ability of clays to effect almost complete removal of metal ions from solution poses some unique analytical problems to characterization of hysteresis using chemical methods.

In the present study ^{65}Zn was used as a tracer to enable characterization of adsorption and desorption of Zn^{2+} by smectite in the trace region. In light of reports of irreversible sorption, precipitation and specific adsorption, there is no guarantee that isotopic equilibria will occur at all substrate levels. The objectives of this study were to determine if the principles of isotopic dilution are valid over a wide range of surface compositions, and to develop techniques to further study adsorption and desorption of trace amounts of Zn^{2+} by Ca smectite. To accomplish these objectives, batch adsorption experiments using ^{65}Zn as a tracer were compared to results obtained over an analytical range in which Zn^{2+} could be determined by standard AA methods.

Materials and Methods

Preparation of Ca smectite

A given weight of smectite (Montmorillonite # 25, Upton, Wyoming) was dispersed in distilled, deionized H_2O by stirring for 24 hr. The colloidal portion was obtained by repeated sedimentation and decantation of the < 2uM fraction. Ca smectite was prepared by equilibrating this fraction with 1 $\underline{M}$ $CaCl_2$ (pH 6.0) for a period of 24 hr. At the end of 5 equilibrations the Ca clay was dialyzed against distilled, deionized H_2O until a negative test for Cl^- was obtained using $AgNO_3$. The resulting clay was suspended in 0.01 $\underline{M}$ $CaCl_2$ and stored until ready for use. The CEC of the clay was determined to be 90 ± 2 cmol (+) kg^{-1} using the NH_4OAC-NaOAC method of Jackson (1958), and the pH was measured to be 6.5 ± 0.2 using a standard reference electrode. XRD was conducted but revealed no other detectable minerals.

Adsorption isotherms

Batch adsorption experiments were initiated by pipetting 25 mL of the rapidly stirred clay suspension into tared 50 mL Oak Ridge centrifuge tubes. The clays were centrifuged at 3000 RPM for 5 min and the mass of clay used ($3.3 \pm 0.1 \times 10^{-4}$ kg) and solvent entrained ($3.6 \pm 0.1 \times 10^{-3}$ kg) were determined gravimetrically on 6 randomly selected tubes by drying at 105 C for 48 hr.

In the nonradioactive study each of the 12 treatments were duplicated and received 21.4 mL 0.01 $\underline{M}$ $CaCl_2$ containing from 13.2 u$\underline{M}$ to 12.8 m$\underline{M}$ Zn^{2+} as $ZnCl_2$ + 1 mL supporting electrolyte. Three replications were run in the tracer study, and 16 initial Zn^{2+} concentrations ranged from 9.3 n$\underline{M}$ to 12.8 m$\underline{M}$. In addition, each tube received 1 mL 1mCi ^{65}Zn L^{-1}. The initial Zn^{2+} concentrations were calculated on a 26 mL basis. All treatments were dispersed on a Vortex mixer and equilibrated for 1 wk at 27 ± 1 C on a wrist action shaker. The samples were separated by centrifugation as previously described, and 4ml was removed for analysis.

For the analytical study Zn^{2+} in the equilibrium solution was determined by standard AA methods using a Varian AA6 with an air-acetylene flame. Radiometric data were obtained on a Packard Tri-Carb spectrometer equipped with a gamma counter by comparing sample radioactivity with that obtained for known ^{65}Zn standards of the same geometry. Equilibrium values were calculated using principles of isotopic dilution. In both cases Zn adsorbed was calculated by difference from the initial concentration. Where appropriate, Zn^{2+} activity was calculated from the extended De Bye-Huckel equation using an ionic strength of 0.03.

Desorption isotherms

Desorption was accomplished by replacing the 4 mL sample with 0.01 $\underline{M}$ $CaCl_2$ and re-equilibrating for 1 wk. At the end of this period radiometric and AA analyses were repeated. In this fashion 6 desorption cycles were accomplished. Data for adsorption and desorption isotherms were calculated using a mass balance approach. For a more detailed description of this calculation the reader is referred to the BASIC computer programs "ZNCALC" and "NUCALC" listed in the appendix.

Results and Discussion

The comparative adsorption of Zn^{2+} as measured by radiotracer or analytical methods is presented as a Freundlich isotherm (Figure 1). Except for the lowest analytically determined Zn^{2+} level, relatively good agreement was obtained between the two methods. Bourg and Filby (1976) also reported that ^{65}Zn was isotopically exchangeable with Zn adsorbed by smectite, however Tiller et al. (1972) reported that ^{65}Zn in alkaline soils did not undergo complete isotopic exchange, possibly due to fixation. Lamm et al. (1963) attributed lower rates of isotopic exchange to high bond energies of P in a Mn phtalate precipitate. Such results suggest isotopic exchange may be useful in studying high affinity adsorption in clay minerals since the existence of such sites could result in non attainment of isotopic equilibria.

Another point to note in figure 1 is that data do not conform to the Freundlich equation. Similar behavior for Zn^{2+} adsorption in soils has been attributed to multiple bonding mechanisms or adsorption at sites of different energies (Kuo and Mikkelsen, 1979; Elrashidi and O'Connor, 1982).

Freundlich desorption isotherms are presented for both methods in figures 2 and 3. Desorption appears to be dependent on the extent of surface coverage. Based on calculations using the CEC, 1 symmetry of Zn^{2+} = 450 uM g^{-1} (or log (X/m) = 2.65). The highest fractional loading of Zn observed in this study was .65 x CEC. In both studies desorption hysteresis begins to occur at log (X/m) = 0.5 or 3.2 uM Zn/g. Thus desorption hysteresis occurs when < 1% of the surface is occupied by Zn. At higher surface occupancies the reaction is completely reversible as

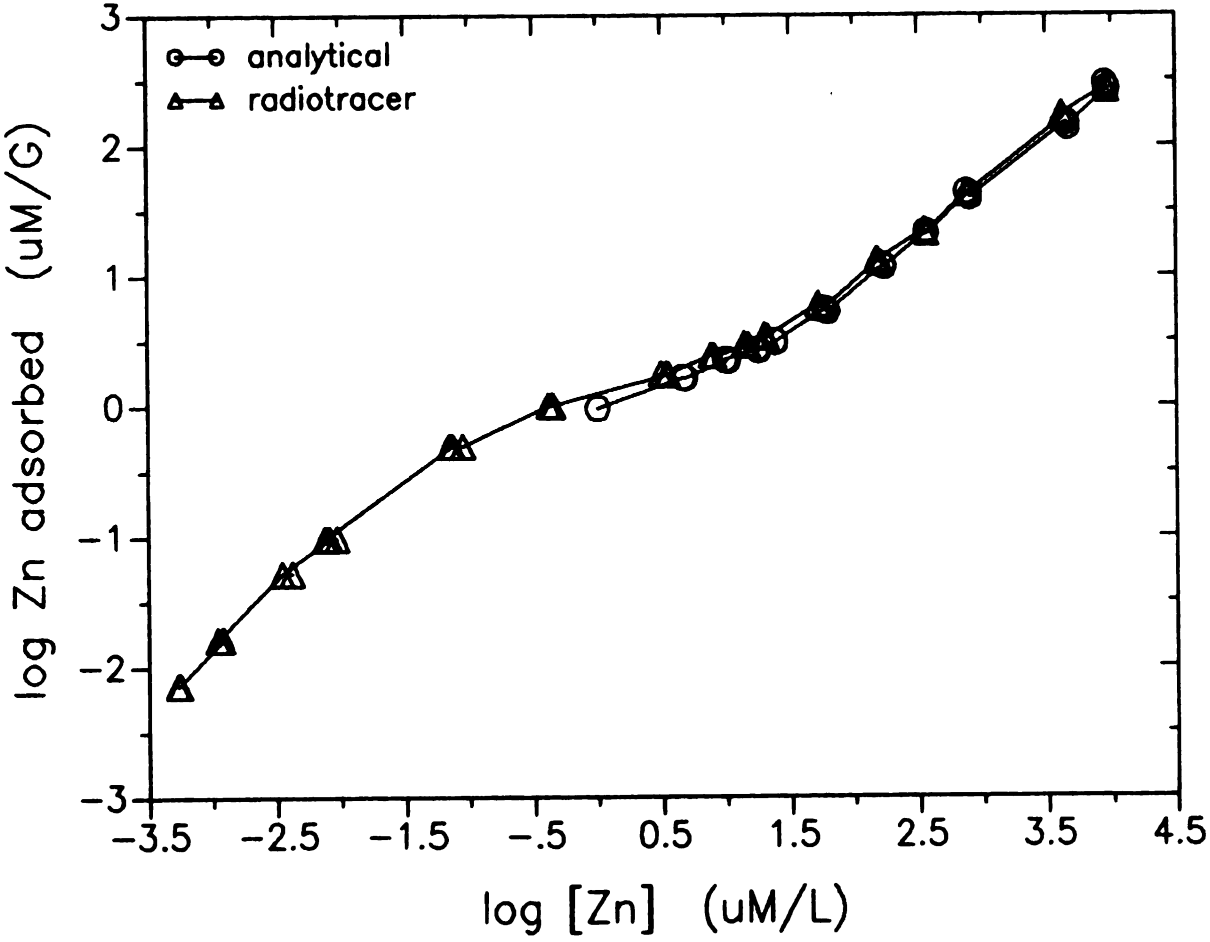

Figure 1. Comparative adsorption of Zn by Ca smectite using analytical and radiotracer methods.

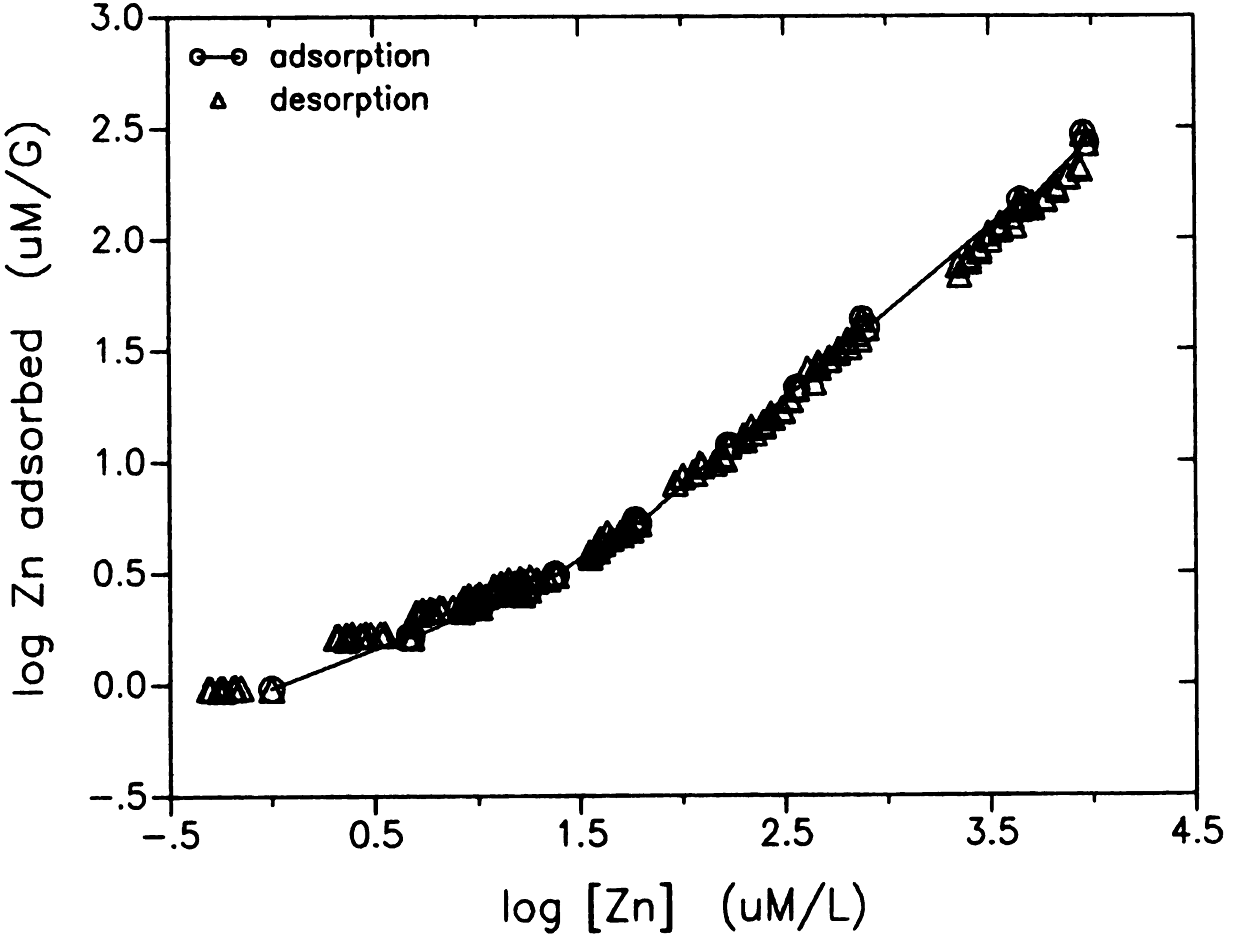

Figure 2. Desorption of Zn from Ca smectite as measured by analytical methods.

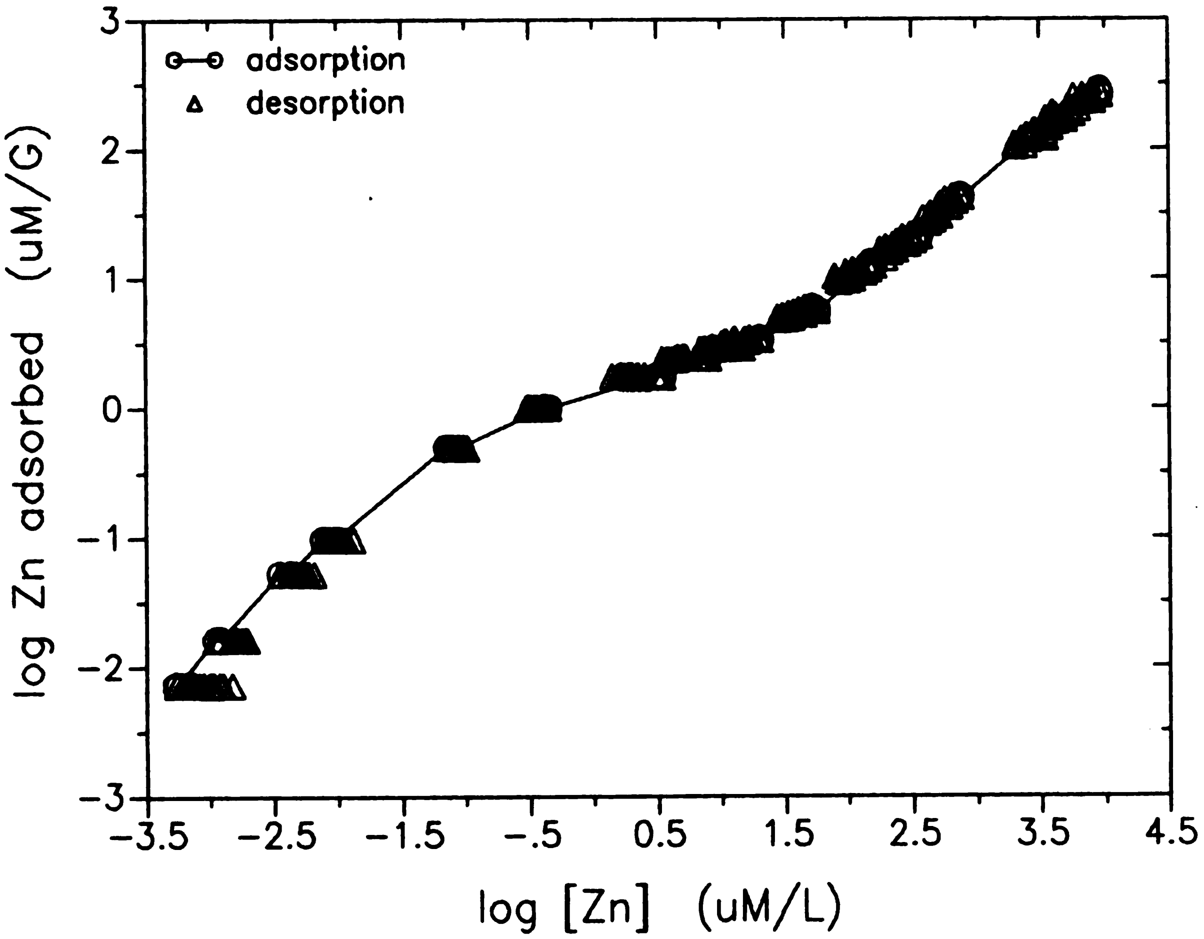

Figure 3. Desorption of Zn from Ca smectite as measured by radiotracer methods.

indicated by the proximity of the desorption points to the adsorption isotherm. The resulting hysteresis may be interpreted as evidence of sites of higher bonding energy at low surface coverage. Tiller et al. (1962) also reported non-reversible adsorption of Zn by smectite at low surface coverage, however Maes and Cremers (1975) observed hysteresis at high surface occupancy. In the later case, smectite was pretreated at pH 3.5 which may have resulted in formation of hydroxy-Al compounds.

There are several interesting points to note in Figure 3. First is the fact that hysteresis begins around the inflection point of the nonlinear isotherm. This again may be an indication of multiple adsorption mechanisms or sites with different bonding energy, however in absence of independent mechanistic evidence, this explanation remains unconfirmed (Veith and Sposito, 1977). Secondly, at intermediate Zn^{2+} levels, sequential dilution of the solution phase produced a horizontal line in the direction of the ordinate (i.e. hysteresis). Desorption points below log (X/m) = -1 depict an increase in solution concentration with no subsequent decrease in solid phase composition, a result which is physically impossible.

Two explanations for this behavior are offered. First, is the probability of experimental error at very low solution levels and the insensitivity of log-log plots to reflect changes in the solid phase composition as a result of minute changes in the solution phase. This fact is evident in both the linear and log transformed data (Table 1). Comparison of figures 3 and 4 further illustrate the insensitivity of the Freundlich equation to depict data variability.

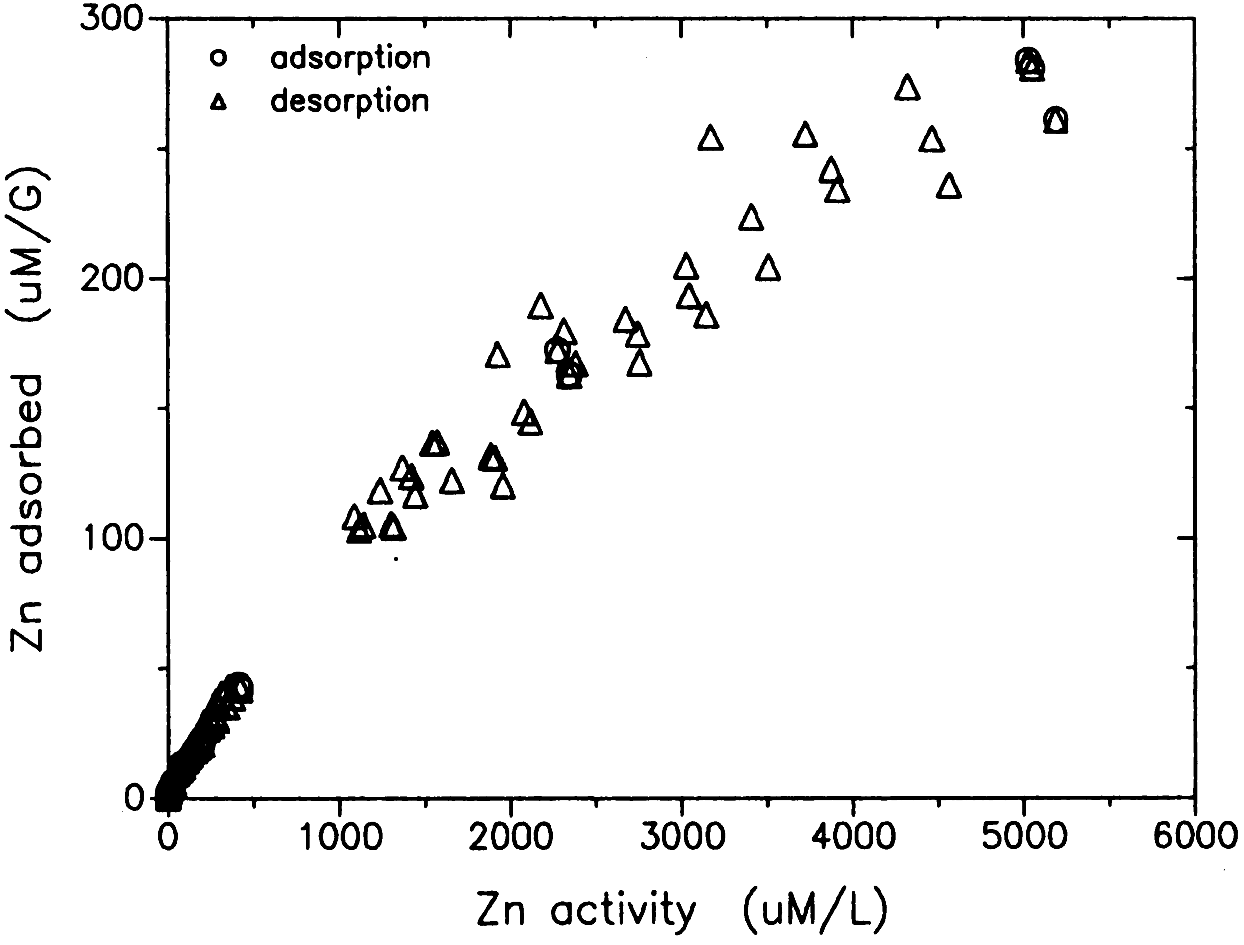

Figure 4. An illustration of the Linear equation data variability for adsorption and desorption of Zn as measured by radiotracer methods.

Second, and more importantly, is the possibility of non-attainment of isotopic equilibria. Experimentally desorption is accomplished by removing and diluting the solution phase. The new position of equilibrium is calculated based on measured changes of ^{65}Zn in solution and mass balance principles. Thus small errors may be compounded in subsequent calculations. Furthermore, if isotopic dilution cannot be assumed then mass balance calculations are not valid. Unfortunately isotopic equilibrium in such dilute solutions cannot be verified analytically since the detection limit of Zn by AA methods was determined to be 0.2 u<u>M</u> (.015 ppm).

Table 1. Comparison of Freundlich and linear isotherm data at the lowest Zn level in the tracer study.

	FREUNDLICH		LINEAR	
#	Log [Zn]	Log uM/g	(Zn) uM/L	uM/g
		REP 1		
1	-3.25609	-2.13917	0.000303	0.00726
2	-2.96962	-2.13949	0.000586	0.00725
3	-2.82611	-2.14226	0.000815	0.00721
4	-3.00788	-2.14093	0.000536	0.00723
5	-3.00788	-2.14165	0.000536	0.00722
6	-2.98833	-2.14258	0.000561	0.00720
7	-2.98833	-2.14333	0.000561	0.00719
		REP 2		
1	-3.27080	-2.13950	0.000293	0.00725
2	-3.18973	-2.13754	0.000353	0.00729
3	-3.14833	-2.13831	0.000388	0.00727
4	-3.18326	-2.13856	0.000358	0.00727
5	-3.21660	-2.13881	0.000332	0.00726
6	-3.11784	-2.13998	0.000416	0.00724
7	-3.08082	-2.14086	0.000453	0.00723
		REP 3		
1	-3.26287	-2.13616	0.000298	0.00731
2	-3.13473	-2.13743	0.000400	0.00729
3	-3.13092	-2.13799	0.000404	0.00728
4	-3.19629	-2.13804	0.000348	0.00728
5	-3.08082	-2.13942	0.000453	0.00725
6	-3.04671	-2.14034	0.000490	0.00724
7	-3.09108	-2.14058	0.000443	0.00723

In the present study a radiotracer method was developed to study trace desorption of Zn from smectite. Two important conclusions may be drawn from this preliminary study. First the principles of isotopic dilution appear to be valid over the adsorption range compared. Since the data in Table 1 reveal that desorption is occuring to some extent, the anomaly in the desorption behavior below Log (X/m) = -1 is attributed to compounded experimental error and insensitivity of log-log plots. Secondly, the extent of non-reversible adsorption is dependent on the surface occupancy. At high occupancy adsorption is perfectly reverible. At Zn occupancies < 1% of the CEC, desorption hysteresis becomes extreme. Interestingly, soil Zn seldom exceeds 1% of the CEC. Hysteresis on clay minerals may therefore contribute to Zn deficiency in plants although the complexity of natural soil systems compared to aqueous solution studies with pure clay minerals is acknowledged. Regardless, the reversibility at high occupancy suggests that pure clays may not be as useful in immobilizing heavy metals in a waste disposal scenario.

Literature Cited

Bingham, F.T., A.L. Page, and J.R. Sims. 1964. Retention of Cu and Zn by H-montmorillonite. Soil Sci. Soc. Am. J. 28:351-354.

Bourg, A.C.M., and R.H. Filby. 1976. Isotopic exchange of Zn^{65} with stable Zn adsorbed on reference clay minerals. Geochim. Cosmochim. Acta. 40:1573-1574.

Brummer, G., K.G. Tiller, V. Herms, and P.M. Clayton. 1983. Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils. Geoderma. 31:337-354.

DeMumbrum, L.E. , and M.L. Jackson. 1956. Infrared adsorption evidence on ecxhange reaction mechanism of copper and zinc with layer silicate clays and peats. Soil Sci. Soc. Am. J. 20:334-337.

Elrashidi, M.A., and G.A. O'Connor. 1982. Influence of solution composition on sorption of zinc by soils. Soil Sci. Soc. Am. J. 46:1153-1158.

Frost, R.R., and R.A. Griffin. 1977. Effect of pH on adsorption of copper, zinc and cadmium from landfill leachate by clay minerals. J. Environ. Sci. Health, Part A. 12:139-156.

Helfferich, F. 1962. Ion exchange, McGraw-Hill. New York.

Jackson, M.L., 1958. Soil chemical analysis. Prentice-Hall. New Jersy.

Kuo, S., and D.S. Mikkelsen. 1979. Zinc adsorption by two alkaline soils. Soil Sci. 128:274-279.

Lamm, C.G., E.H. Hansen, and J.A. Jorgensen. 1963. Isotopic exchange in soil fertility studies. Soil Sci. 94:16-23.

Maes, A., and A. Cremers. 1975. Cation-exchange hysteresis in montmorillonite: a pH dependent effect. Soil Sci. 119:198-202.

McBride, M.B., and M.M Mortland. 1974. Copper (II) interactions with montmorillonite: evidence from physical methods. Soil Sci. Soc. Am. J. 38:408-414.

McLaren, R.G., and J.G. Williams, and R.S. Swift. 1983. Some observations on the desorption and distribution behavior of copper with soil components. J. Soil Sci. 134:325-331.

Tabikh, A.A., I. Barshad, and R. Overstreet. 1960. Cation exchange hysteresis in clay minerals. Soil Sci. 104:219-226.

Tiller, K.G., J. Gerth, and G. Brummer. 1984. The relative affinities of Cd, Ni, and Zn for different soil clay fractions and goethite. Geoderma. 34:17-35.

Tiller, K.G., and J.F. Hogdson. 1962. The specific adsorption of cobalt and zinc by layer silicates. p393-403. In Proceedings of the 9th (1960) National Conference on Clays and Clay Minerals. Pergamon Press. New York.

Tiller, K.G., J.L. Honeysett, and M.P.C. de Vries. 1972. Soil zinc and its uptake by plants. I. Isotopic exchange equilibria and the application of tracer techniques. Aust. J. Soil Res. 10:151-164

Van Bladel, R., and H. Laudelout. 1967. Apparent irreveribility of ion-exchange reactions in clay suspensions. Soil Sci 104:134-137.

Veith, J.A., and G. Sposito. 1977. On the use of the Langmuir equation in the interprtation of "adsorption phenomenon. Soil Sci. Soc. Am. J. 41:697-702.

CHAPTER III

DESORPTION OF ZINC FROM RESIN, SMECTITE AND CHARITY CLAY

Introduction

The use of solubility product principles to describe reactivity of Zn^{2+} with soil components has met with limited success. It is more likely that Zn^{2+} is controlled by adsorption-desorption reactions rather than precipitation-dissolution reactions (Krauskopf, 1972; Brummer et al. 1983). In describing adsorption of heavy metals in soils and clays, extensive use has been made of three models; the Linear, Freundlich and Langmuir equations. However, there are few reports of their use in modeling desorption.

There are no known published reports on the use of the Langmuir equation to model desorption from soil components, however McLaren et al. (1983) used the linear equation to model Cu^{2+} desorption from smectite. Barney (1984) used the Freundlich equation to model desorption of radionuclides from basalt materials. Elrashidi and O'Connor (1982) also used the Freundlich equation to model desorption of Zn^{2+} from nine soils of varying chemical and physical properties. An equilibrium dialysis approach was used by Maes and Cremers (1975) to model desorption of Co^{2+} and Zn^{2+} from smectite. In all cases desorption hysteresis was reported and some nonlinear isotherms were observed.

Historically, nonlinear adsorption isotherms have been attributed to sites of different bonding energy or multiple adsorption mechanisms (Shuman, 1976). It is well recognized that whole soils have an extremely large number of sites which may provide for different adsorption mechanisms or bonding energies. Smectites are considered to have two different types of sites, those resulting from isomorphic substitution, and pH dependent sites resulting from broken edge OH's. Ion exchange resins on the other hand, are considered to have only one type of functional group and bonding mechanism. Comparative studies using simple, well characterized adsorbents could be used to determine the utility of different models to characterize adsorption and desorption in more complex systems such as pure clay minerals and whole soils.

The objective of the present study was to investigate the use of the Linear, Freundlich and Langmuir equations in modeling adsorption and desorption from Ca smectite, a Charity clay, a weak acid cation exchange-chelating resin (Chelex) and a strong acid cation exchange resin (Dowex). The later materials were chosen for their well characterized adsorption mechanism and possible conformity to the assumptions of uniform bonding energy and monolayer adsorption.

Materials and Methods

Preparation of adsorbents

Ca smectite (montmorillonite #25, Upton, Wyoming) was prepared by sedimentation and decantation of the <2uM fraction in distilled H_2O followed by repeated saturation with 1M $CaCl_2$ (pH 6.0). The flocculated Ca-clay was dialyzed against distilled H_2O until a negative test for Cl^- was obtained using $AgNO_3$. The resulting Ca-clay was stored in 0.01 M $CaCl_2$ until ready for use. The Charity clay (aeric haplaquept) was collected from the top 20 cm, air dried, ground to pass a 20 mesh sieve and stored until ready for use.

Ca Dowex (Dowex 50W-X8) and Ca Chelex (Chelex-100) were prepared from their Na forms by column elution with 0.1 M $CaCl_2$ (pH 6.0) until the pH stabilized and Na^+ could no longer be detected in the effluent. The resins were then eluted with 5 bed volumes of distilled H_2O, 5 bed volumes of 0.01 M $CaCl_2$ (pH 6.0), vacuum filtered and stored in sealed containers until ready for use.

Physical and chemical analyses

Table 1 contains results of chemical analyses conducted on the adsorbents. The CEC of the smectite and Charity soil were determined by the NH_4OAC-NaOAC method of Jackson (1958). The CEC of the resins were determined by summation of cations (Ca^{2+} + Na^+) eluted with 5 .020 L washings with 0.1 M HCl. The pH was determined on the equilibrium solutions described below using a combination electrode. The equilibrium pH's for Ca Chelex changed drastically upon Zn^{2+} adsorption and are presented in the discussion section. For the Charity clay, the texture was determined by the hydrometer method and the soil was found to contain 15 % sand, 39.3 % silt and 45.7 % clay. XRD peak intensity, d(001) spacings and CEC determinations after various treatments revealed the clay fraction contained mostly vermiculite with smaller amounts of smectite, chlorite, kaolinite and illite. Organic C was 1.53 ± .08% as determined by a modified Walkley-Black method.

Table 1. Chemical properties and mass of adsorbent used in batch adsorption experiments.

Adsorbent	pH	CEC	mass
		cmol(+) kg^{-1}	kg x 10^3
Ca Dowex	5.9 ± .2	186 ± 5	.1
Ca Chelex	--	161 ± 3	.1
Ca smectite	6.6 ± .2	90 ± 2	.226
Charity clay	7.4 ± .2	29 ± 1	2.35

Batch adsorption experiments

Duplicate batch adsorption experiments were conducted in 50 mL Oak Ridge centrifuge tubes. Adsorption was initiated by adding 28 mL 0.01 M $CaCl_2$ containing 8 levels of Zn^{2+} as $ZnCl_2$ ranging from 0.46 uM to 14.7 mM (Table 3) to a given mass of adsorbent (Table 1). Each sample was radiolabeled with 1 mL, 1mCi ^{65}Zn L^{-1}, and equilibrated on a wrist action shaker for 24 hr at 26 ± 2 C. At the end of this period the samples were centrifuged at 3000 rpm for 5 min and 4 mL was removed for analysis. Three desorption cycles were accomplished by replacing the 4 mL portion with 0.01 $\underline{\underline{M}}$ $CaCl_2$ and equilibrating as described above.

Radiometric data were obtained on a Packard Tri-Carb spectrometer equiped with a gamma counter by comparing sample radioactivity with that observed for known ^{65}Zn standards of the same geometry. Equilibrium Zn^{2+} concentrations or activities were calculated from principles of isotopic dilution and mass balence. In all cases the amount of Zn adsorbed was calculated by difference from the initial concentration.

Adsorption-desorption isotherms

Adsorption-desorption data were calculated and isotherms constructed for the three adsorption equations given below. A detailed description of these equations is not intended, however an excellent review is presented by Travis and Etnier (1981).

1.) Linear equation

$X/m = KC$

where X = amount of Zn^{2+} adsorbed, m = mass of adsorber, K = a distribution coefficient and C = the Zn^{2+} activity calculated from the extended Debye-Huckel equation. For purposes of this discussion, this model will be distinguished from the linear equation ($y = mx + b$) by capitalization (eg. Linear equation).

2.) Freundlich equation

$$\log(X/m) = \log(K) + 1/n \log(C)$$

where X and m are defined as before, K and n are empirical constants and C is the equilibrium Zn^{2+} concentration.

3.) Langmuir equation

$$C/X/m = 1/(Kb) + C/b$$

where K and b are the bonding coefficient and adsorption capacity, respectively, and C is the equilibrium Zn^{2+} activity.

Results and Discussion

Conformity of adsorption data to a particular equation is typically determined by fitting the data to the linearized form of the equation via a linear regression approach. The value of the regression coefficient (r^2) is taken as a measure of fit of the data to the adsorption model (Table 2). A graphical approach is clearly more useful for characterizing desorption, since the proximity of the desorption points to the adsorption isotherm is a measure of reversibility even when nonlinear isotherms are observed (McLaren et al. 1983, Elrashidi and O'Connor, 1982).

Table 2. Summary of linear regression equations for Zn^{2+} adsorption by Ca Chelex, Ca Dowex, Ca smectite and Charity clay.

Adsorbent	Equation	Regression Coefficient	Capacity
		r^2	cmol (+) kg^{-1}
	Linear[1]		
Ca Dowex	$Y = 7.32 \times 10^{-2}X + 21.2$	.97	-
Ca Chelex	$Y = 7.86 \times 10^{-2}X + 133$	.61	-
Ca smectite	$Y = 3.42 \times 10^{-2}X + 11.0$	.97	-
Charity clay	$Y = 1.93 \times 10^{-2}X + 7.68$	.89	-
	Freundlich[1]		
Ca Dowex	$Y = .939X - .972$	.99	-
Ca Chelex	$Y = .458X + 1.36$	.86	-
Ca smectite	$Y = .582X - .182$	.98	-
Charity clay	$Y = .660X - .211$	.94	-
	Langmuir[1]		
Ca Dowex	$Y = 1.08 \times 10^{-3}X + 5.99$	.98	185
Ca Chelex	$Y = 1.60 \times 10^{-3}X + .114$	.99	130
Ca smectite	$Y = 3.32 \times 10^{-3}X + 7.26$	.76	60
Charity clay	$Y = 1.13 \times 10^{-3}X + 1.64$	.98	17.8

[1] Adsorption model.

Adsorption of Zn^{2+} by Dowex is clearly nonlinear for the Linear (Figure 1) and Langmuir (Figure 3) adsorption models, despite the fact that the regression coefficients indicate a good fit to the model (r^2 = .97 and .98, respectively, Table 2). The Freundlich equation is linear over 5 decades of Zn^{2+} in solution (Figure 2). More importantly, adsorption appears to be completely reversible at all surface occupancies observed. The Freundlich equation has one advantage in that it can be used to view adsorption and desorption phenomena over several orders of magnitude at a single glance, however log-log plots are generally insensitive and tend to minimize data variability.

Unlike the Freundlich equation, the Linear model does not mask data variability since the relationship between solid and solution Zn is viewed directly. As such, it appears useful in characterizing desorption (Figure 1), although scale expansion in necessary to view adsorption and desorption of trace amounts of Zn (Figure 4).

That the adsorption data did not conform to the Langmuir equation appears unusual at first glance, since Ca Dowex is expected to fulfill the assumptions of monolayer adsorption and uniform bonding energy. This anomaly may be explained in terms of the ion exchange distribution coefficient D_g where

$$D_g = (\text{ion conc. in resin/ion conc. in soln}) = (X/m)/C$$

Typically D_g decreases as the fractional loading of a particular ion increases, while in dilute solution D_g is constant (Fritz and Schenk, 1979). The adsorption data for Dowex exhibit this behavior. Only at the 2 highest Zn levels does D_g^{-1} change (column 2, Table 3).

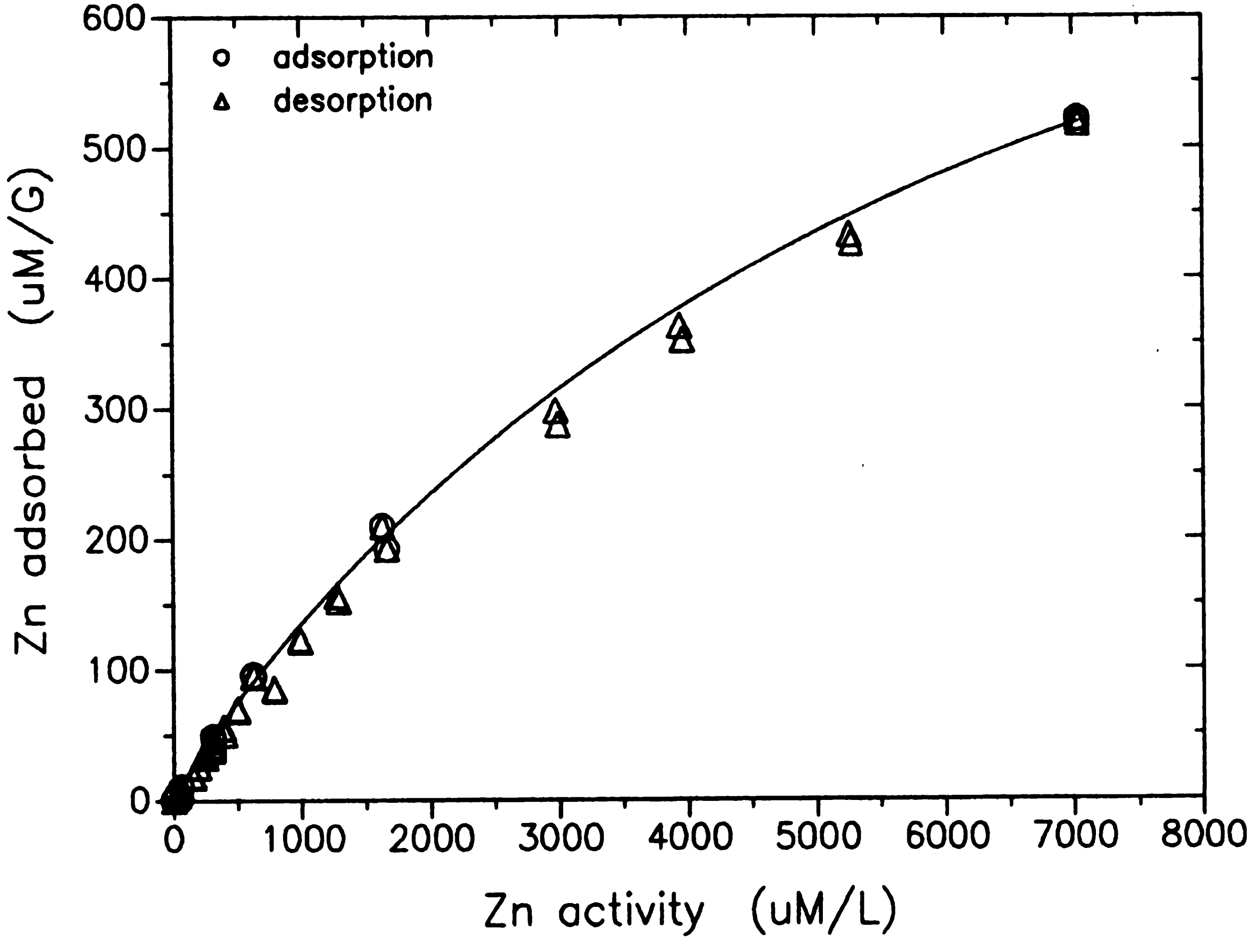

Figure 1. Adsorption and desorption of Zn by Ca Dowex ion exchange resin fit to the Linear equation.

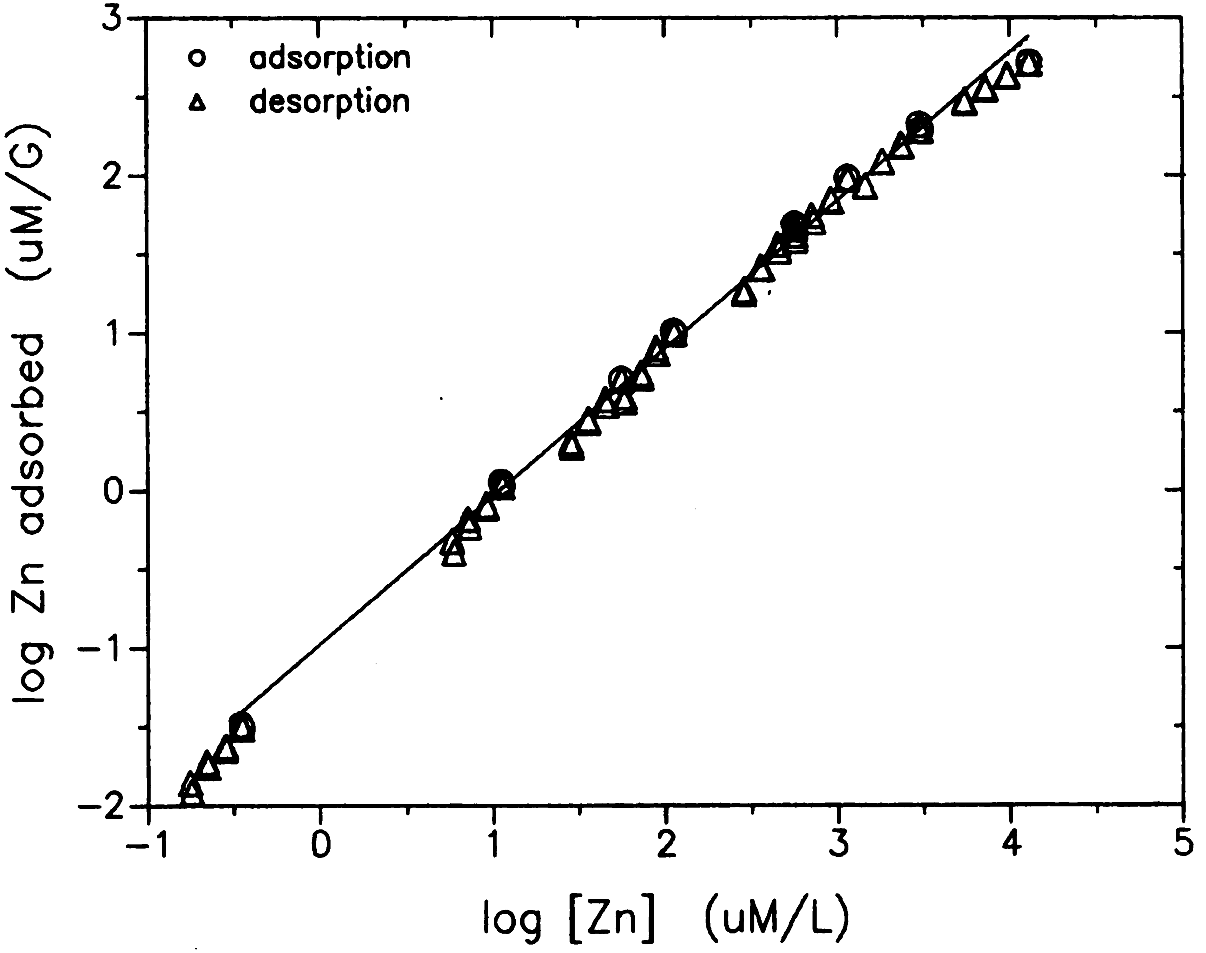

Figure 2. Adsorption and desorption of Zn from Ca Dowex ion exchange resin fit to the Freundlich equation.

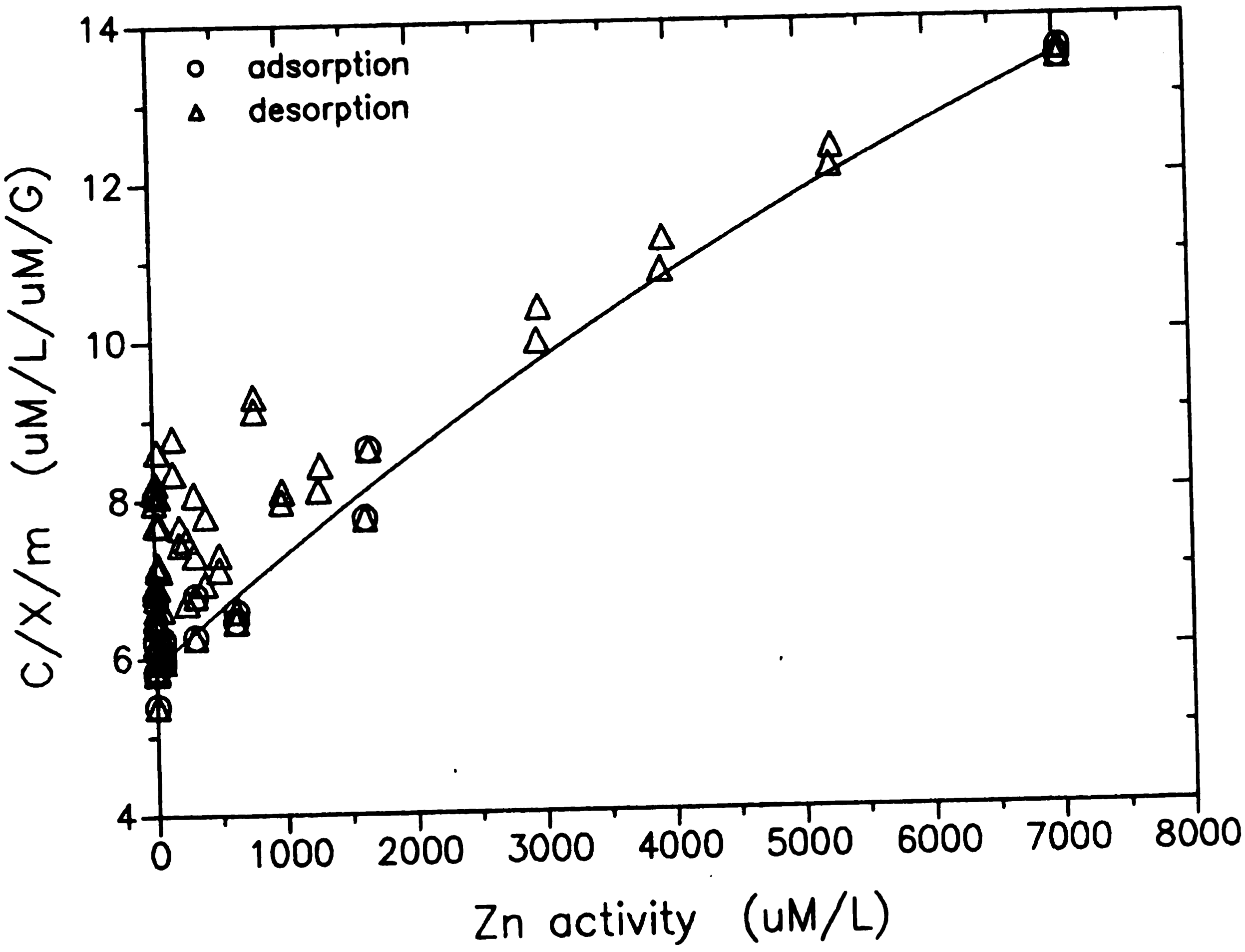

Figure 3. **Adsorption and desorption of Zn by Dowex ion exchange resin fit to the Langmuir equation.**

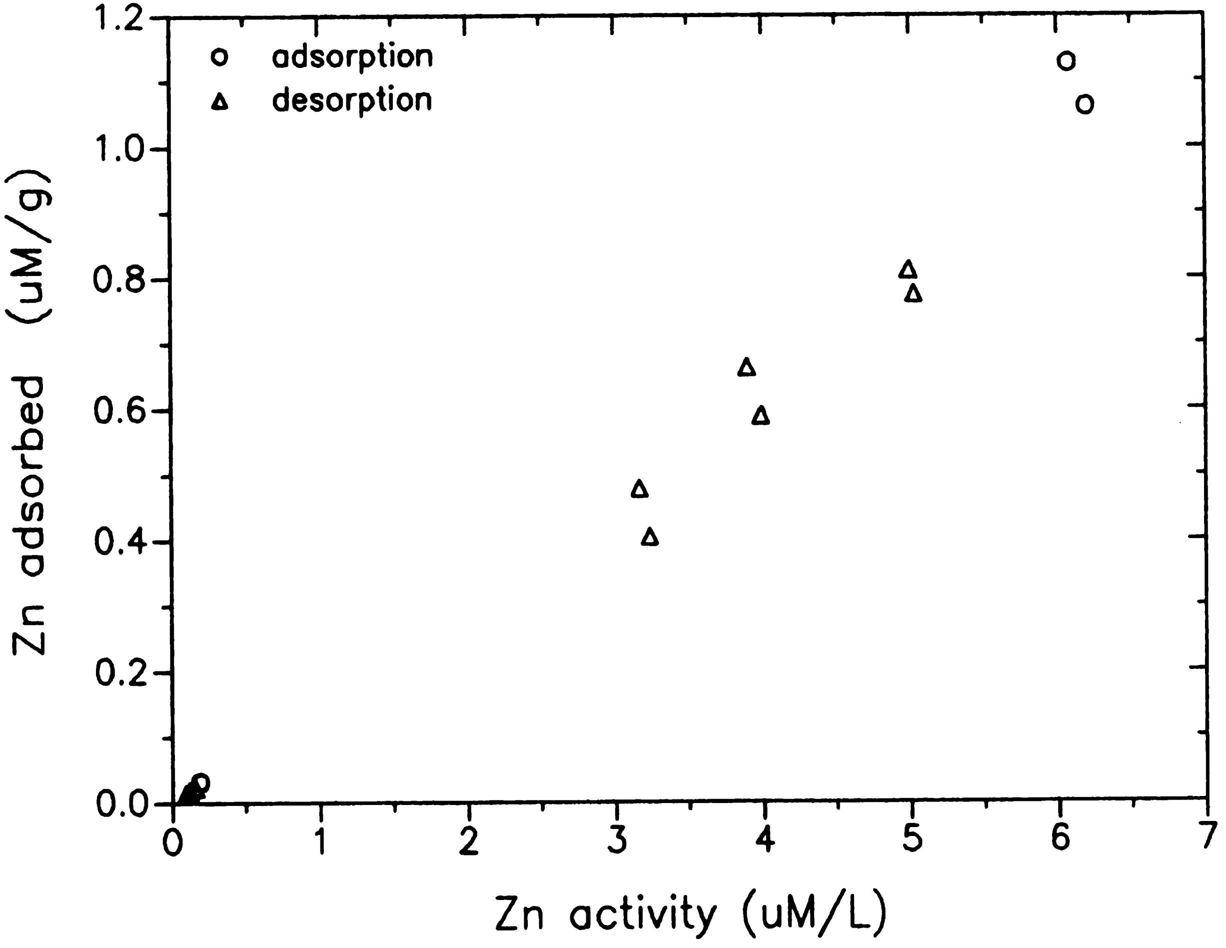

Figure 4. Desorption of trace amounts of Zn by Ca Dowex ion exchange resin as measured by the Linear equation.

Furthermore, variability of C/X/m may become extreme in the Langmuir model since analytical errors are associated with both C and X/m. As a result, the Langmuir equation appears to be of little use in characterizing either adsorption or desorption of Zn^{2+} by Ca Dowex despite the fact that the predicted adsorption capacity (185 cmol (+) kg^{-1}, Table 2) corresponds nicely with the CEC (186 cmol (+) kg^{-1}, Table 1).

Table 3. Values of D_g^{-1} for adsorption of Zn^{2+} on Ca Dowex, Ca Chelex, Ca smectite and Charity clay.

Initial Zn	Ca Dowex	Ca Chelex	Ca smectite	Charity
uM L^{-1}		L g^{-1}		
0.46	6.20	0.00358	0.0527	0.573
	5.81	0.00182	0.0778	0.576
15.0	5.38	0.00556	2.29	0.492
	5.84	0.00284	2.28	0.492
73.0	5.95	0.00358	6.86	0.345
	6.06	0.00380	6.54	0.352
147	5.95	0.00424	8.68	0.476
	6.22	0.00270	8.79	0.495
728	6.77	0.0252	12.4	1.26
	6.25	0.0293	12.6	1.11
1470	6.45	0.461	12.9	2.82
	6.58	0.484	13.9	2.87
3705	7.75	2.39	16.4	11.4
	8.62	2.55	18.3	11.2
14670	13.4	11.1	28.6	49.0
	13.5	10.7	29.0	47.7

Adsorption of Zn^{2+} by Ca chelex did not conform to the Linear model as indicated by graphical methods (Figure 5) or linear regression methods ($r^2 = 0.61$, Table 2). Adsorption is completely reversible above 200 uM Zn g^{-1}, however desorption hysteresis becomes extreme below 50 uM Zn g^{-1} (Figure 6). Adsorption of Zn^{2+} by Chelex also did not conform to the Freundlich model (Figure 7). In fact, there are two linear portions with very different slopes. In soils and clays this behavior has been attributed to sites of uniquely different bonding energies, but in the present case it was assumed that there was only one type of exchange site present. That adsorption conformed to the Langmuir equation (Figure 8, $r^2 = 0.99$, Table 2) is further evidence to support this assumption.

The "two surface" result may be related to reduced selectivity for Zn^{2+} resulting from changes in the pH as the degree of fractional loading increased (Table 4). Hydrogen ions were released into the solution as Zn was adsorbed. Comparison of the Zn adsorption capacity determined from the Langmuir equation (b = 130 cmol (+) kg^{-1}, Table 2) with the CEC(161 cmol (+) kg^{-1}, Table 1) may be an indication of a mixed H^+-Ca^{2+} resin. Hendrickson et al. (1982) also reported that Ca Chelex retained considerable H^+ in the pH range 5.5 - 6.0. More importantly, they observed and quantified the pH dependence of the selectivity coefficient using the following equation:

$$\log K_d = 0.815\text{pH} - 2.37 \quad (r = .986)$$

While this equation may explain the unusual "two surface" behavior, it does not account for the occurrence of desorption hysteresis in very dilute solution. Furthermore, these results are in

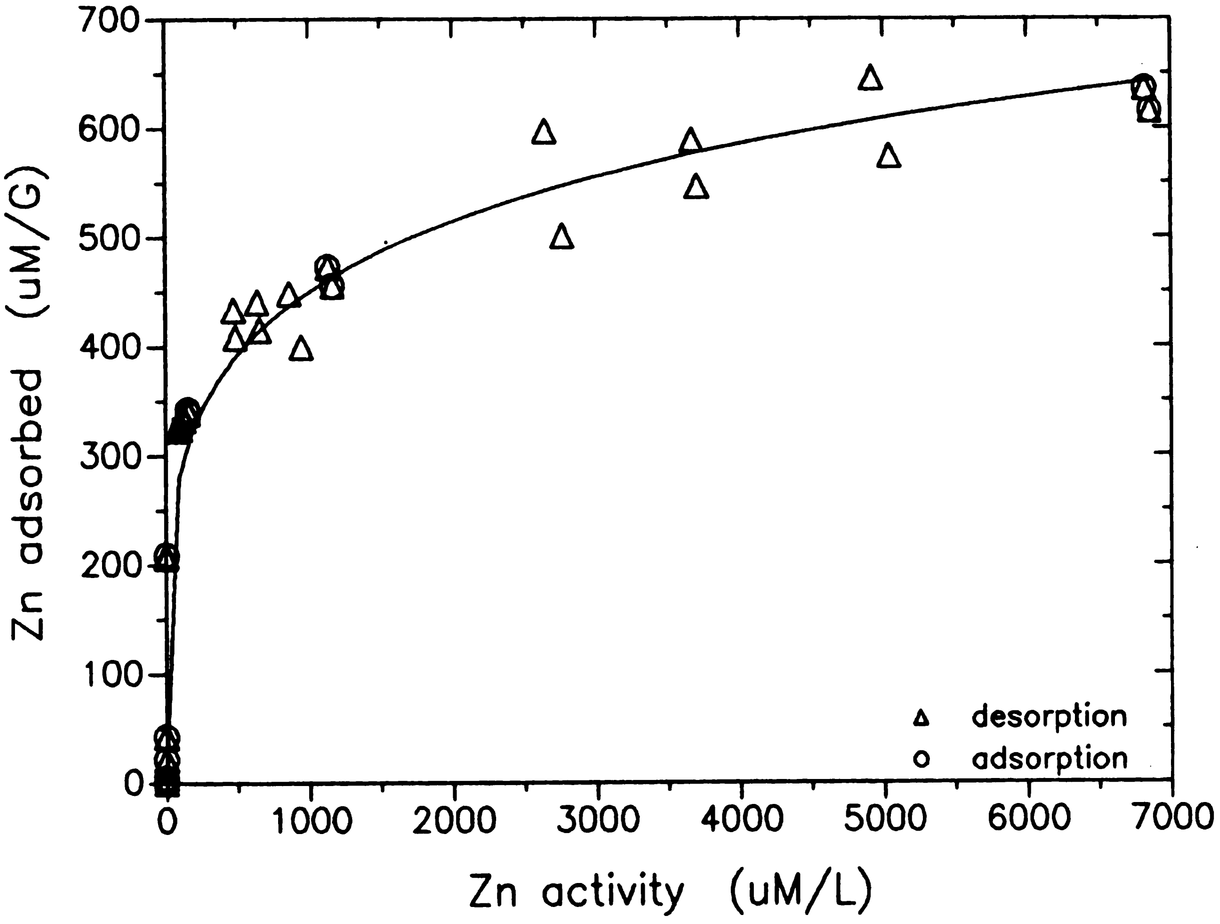

Figure 5. Adsorption and desorption of Zn by Ca Chelex ion exchange resin fit to the Linear equation.

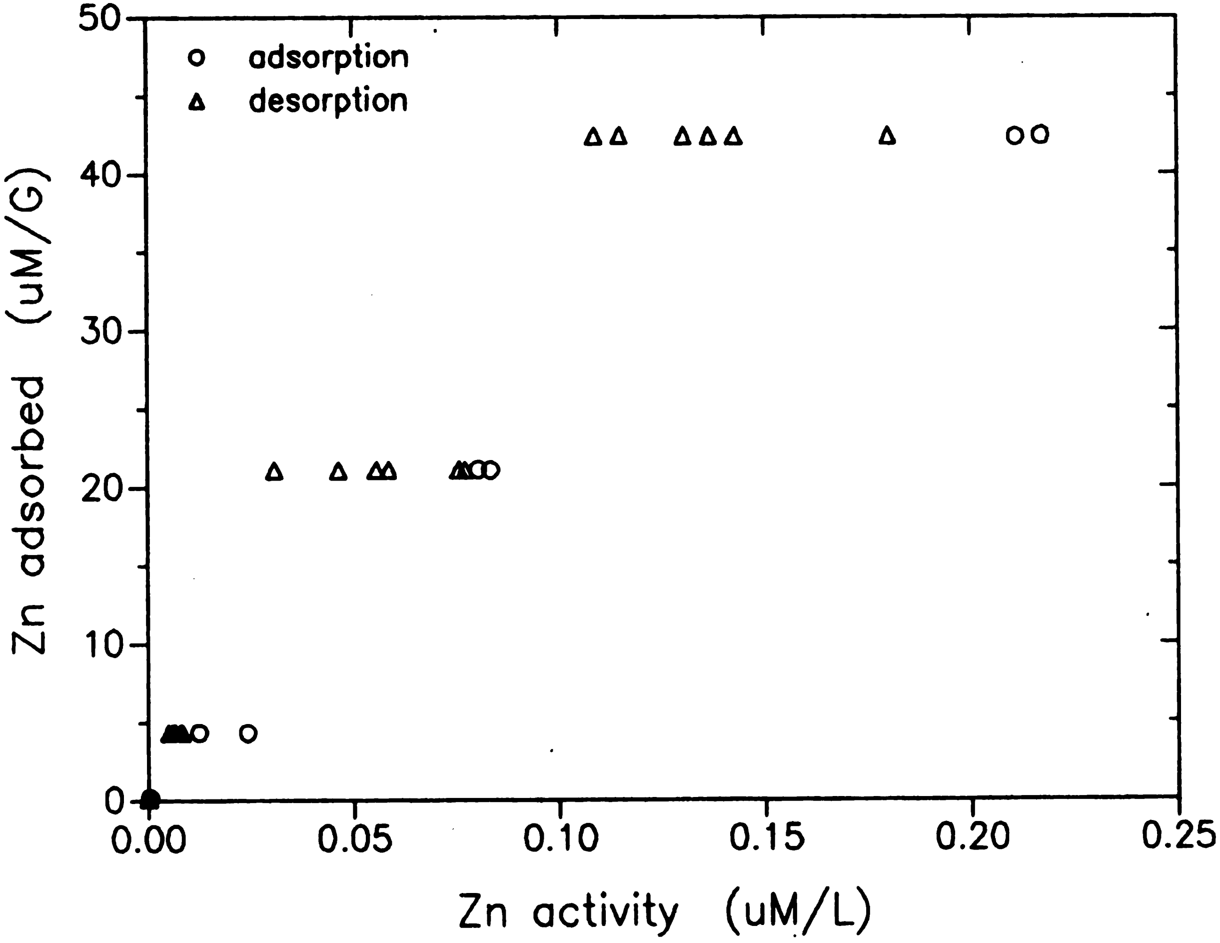

Figure 6. Desorption of trace amounts of Zn by Ca Chelex ion exchange resin as measured by the Linear equation.

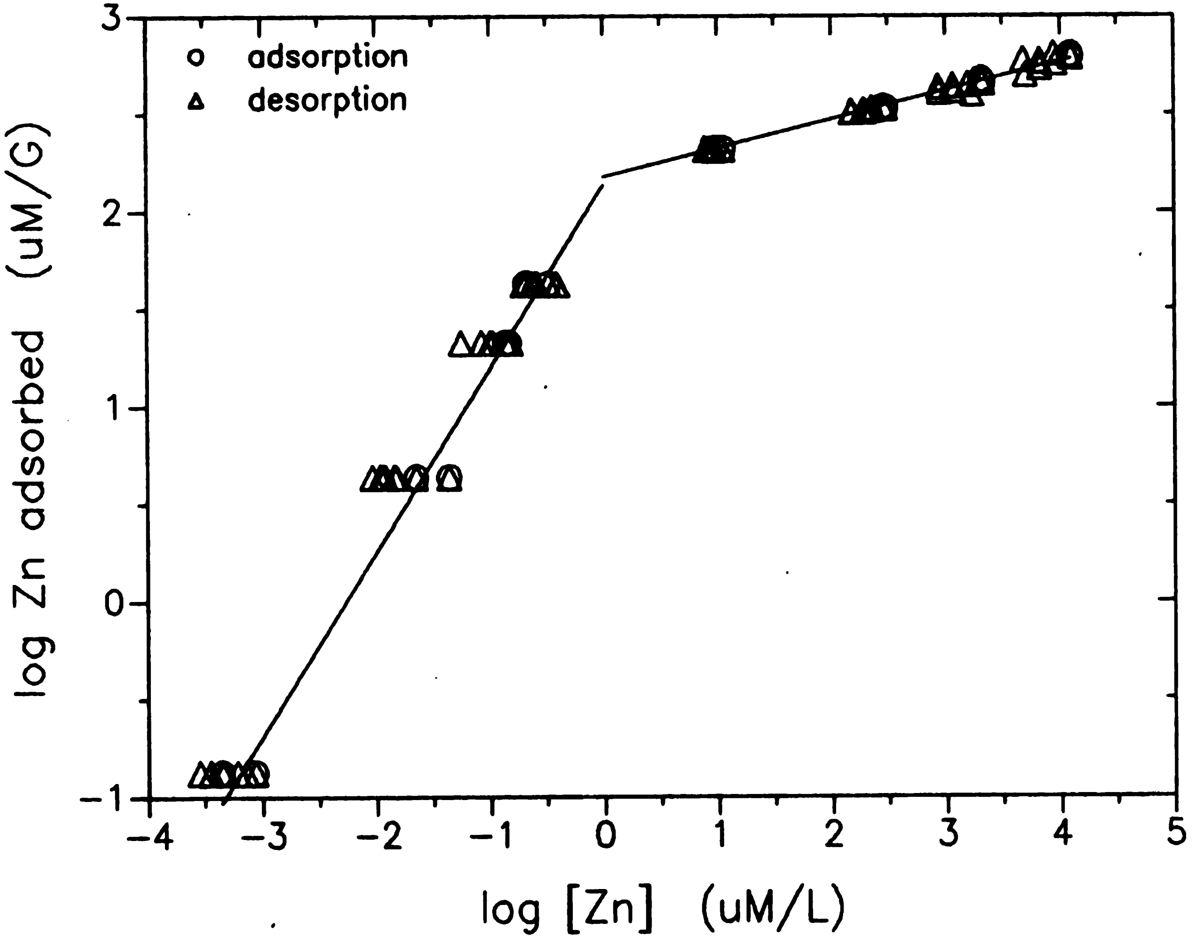

Figure 7. Adsorption and desorption of Zn from Ca Chelex ion exchange resin fit to the Freundlich equation.

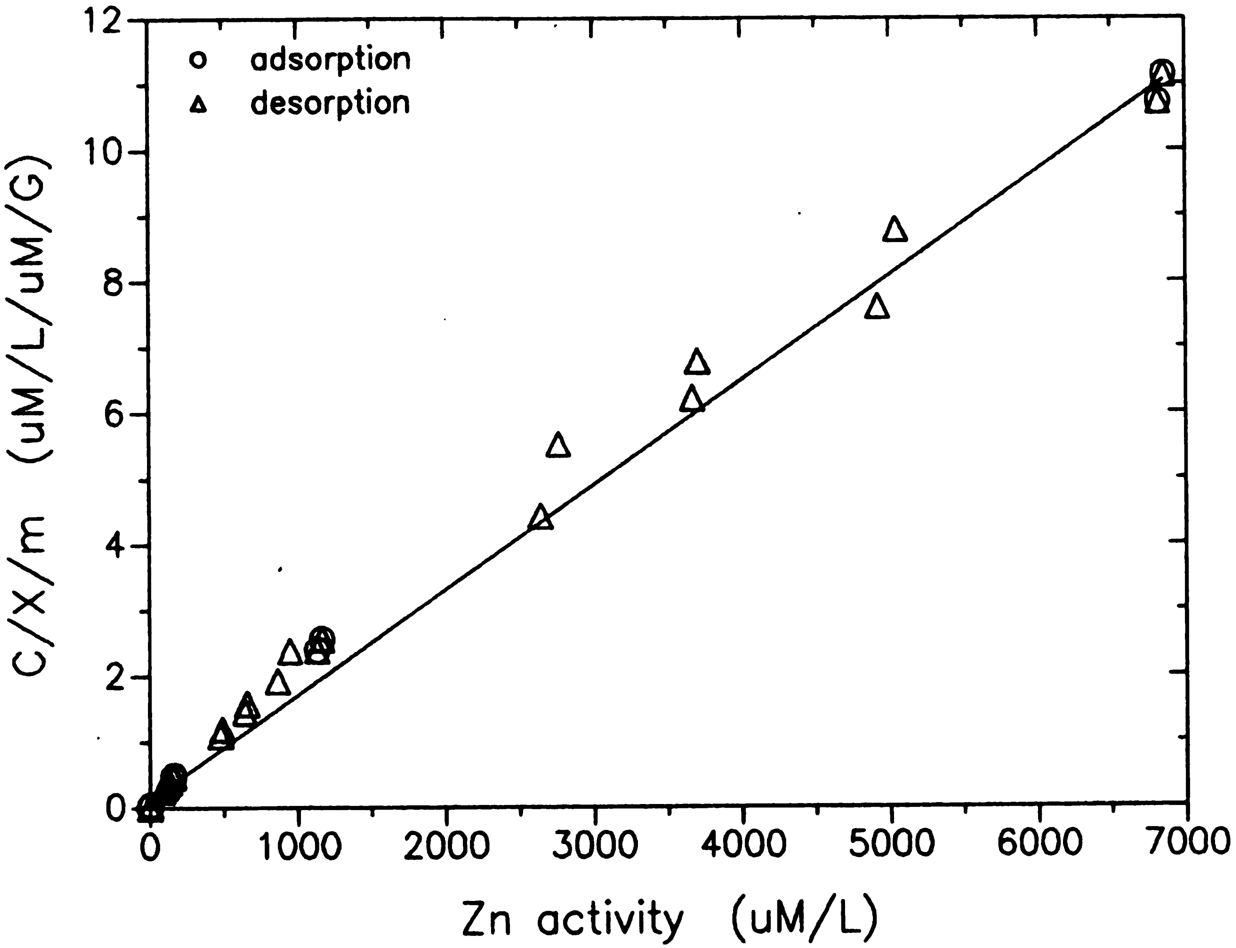

Figure 8. Adsorption and desorption of Zn by Ca Chelex ion exchange resin fit to the Langmuir equation.

contrast to previous reports that Chelex can act as a solid phase buffer to maintain pH and constant metal activity below analytical detection limits (Turner et al. 1984; Hendrickson et al. 1982; Hendrickson and Corey, 1983)

One possible explaination for this behavior may be that the driving force resulting from diluting the solution phase after a sample is removed may not be enough to effect desorption, or that the extent of desorption is so small that it cannot be measured accurately.

Table 4. Equilibrium pH and Zn activity for Ca Chelex adsorption isotherms.

Zn activity uM L-1	pH
.000476	5.9
.000243	6.0
.0241	5.7
.0124	5.8
.0756	5.9
.0802	5.8
.180	6.0
.114	6.0
5.26	4.9
6.10	4.8
157	4.0
164	4.0
1130	3.8
1160	3.8
6860	3.7
6820	3.7

Adsorption of Zn^{2+} by Ca smectite did not conform to the Linear (Figure 9), Freundlich (Figure 10), or Langmuir models (Figure 11) over the range of surface occupancy studied, even though regression coefficients indicate a reasonable fit of the data to the first two equations (r^2 = 0.97 and 0.98 respectively, Table 2). Adsorption appears to be completely reversible down to 3 uM Zn g^{-1}, however extreme desorption hysteresis occurs at 1.2 uM g^{-1} or when < 1% of the CEC is occupied by Zn (Figure 12). In contrast, Maes and Cremers (1975) reported reversibility at low surface coverage and desorption hysteresis of Zn at high occupancy. This behavior was attributed to specific adsorption involving structural OH groups or Al-hydroxy species which might have formed during acid pretreatment.

The fact that adsorption was completely reversible for all compositions of a pure ion exchanger (Figure 2) is further evidence that ion exchange is the mechanism operating above 1.2 uM g^{-1} (Figure 12). Desorption below this value behaved more like the chelating resin (Figure 6) which is known to have a high bonding energy (12-15 kcal mol^{-1}) and a large selectivity for Zn over Ca of approximately $10^{5.5}$ times (Gamble and Schnitzer, 1973). It is doubtful that hysteresis is due to inadequate driving force since McLaren et al. (1983) observed hysteresis for Cu^{2+} desorption from smectite at a level 5 times higher (6.3 uM Cu^{2+} g^{-1}) even though a larger displacement from equilibrium was used by removing and replacing the entire solution phase before re-equilibration. As a result, desorption hysteresis must be attributed to some type of unusually strong bonding, irreversible bonding or a reaction with a high activation energy (chemisorption).

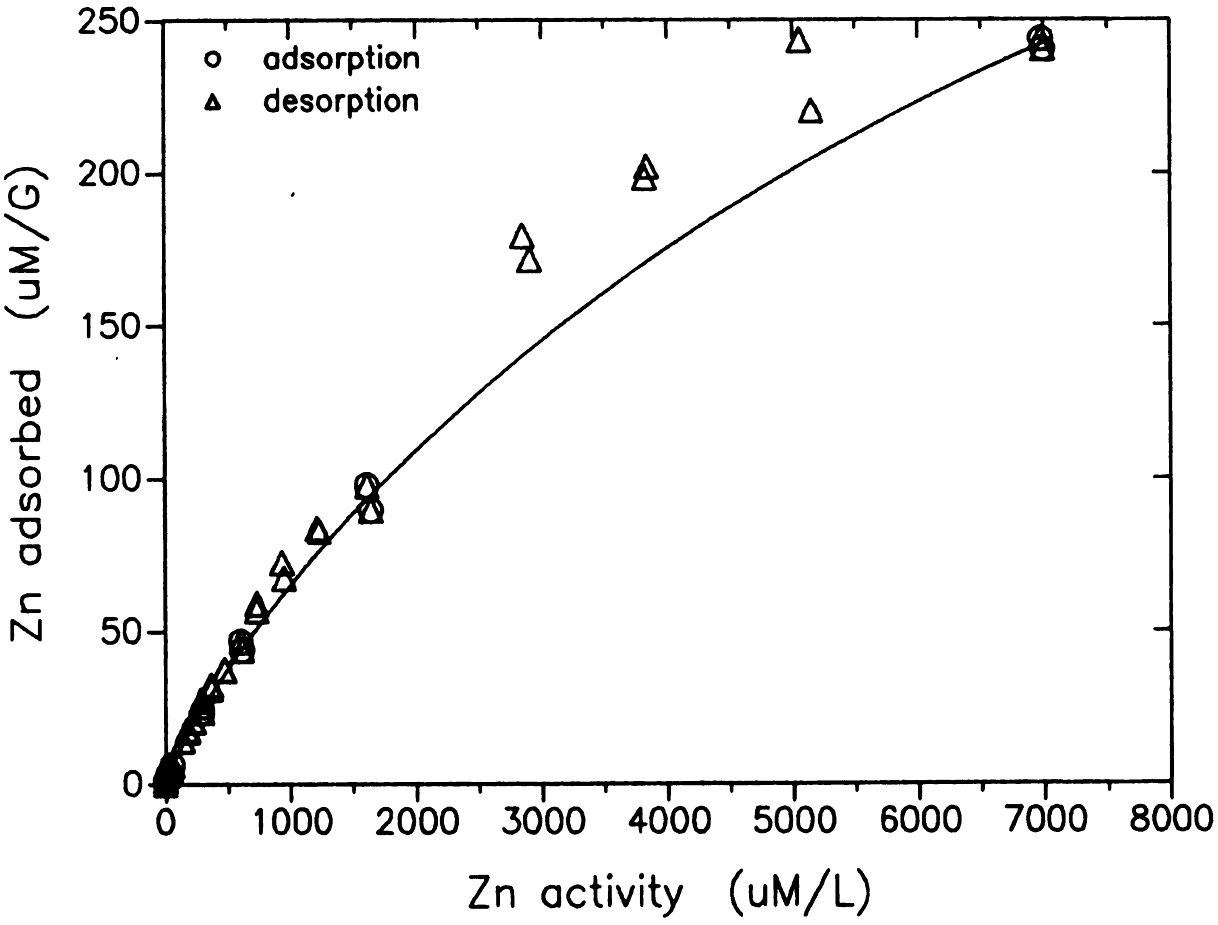

Figure 9. Adsorption and desorption of Zn by Ca smectite at pH 6.6 fit to the Linear equation.

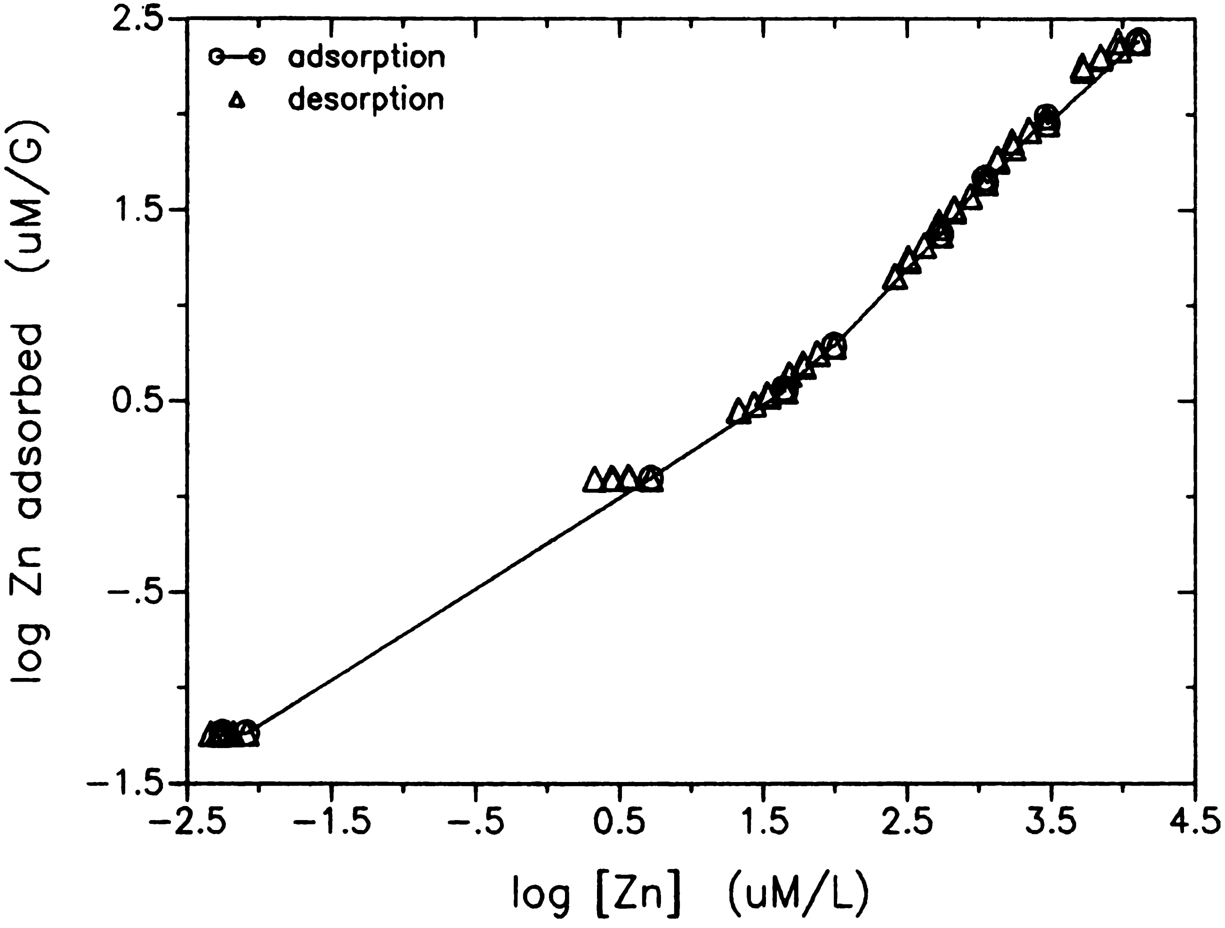

Figure 10. Adsorption and desorption of Zn by Ca smectite at pH 6.6 fit to the Freundlich equation.

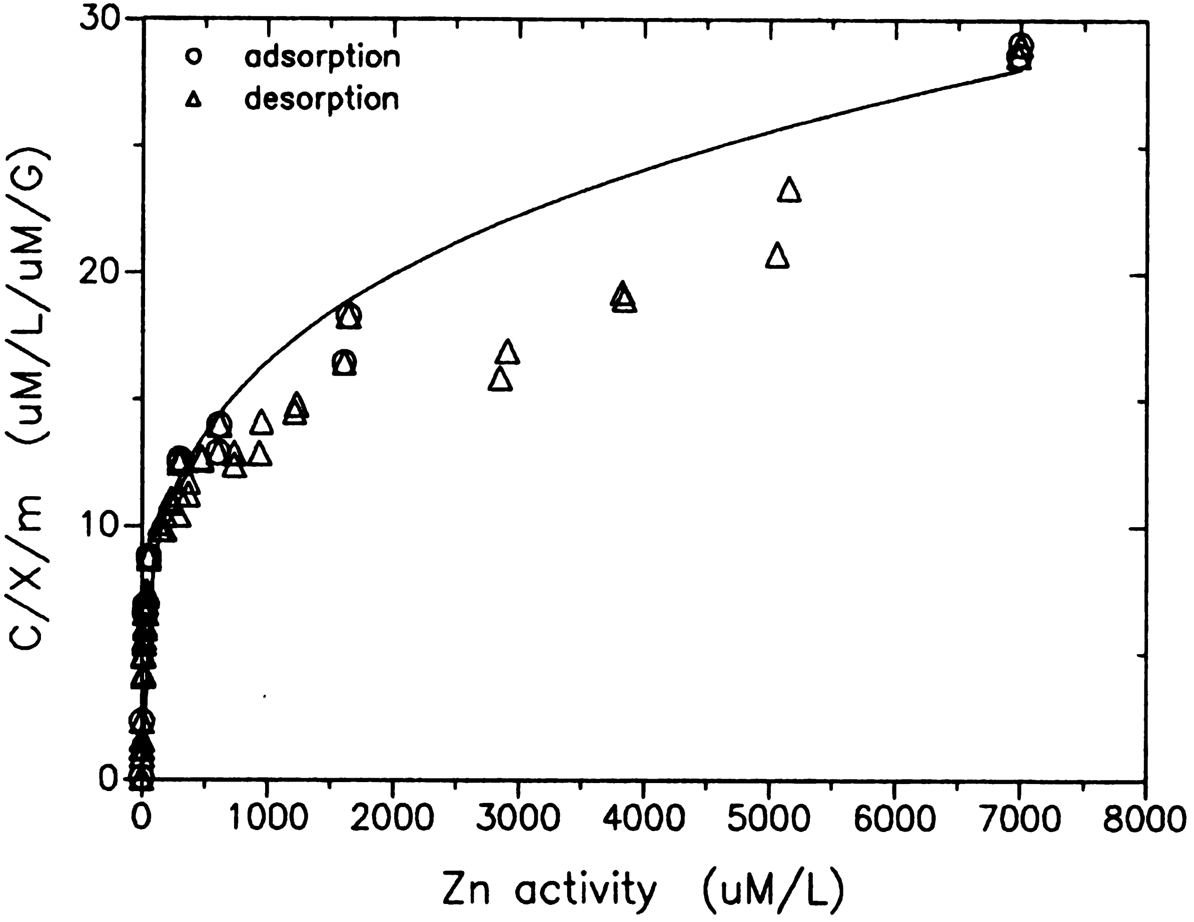

Figure 11. Adsorption and desorption of Zn by Ca smectite at pH 6.6 fit to the Langmuir equation.

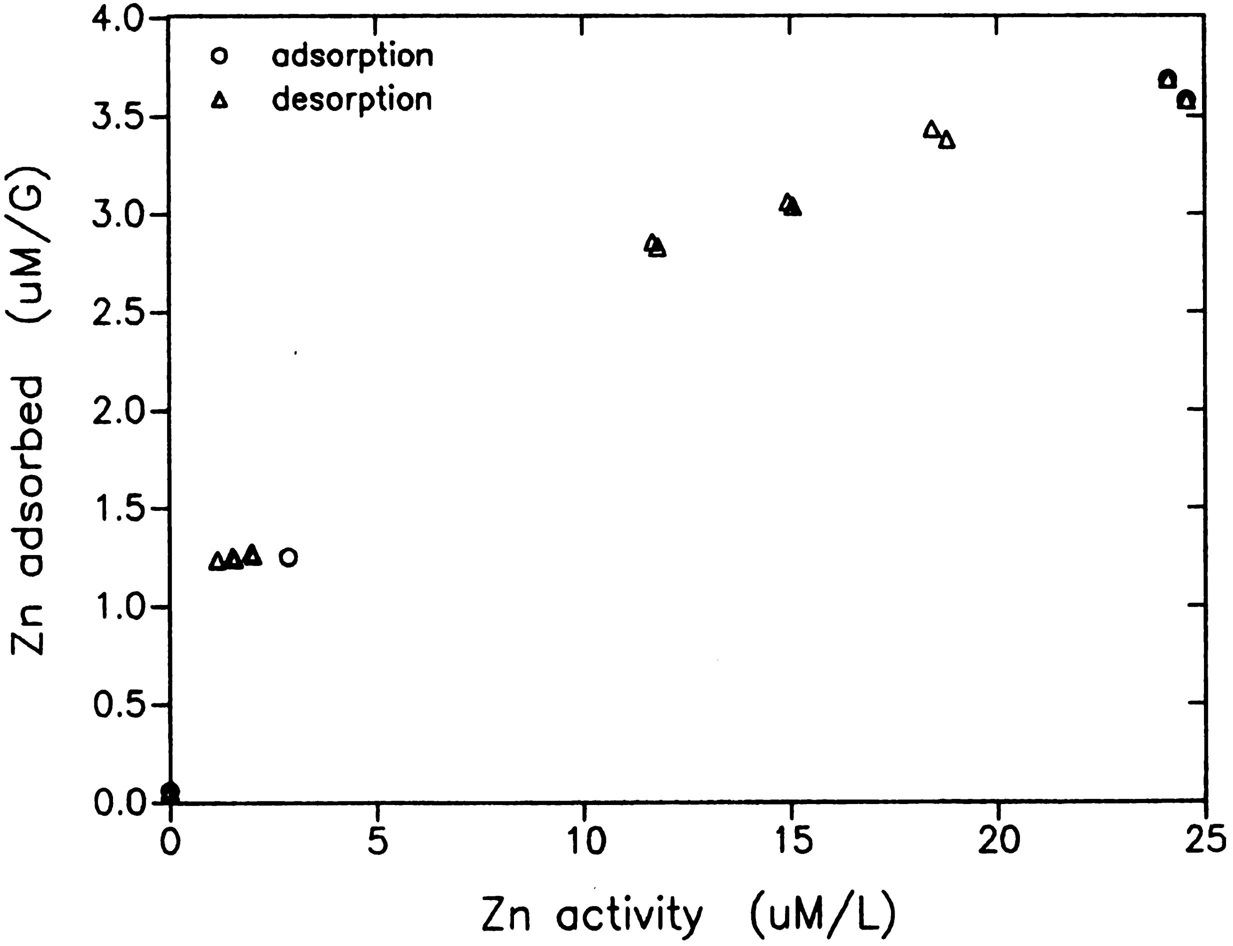

Figure 12. Desorption of trace amounts of Zn by Ca smectite pH 6.5 as measured by the Linear equation.

Adsorption and desorption of Zn^{2+} by Charity clay using the Linear (Figure 13), Freundlich (Figure 14), and Langmuir models (Figure 15) produced nonlinear adsorption isotherms in spite of the apparent good fit of the data to the models as indicated by the regression coefficients (r^2 = 0.89, 0.94, 0.98 respectively, Table 2). Desorption hysteresis is extreme at all surface occupancies studied (Figure 14). Elrashidi and O'Connor (1982) also reported extreme hysteresis for Zn desorption from 9 soils of varying physical and chemical composition, though their work did not cover the desorption range investigated in these studies.

The Charity clay is an alkaline soil (Table 1) with free carbonates and was expected to adsorb a significant amount of Zn^{2+}. Using the Arrhenius equation, Kuo and Mikkelsen (1979) determined the activation energy for Zn^{2+} adsorption by two alkaline soils. Since this value was considered too high to be due to electrostatic attraction, the stability of adsorbed Zn was attributed to chemisorption. Similar behavior in alkaline soils has been attributed to precipitation of $ZnOH_2$ (Saeed and Fox, 1977), however recent evidence suggests that precipitation-dissolution reactions are masked by the presence of a wide variety of other sites, and hence will occur only when sufficient Zn^{2+} is added to ensure complete saturation of the exchange complex (Brummer et al., 1983).

In the present study the highest surface occupancy attained was 80 uM Zn g^{-1} or 16 cmol (+) kg^{-1} (Figure 13) which was not enough to saturate the CEC (29 cmol kg^{-1}, Table 1). Regardless, even $ZnOH_2$ is expected to dissolve in response to changes in the solution activity of

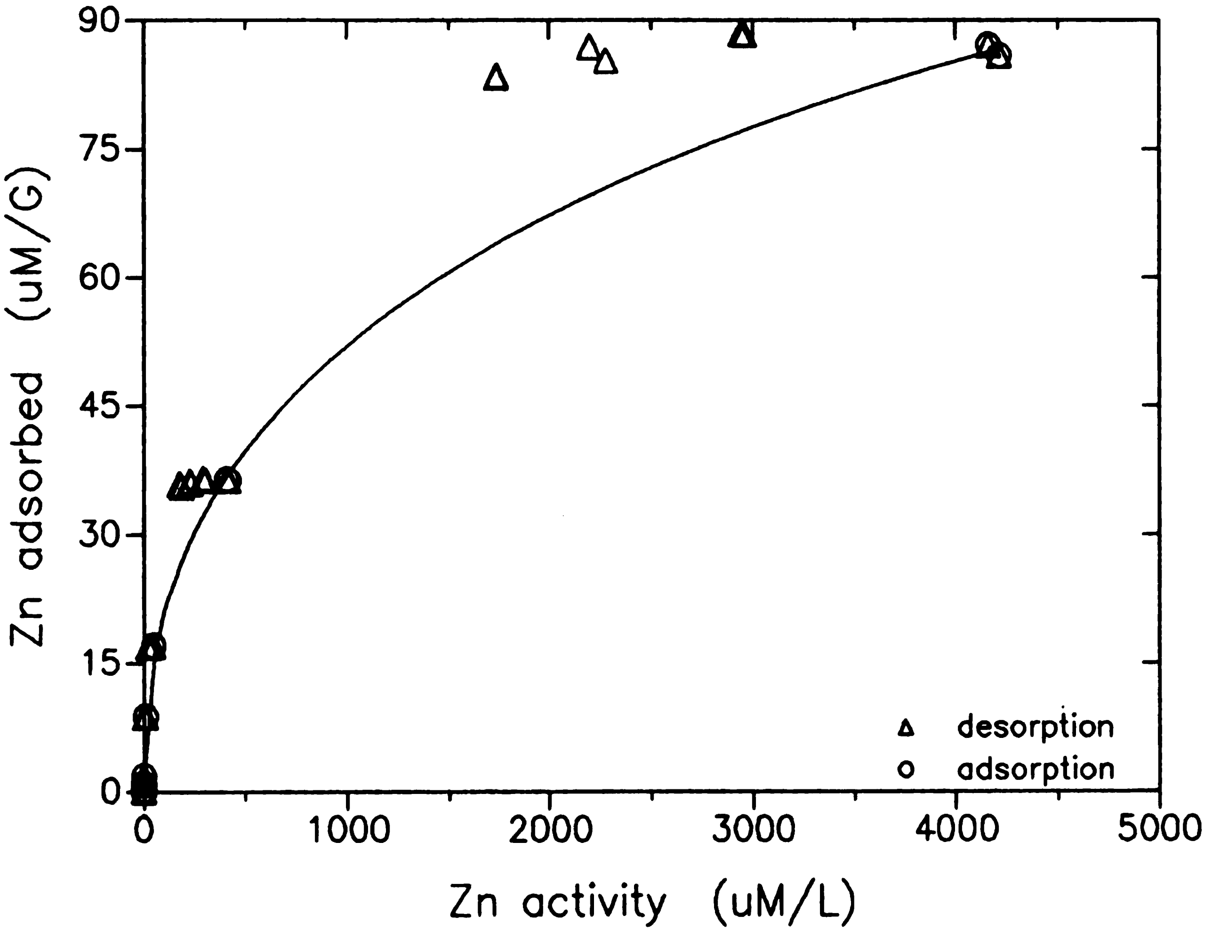

Figure 13. Adsorption and desorption of Zn by a Charity clay at pH 7.4 fit to the Linear equation.

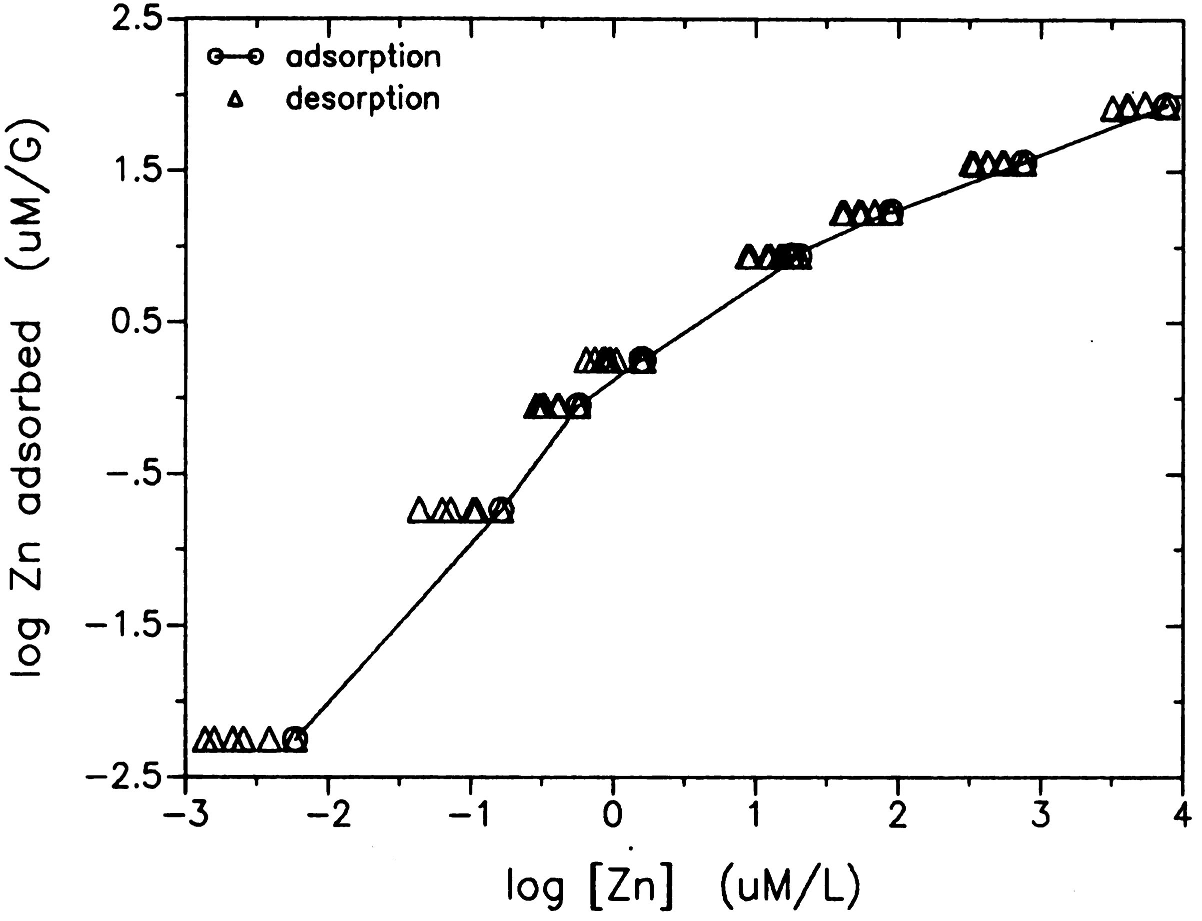

Figure 14. Adsorption and desorption of Zn by a Charity clay at pH 7.4 fit to the Freundlich equation.

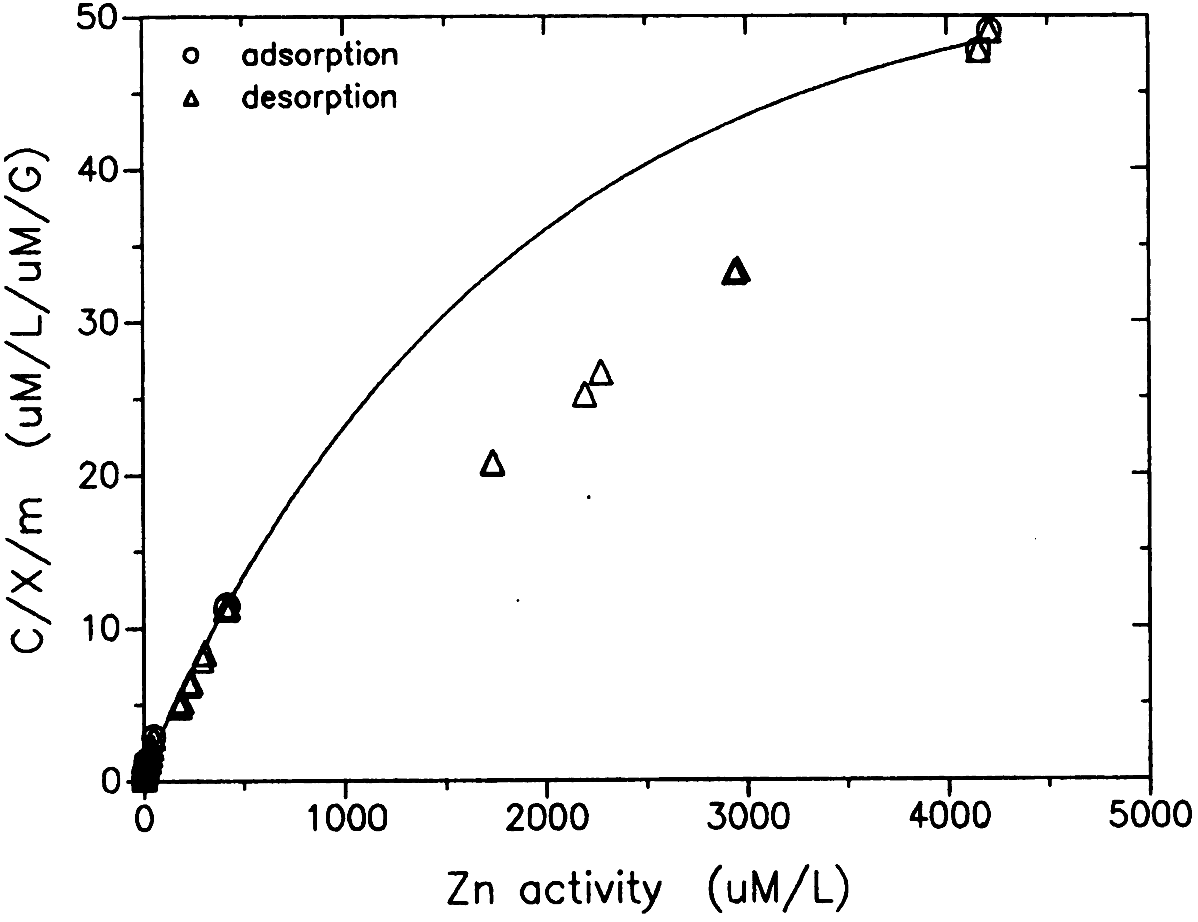

Figure 15. Adsorption and desorption of Zn by a Charity clay at pH 7.4 fit to the Langmuir equation.

Zn^{2+} (Lindsay, 1979). As such, strong retention of Zn by the Charity clay cannot be attributed to precipitation. Chemisorption seems to be a more realistic possibility.

Two important points regarding the use of the Langmuir equation in modeling adsorption-desorption reactions in soils should be mentioned. First is the fact that desorption isotherms appear to be linear at the two highest Zn levels for the Charity clay (Figure 15). Similar behavior was observed for Chelex (Figure 8). In the later case, adsorption was truly reversible over a certain range. In Figure 13 it is easy to see that dividing an evenly spaced variable (C) by a constant (X/m) will result in a straight line with a slope similar to the adsorption isotherm. Secondly, the adsorption maximum predicted by the Langmuir equation (17.8 cmol (+) kg^{-1}, Table 2) was very close to the highest surface occupancy observed in the Linear adsorption isotherm (16 mmol (+) kg^{-1}, Figure 13). Significant errors can result if the adsorption capacity is calculated from adsorption data which does not approach the true adsorption maximum, in which case the Linear equation is just as useful. One must therefore conclude that the Langmuir equation is of limited use in describing either adsorption or desorption of heavy metals in soils.

In summary, a number of important observations should be emphasised. None of the adsorption models investigated quantitatively described adsorption or desorption of Zn^{2+} by Ca smectite or a Charity clay. Adsorption-desorption data for Dowex 50W-X8 did obey the Freundlich equation, while the Langmuir equation could adequately describe adsorption and desorption from Chelex-100. The Langmuir equation proved to be of little use in describing adsorption-desorption reactions by soil materials, however the utility of the Linear and Freundlich equations should not be discounted even though nonlinear adsorption isotherms were obtained. Both equations provide a useful approach to viewing adsorption-desorption phenomena.

Comparison of the smectite and Charity clay data to model systems provided some interesting empirical insights regarding adsorption and desorption mechanisms. Adsorption of Zn^{2+} was completely reversible on smectite, except when < 1% of the CEC was occupied by Zn. This reversibility was attributed to an exchange mechanism. Conversely, extreme hysteresis was observed at all levels of Zn on a Charity clay. Retention in both cases was similar to that for a chelation reaction which had a strong preference for Zn. Since insufficient Zn^{2+} was added to saturate the exchange complex of either soil material, precipitation seemed unlikely. Desorption hysteresis is likely the result of some form of chemisorption.

Literature Cited

Barney, G.S., 1984. Geochemical behavior of disposed radioactive waste. ACS Symposium Series No. 244:3-23. American Chemical Society, Washington D.C.

Brummer, G., K.G. Tiller, V. Herms, and P.M. Clayton. 1983. Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils. Geoderma. 31:337-354.

Elrashidi, M.A., and G.A. O'Connor. 1982. Influence of solution composition on sorption of zinc by soils. Soil Sci. Soc. Am. J. 46:1153-1158.

Fritz, J.S., and G.H Schenk. 1979. Quantitative analytical chemistry. Allyn an Bacon, Boston.

Gamble, D.S., and M. Schnitzer. 1973. Trace metals and metal organic interactions in natural waters. Ann Arbor Science, Ann Arbor

Grim, R.E. 1968. Clay mineralogy. 2nd ed. McGraw-Hill, New York.

Hendrickson, L.L., and R.B. Corey. 1983. A chelating resin method for characterizing soluble metal complexes. Soil Sci. Soc. Am. J. 47:467-474.

Hendrickson, L.L., M.A. Turner, and R.B. Corey. 1982. Use of Chelex-100 to maintain constant metal activity and its application to characterization of metal complexation. Anal. Chem. 54:1633-1637.

Maes, A., and A. Cremers. 1975. Cation-exchange hysteresis in montmorillonite: a pH dependent effect. Soil Sci. 119:198-202.

McLaren, R.G., J.G Williams, and R.S. Swift. 1983. Some observations on the desorption and distribution of copper with some soil components. J. Soil Sci. 134:325-331.

Shuman, L.M. 1976. Zinc adsorption isotherms for soil clays with and without iron oxides removed. Soil Sci. Soc. Am. J. 40:349-352.

Travis, C.C., and E.L. Etnier. 1981. A survey of sorption relationships for reactive solutes in soil. J. Environ. Qual. 10:8-17.

Turner, M.A., L.L. Hendrickson, and R.B. Corey. 1984. Use of chelating resins in metal adsorption studies. Soil Sci. Soc. Am. J. 48:763-769.

CHAPTER IV

EFFECT OF pH ON ADSORPTION AND DESORPTION OF ZINC BY SMECTITE

Introduction

Among the properties known to affect Zn^{2+} and other metal sorption by soil materials, none has been more intensely studied or more poorly understood than pH. Even in pure clay mineral studies there is a general lack of distinction between adsorption and precipitation. Several researchers have reported marked uptake of metals by smectites when the pH exceeds that required for formation of hydroxy species in pure solution. For Zn^{2+}, precipitation in the presence of smectite has been reported in the pH range 6.0-6.5 (Farrah and Pickering, 1976; Frost and Griffin, 1977). Conversely, recent evidence by Brummer et al. (1983) suggests that Zn^{2+} is controlled exclusively by adsorption-desorption reactions unless sufficient Zn^{2+} has been added to ensure complete saturation of the exchange complex. The ability of chelating ligands to mask precipitation has also been reported (Maquire et al. 1983).

Irreversible adsorption of metals below the pH required for precipitation and the pH dependence of such adsorption has been attributed to chemisorption or specific bonding. Maes and Cremers (1975) attributed irreversible Zn^{2+} adsorption by Na smectite at high surface occupancies to strong pH dependent bonding at broken edge OH's or Al-OH compounds which may have resulted from dissolution of the clay during acid pretreatment. However, this behavior is unusual since specific adsorption is expected to occur at low surface occupancies.

Smectites are not considered to have extensive pH dependent charge, but their ability to irreversibly sorb Al-OH compounds is well documented (Keren, 1980). Irreversible pH dependent adsorption of Cu^{2+} and Zn^{2+} by soil clays which contain coatings of Al and Fe oxide has been attributed to chemisorption (Cavallaro and McBride, 1984). Using ESR, Cu^{2+} adsorption on a Al-OH-montmorillonite complex was shown to be both physi-(electrostatic) and chemi-sorbed (Harsh and Donner, 1984).

While these results may explain Zn^{2+} retention by soils and clays which contain microcrystalline and noncrystalline oxides, they do not account for desorption hysteresis of Zn on smectite observed in earlier studies by this laboratory (Zielke, Chapter III). In these studies, extreme desorption hysteresis occurred in the trace region while adsorption of Zn by smectite at moderate to high surface occupancy was completely reversible even at pH's where precipitation has been reported by others. In light of these differences, the objective of the present study was to investigate the effect of pH on the reversibility of Zn^{2+} adsorption by Ca smectite over a wide range of surface coverage.

Materials and Methods

Preparation of adsorbents

Ca smectite (montmorillonite # 25, Upton, Wyoming) was prepared by sedimentation and decantation of the <2um fraction in distilled H_2O followed by repeated saturation with 1M $CaCl_2$. The flocculated Ca clay was dialyzed against distilled H_2O until a negative test for Cl^- was obtained using $AgNO_3$. The resulting clay was diluted with 0.01 M $CaCl_2$ to give a 1% w/w suspension, split into several portions and the pH was adjusted twice a day with 0.01 M HCl or saturated $Ca(OH)_2$ until a stable reading (± 0.05 pH units) was obtained for 3 consecutive days. This process required approximately three weeks. The CEC was determined on unadjusted Ca clay and was found to be 90 ± 2 cmol (+) kg^{-1}.

Adsorption isotherms

Batch adsorption experiments were conducted in duplicate at each of 6 pH levels by adding 3 mL of the rapidly stirred clay suspensions to 5 mL RIA polypropylene test tubes. Each tube received 0.2 mL of an appropriate Zn solution (Table 1) and 0.2 mL of a ^{65}Zn solution containing 1 mCi ^{65}Zn L^{-1}. The mass of clay used at each pH level was determined gravimetrically. The tubes were then sealed, dispersed on a vortex mixer and equilibrated on a wrist action shaker at 26 ± 2 C for 2 wks. At the end of this time the samples were separated by centrifugation at 3000 rpm for 5 min, and a 1 mL aliquot was removed for radioassay. Six desorption cycles were accomplished by replacing the 1 mL sample with 0.01 M $CaCl_2$ and re-equilibrating for 24 hr.

Radiometric data were obtained on a Packard Tri-Carb spectrometer equipped with a gamma counter by comparing sample radioactivity with that observed for known ^{65}Zn standards of the same geometry. Equilibrium Zn^{2+} concentrations were calculated from principles of isotopic dilution and mass balance. In all cases the amount of Zn adsorbed was calculated by difference from the initial concentration. The equilibrium pH was determined on the 1 mL aliquot using a combination pH electrode.

The rate of Zn adsorption at the lowest Zn^{2+} level was investigated by equilibrating duplicate samples for periods of .5, 1, 2, 4, 8, and 20 hr, and determining the amount of Zn adsorbed as described above. The effect of equilibration time on adsorption and desorption was investigated at the 3 lowest Zn^{2+} levels by equilibrating duplicate samples for 24, 72, 168 and 672 hr. Three desorption cycles were conducted as described earlier.

Table 1. Initial Zn^{2+} levels and equilibrium pH's for Zn adsorption by Ca smectite.

Initial Zn^{2+}	Equilibrium pH^1					
$uM\ L^{-1}$						
.0097	3.47	4.44	5.88	6.51	6.94	7.70
.430	3.45	4.45	5.92	6.57	7.03	7.73
4.47	3.45	4.49	5.91	6.57	7.02	7.74
44.9	3.45	4.50	5.86	6.53	6.98	7.76
426	3.44	4.47	5.76	6.43	6.80	7.76
4380	3.44	4.40	5.56	6.23	6.59	6.94

[1] Means of duplicate samples

Results and Discussion

The equilibrium pH for adsorption by the 6 different clay suspensions is presented in Table 1. In all cases the pH in subsequent desorption cycles did not change by more than ± 0.1 pH units. There was a tendency for the pH to decrease at the higher initial Zn^{2+} levels (column 4,5, 6, and 7, Table 1). This decrease is most likely the result of hydrolysis via the reaction:

$$Zn^{2+} + H_2O = ZnOH^+ + H^+$$

Adsorption of Zn by smectite at pH 3.5 conformed to the Freundlich equation and was completely reversible at all Zn^{2+} levels as indicated by the proximity of the desorption points to the initial adsorption isotherm (Figure 1). At this pH, smectite is most likely a mixed Al-Ca-

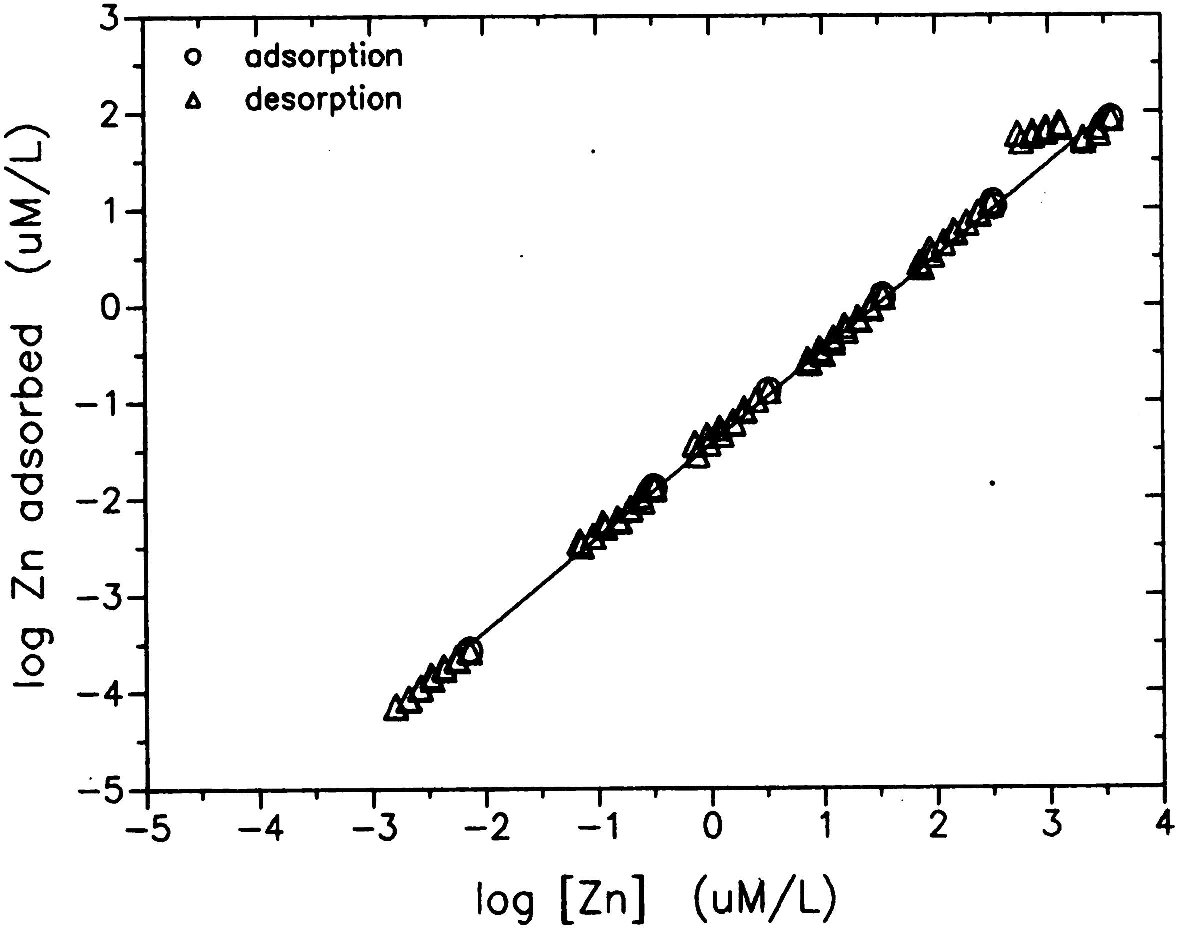

Figure 1. Adsorption and desorption of Zn by Ca Smectite at pH 3.5.

Zn clay (Pionke and Corey, 1967), and any pH dependent sites capable of strong bonding remain undissociated or are associated with Al^{3+}. Zinc adsorption appears completely reversible under these conditions because it is competing with Ca^{2+} for sites which do not lead to specific bonding.

At pH 4.5 Zn adsorption still conforms to the Freundlich equation over the entire range observed (Figure 2), but moderate desorption hysteresis occurs below log (X/m) = -0.5. Three explanations are offered for this behavior. First, at this pH smectite may be subject to acidic dissolution, however exchangeable Al is probably very low and Al-OH complexes which contribute to hysteresis might be forming on the surface (Harsh and Donner, 1984). Secondly, is the possibility that desorption hysteresis is the result of strong bonding at broken edge OH's, and that these sites dissociate at a lower pH than originally thought. Still another possibility is that some other type of pH dependent site capable of effecting desorption hysteresis is present.

At pH 5.9 and above, data no longer conform to the Freundlich equation and nonlinear isotherms are observed (Figures 3,4,5 and 6). Adsorption appears to be completely reversible above log (X/m) = 0, but hysteresis becomes extreme below this value (Figure 3). Irreversible adsorption on pH dependent sites such as broken edge OH's may be responsible since Zn adsorbed on the surface at this level represents <1 % of the CEC.

As the pH is increased further, more Zn was adsorbed in the range where hysteresis was observed, while adsorption at the high end remained relatively constant. For example, log [Zn] where hysteresis begins at

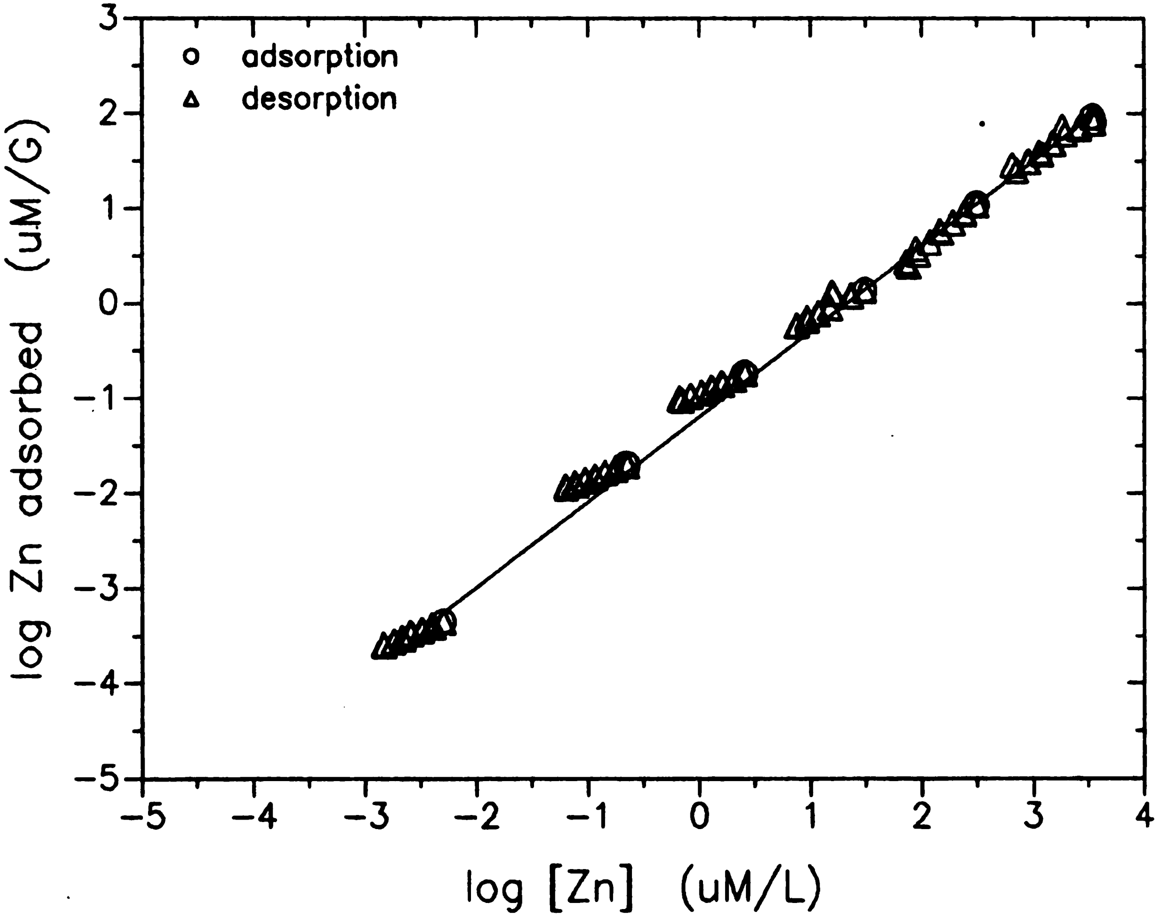

Figure 2. Adsorption and desorption of Zn by Ca smectite at pH 4.5.

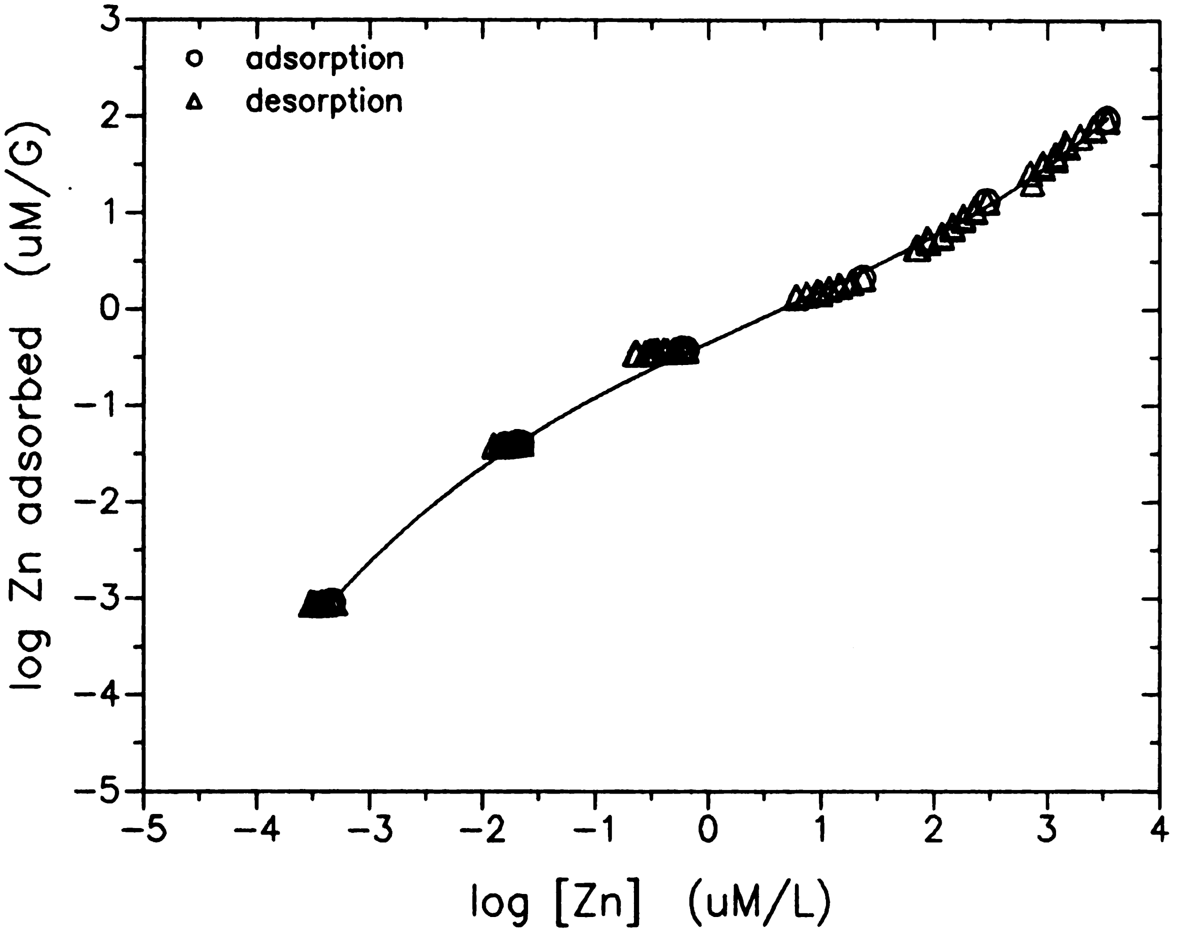

Figure 3. Adsorption and desorption of Zn by Ca smectite at pH 5.9.

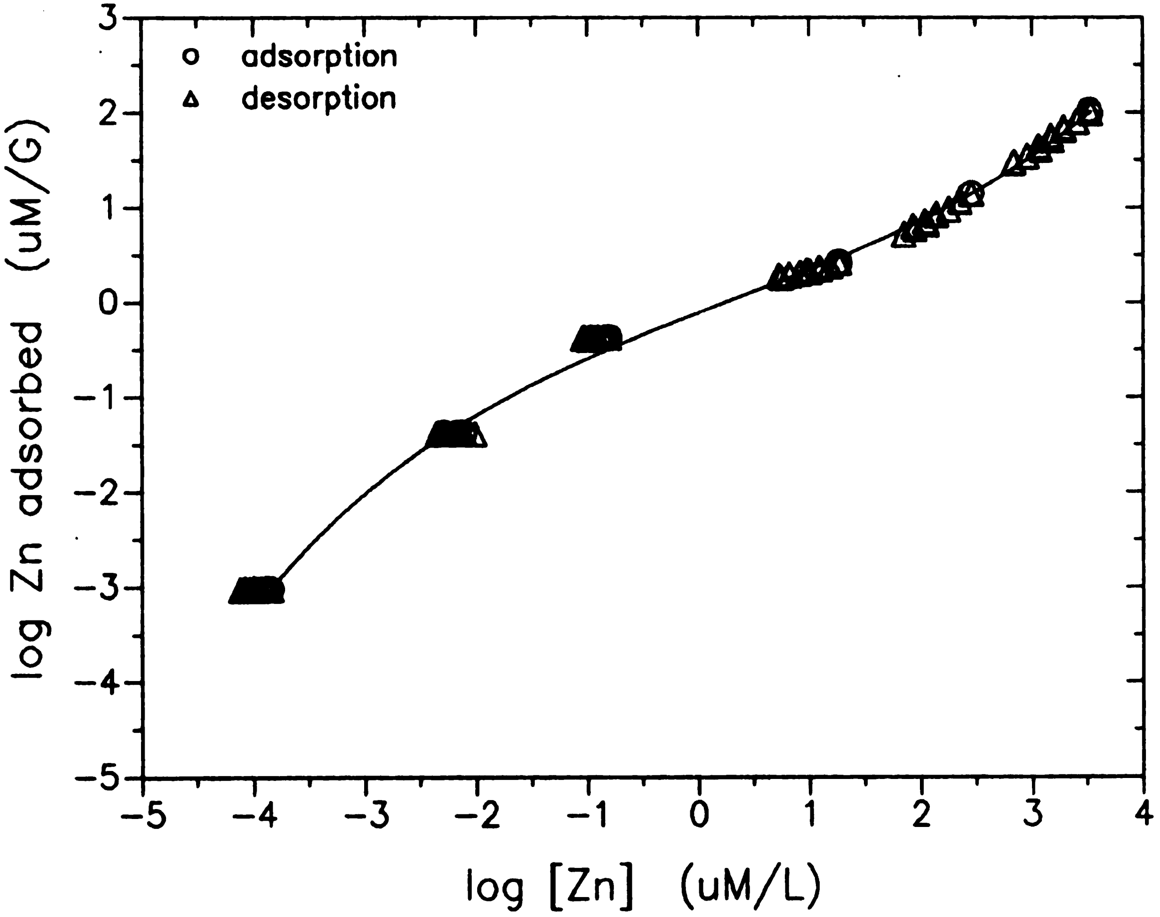

Figure 4. Adsorption and desorption of Zn by Ca smectite at pH 6.5.

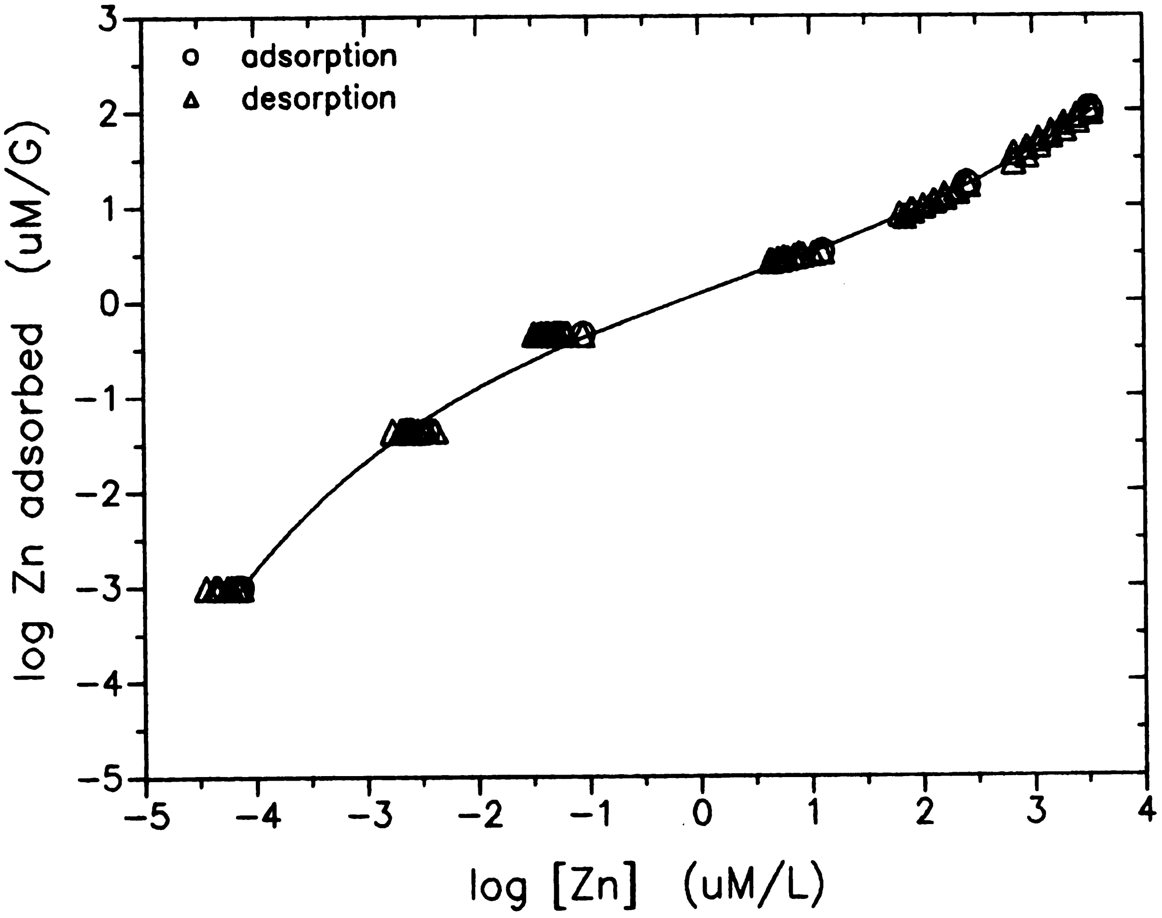

Figure 5. Adsorption and desorption of Zn by Ca smectite at pH 7.0.

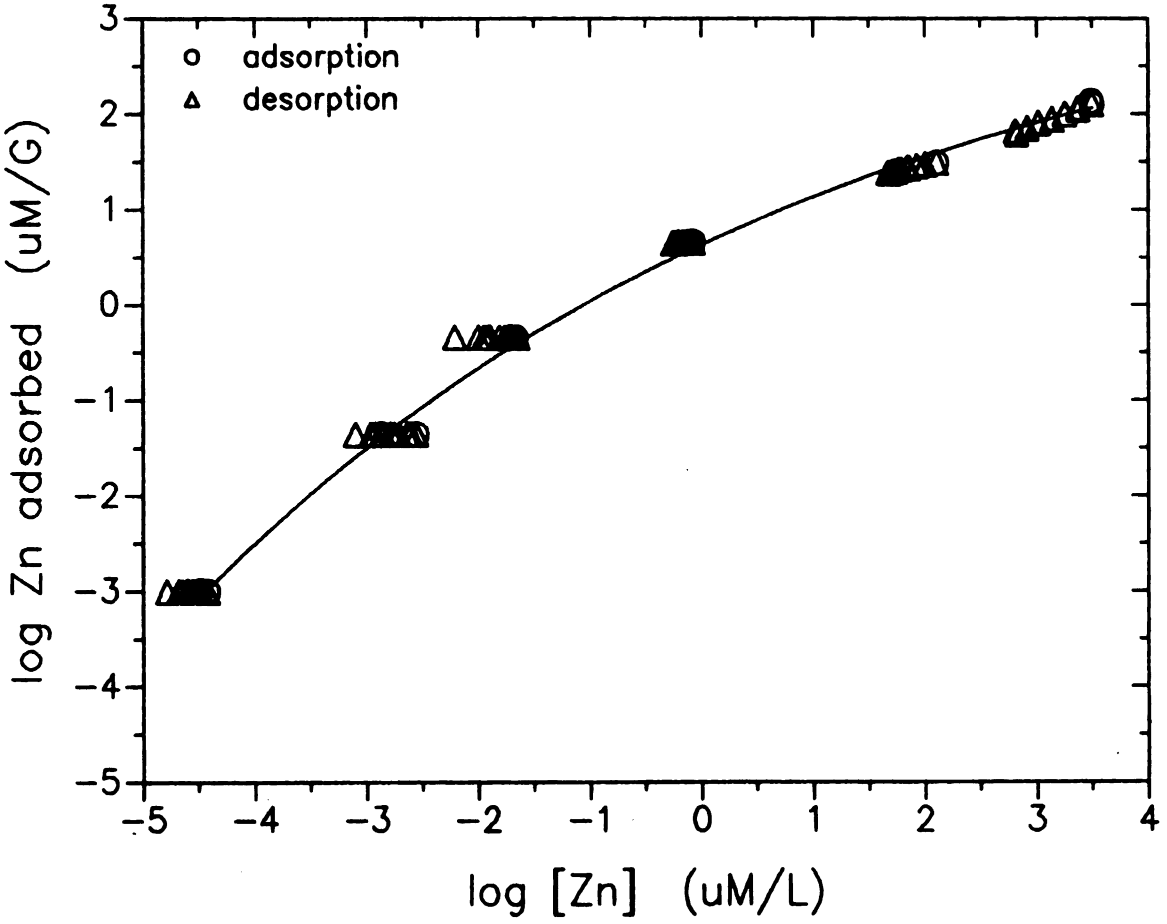

Figure 6. **Adsorption and desorption of Zn by Ca smectite at pH 7.7.**

pH 5.9 (Figure 3) is approximately 0. At pH 6.5, log [Zn] = -.75 (Figure 4), and at pH 7.0, log [Zn] is approximately -1 (Figure 5). At pH 7.7 this value shifts to log [Zn] = -1.5, and hysteresis is observed at the next highest initial Zn^{2+}level (Figure 6). In contrast, adsorption at the highest initial Zn level was completely reversible and occurs uniformly at log (X/m) = 2 and log [Zn] = 3.5. Mathematically, these results contribute to increasing nonlinearity of the Freundlich isotherm. Mechanistically, they confirm that hysteresis is occurring on pH dependent sites while complete reversibility is exhibited at the permanently charged sites.

Maes and Cremers (1975) first suggested that hysteresis was a pH dependent phenomenon, however the results presented here are in no way similar to those previously presented, since desorption hysteresis was observed in the high end of the adsorption envelope. One explanation offered for this observation was the formation of Al-OH complexes which selectively retained Zn.

Harsh and Donner (1984) studied specific adsorption of Cu^{2+} on Al-OH complexes which were precipitated on smectite. Adsorption was extremely energetic and time dependent. After 168 hr only 0.6% of the Cu adsorbed could be removed with 0.25 M $Ba(NO_3)_2$. In the present study, adsorption at the lowest Zn^{2+} level was nearly complete in less than 24 hr at all pH's (Figure 7). Rapid adsorption was observed at higher Zn levels as well (Figure 8). More importantly, there was no significant effect of time on the desorbability of Zn at 72 and 672 hr (Figure 9). While results are shown only for pH 4.5, similar behavior was observed throughout the pH range investigated.

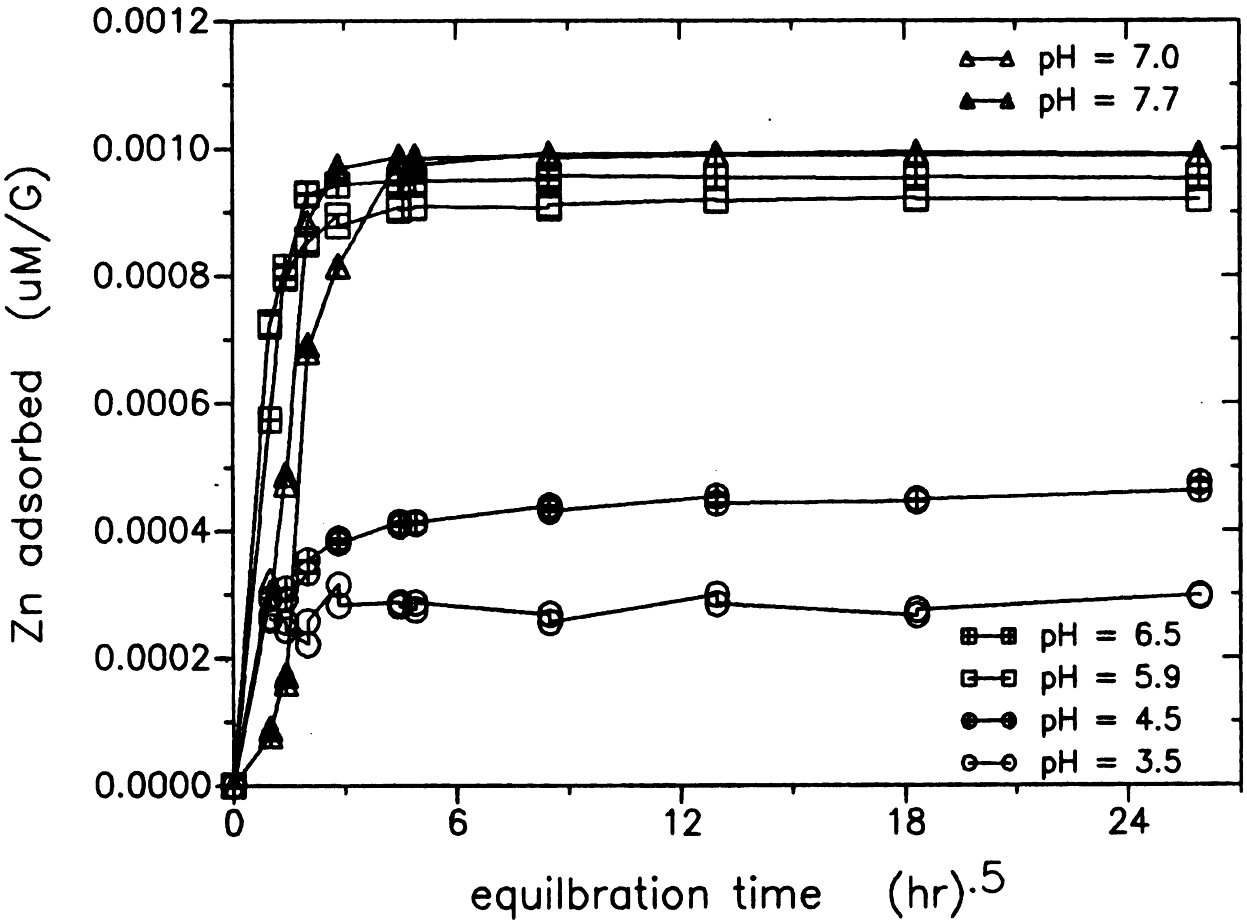

Figure 7. **Adsorption of Zn by Ca smectite as a function of time and pH.**

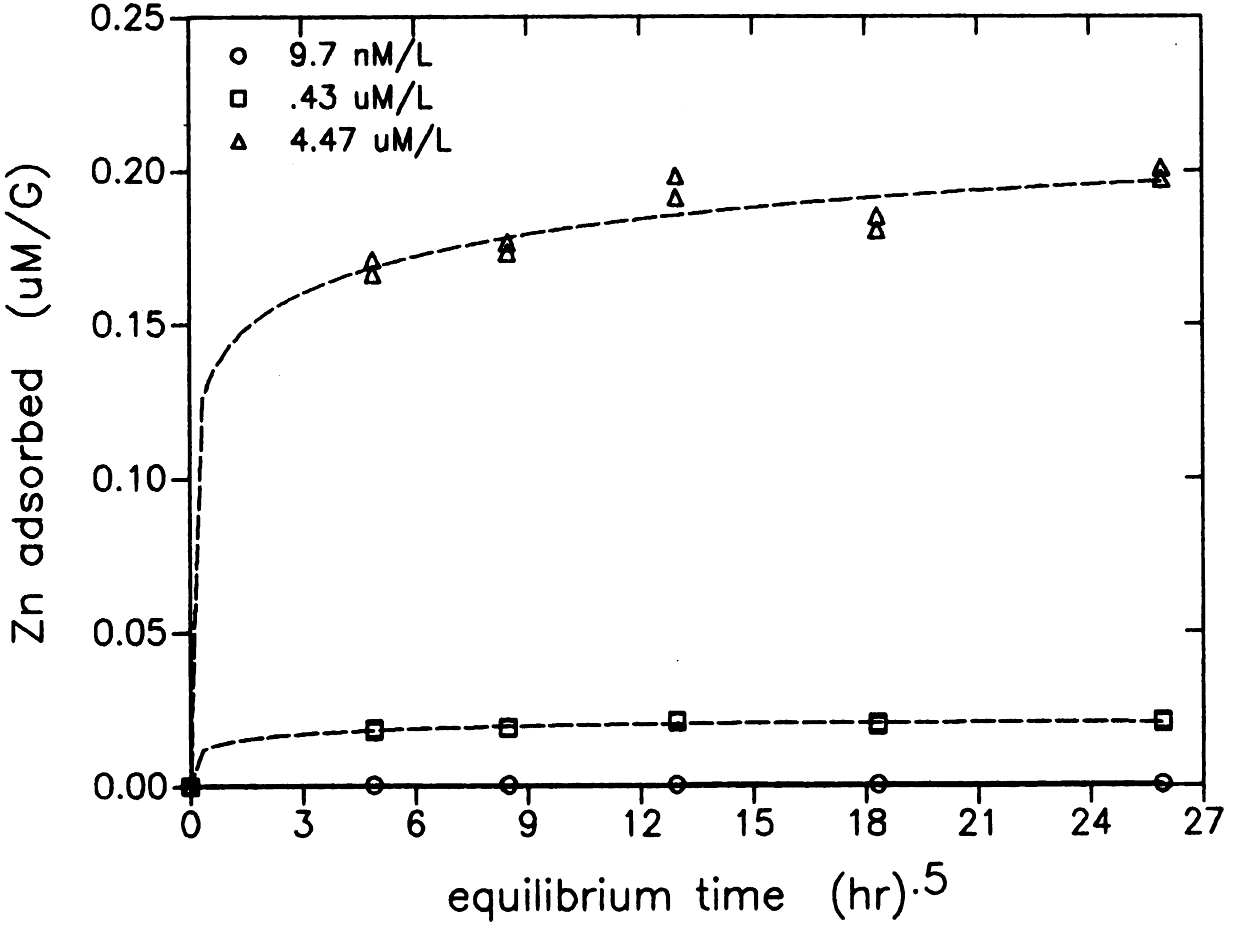

Figure 8. **Effect of time on the adsorption of Zn by pH 4.5 Ca smectite at three initial Zn levels.**

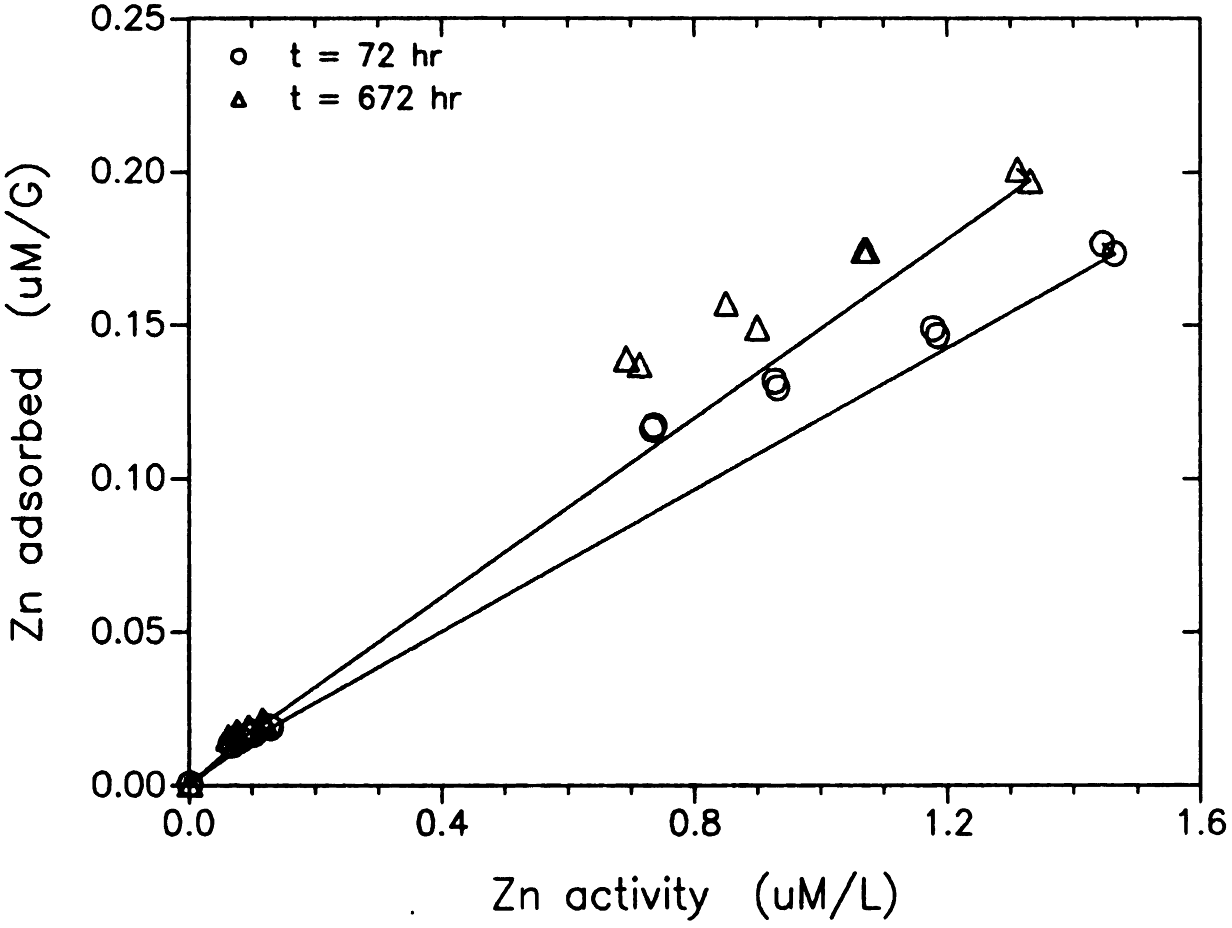

Figure 9. Effect of time on adsorption and desorption of Zn by Ca smectite at pH 4.5.

Two important conclusions can be drawn from these time dependent studies. First, it is unlikely that precipitation occurred at any pH or Zn level since equilibria was attained in <24 hrs. Secondly, hysteresis cannot be accounted for by chemisorption on aluminum polymers as was suggested in data by Harsh and Donner (1984) since these types of reactions exhibit strong time dependence. Furthermore the smectite used in this study was prepared to exclude the formation of aluminum polymers.

In conclusion, adsorption of Zn was observed to be pH dependent. At high surface occupancy, adsorption was completely reversible as expected for an ion exchange reaction. Desorption hysteresis in the trace region did not behave like chemisorption on Al-OH polymers and hence must be attributed to the presence of some other pH dependent site. One possibility would be broken edge OH's; however, moderate desorption hysteresis was observed even at pH 4.5, which is below the pH where such sites are expected to be ionized. One fact is known for certain; smectite clays have a demonstrated ability to mask Zn precipitation even in alkaline solution. This observation raises serious doubt as to the effectiveness of pH control as a means to immobilize heavy metals in waste disposal processes that utilize smectite clays. If the sites contributing to hysteresis could be identified and optimized, smectites would have greater appeal as an adsorbent for heavy metals.

Literature Cited

Brummer, G., K.G. Tiller, V. Herms, and P.M. Clayton. 1983. Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils. Geoderma. 31:337-354.

Cavallaro, N., and M.B. McBride. 1984. Zinc and copper sorption and fixation by an acid soil clay: effect of selective dissolutions. Soil Sci. Soc. Am. J. 48:1050-1054.

Farrah, H., and W.F. Pickering. 1976. The sorption of zinc species by clay minerals. Aust. J. Chem. 29:1649-1656.

Frost, R.R., and R.A. Griffin. 1977. Effect of pH on adsorption of copper, zinc and cadmium from landfill leachate by clay minerals. J. Environ. Sci. Health, Part A. 12:139-156.

Harsh, J.B, and H.E. Donner. 1984. Specific adsorption of copper on an hydroxy-aluminum-montmorillonite complex. Soil Sci. Soc. Am. J. 48:1034-1039.

Keren, R. 1980. Effects of hydroxy aluminum precipitation on the exchange capacity reduction and aggregate size distribution of montmorillonite hydroxy-aluminum complexes. Soil Sci. Soc. Am J. 44:1209-1212.

Maes, A., and A. Cremers. 1975. Cation-exchange hysteresis in montmorillonite: a pH dependent effect. Soil Sci. 119:198-202.

Maquire, M., J. Slavek, I. Vimpany, F.R. Higginson, and W.F. Pickering. 1981. Influence of pH on copper and zinc uptake by soil clays. Aust. J. Soils Res. 19:217-229.

Pionke, H.B. and R.B. Corey. 1967. Relations between acidic aluminum and soil pH, clay and organic matter. Soil Sci. Soc. Am. Proc. 31:749-752.

CHAPTER V

EFFECT OF INITIAL EXCHANGEABLE ION ON ADSORPTION AND DESORPTION OF ZINC FROM SMECTITE

Introduction

Several researchers have studied the effect of solution composition on metal adsorption by soils and clays (Elrashidi and O'Connor, 1982; Egozy, 1980). However, there are few reports of the effect of initial exchange ion on adsorption. Furthermore, there are no known studies where metal desorption is systematically studied relative to the initial exchange ion.

Logically, most of the studies conducted have been on soil materials saturated with ions of agricultural importance. Nelson and Melsted (1955) reported the relative order of affinity of different cations by clay minerals was $H^{+}(Al^{3+}) > Zn^{2+} > Ca^{2+} > Mg^{2+} > K^{+}$. Garcia-Miragaya and Page (1977) reported that Cd^{2+} sorption by different homoionic montmorillonites followed the order Na > K > Ca > Al. Shukla et al. (1980) found that Zn adsorption by whole soils which were saturated with different cations followed the order H(Al) < Ca < Mg < K ,Na. Adsorption of alkali metal cation on smectite followed the order Li < Na < K < Rb < Cs. The free energy of adsorption was related to ion size parameters and polarizability factors (Gast, 1969).

Although the cation composition of soils varies widely, there can be little doubt the initial exchange ion and associated adsorption energy will affect the position of equilibria in heavy metal adsorption-desorption studies and in natural systems. Since different cations affect the basal spacings of smectite minerals, these effects may be steric as well as electrostatic (MacEwan and Wilson, 1980).

The objective in the present study was to determine the effect of initial exchange ion on adsorption and desorption of Zn by a smectite clay. Homoionic alkali metal smectites were prepared in an attempt to systematically vary the hydrated ion size and adsorption energy of the initial exchange ion. In this fashion, the periodic nature of homoionic clays and their reactivity toward Zn^{2+} could be investigated.

Materials and Methods

Preparation of adsorbents

Sodium and K saturated smectites (montmorillonite # 25, Upton, Wyoming) were prepared by repeated saturation with the appropriate 1 M MCl salt at pH 5.0. Rubidium and Cs smectites were prepared by repeated saturation with a 0.1 M MCl salt. In all cases, smectites were prepared from the < 2 um fraction which was recycled from previous Ca-Zn adsorption experiments. The saturated alkali metal smectites were dialyzed against distilled H_2O until a negative test for Cl^- was obtained using $Ag(NO_3)_2$. The resulting clay was diluted with the appropriate 0.03 MCl salt solution and stored until ready for use.

Adsorption isotherms

Batch adsorption experiments were conducted in duplicate for each of the alkali metal saturated clays by pipetting 3 mL of the rapidly stirred clay suspensions into 5 mL RIA polypropylene test tubes. Each tube received 0.2 mL of an appropriate Zn solution (Table 1) and 0.2 mL of a ^{65}Zn solution containing 1mCi ^{65}Zn L^{-1}. The mass of each clay used was determined gravimetrically. The tubes were then sealed, dispersed on a vortex mixer and equilibrated on a wrist action shaker at 26 ± 2 C for 2 wks. At the end of this period the samples were separated by centrifugation at 3000 rpm for 5 min, and a 1 mL aliquot was removed for radioassay. Eight incremental desorption cycles were accomplished by replacing the 1 mL sample with the appropriate 0.03 M MCl solution and re-equilibrating for 24 hrs.

Radiometric data were obtained on a Packard Tri-Carb spectrometer equipped with a gamma counter by comparing sample radioactivity with that obtained for known ^{65}Zn standards of the smae geometry. Equilibrium Zn concentrations were calculated from principles of isotopic dilution and mass balance. the amount of Zn adsorbed was calculated from the initial concentration. The equilibrium pH was determined on the 1 mL aliquot using a combination electrode.

The rate of Zn adsorption at the lowest Zn^{2+} level was investigated by equilibrating duplicate samples for periods of 1, 2, 4, 8 and 16 hr. Adsorbed Zn was determined as described above. The effect of longer equilibration times on adsorption was investigated at the 3 lowest Zn^{2+} levels by equilibrating duplicate samples for 24, 72, 168 and 672 hrs.

Table 1. Initial Zn^{2+} concentrations and equilibrium pH's for the adsorption of Zn by homoionic smectites

Initial Zn^{2+}	Equilibrium pH[1]			
	Na	K	Rb	Cs
uM L^{-1}				
.0097	5.49	5.66	5.73	5.45
.147	5.48	5.69	5.74	5.43
1.45	5.50	5.62	5.73	5.53
146	5.49	5.65	5.72	5.40
1450	5.13	5.21	5.36	5.18

[1] Means of duplicate samples

Results and Discussion

In this study an attempt was made to maintain the pH at a constant value so that adsorption-desorption effects could be attributed to the exchangeable ion rather than to differences in the equilibrium pH. This objective was attained as the pH in subsequent desorption cycles did not change by mnore than ± 0.1 unit, however the equilibrium pH's at the highest Zn level were lower, possibly due to hydrolysis in the bulk solution.

Adsorption data for the different homoionic clays are presented as Freundlich isotherms. For Na smectite, adsorption obeyed the Freundlich equation over 6 orders of magnitude and appears to be completely reversible over the entire range studied (Figure 1). Conformity to the Freundlich equation and complete reversibility was observed for Zn

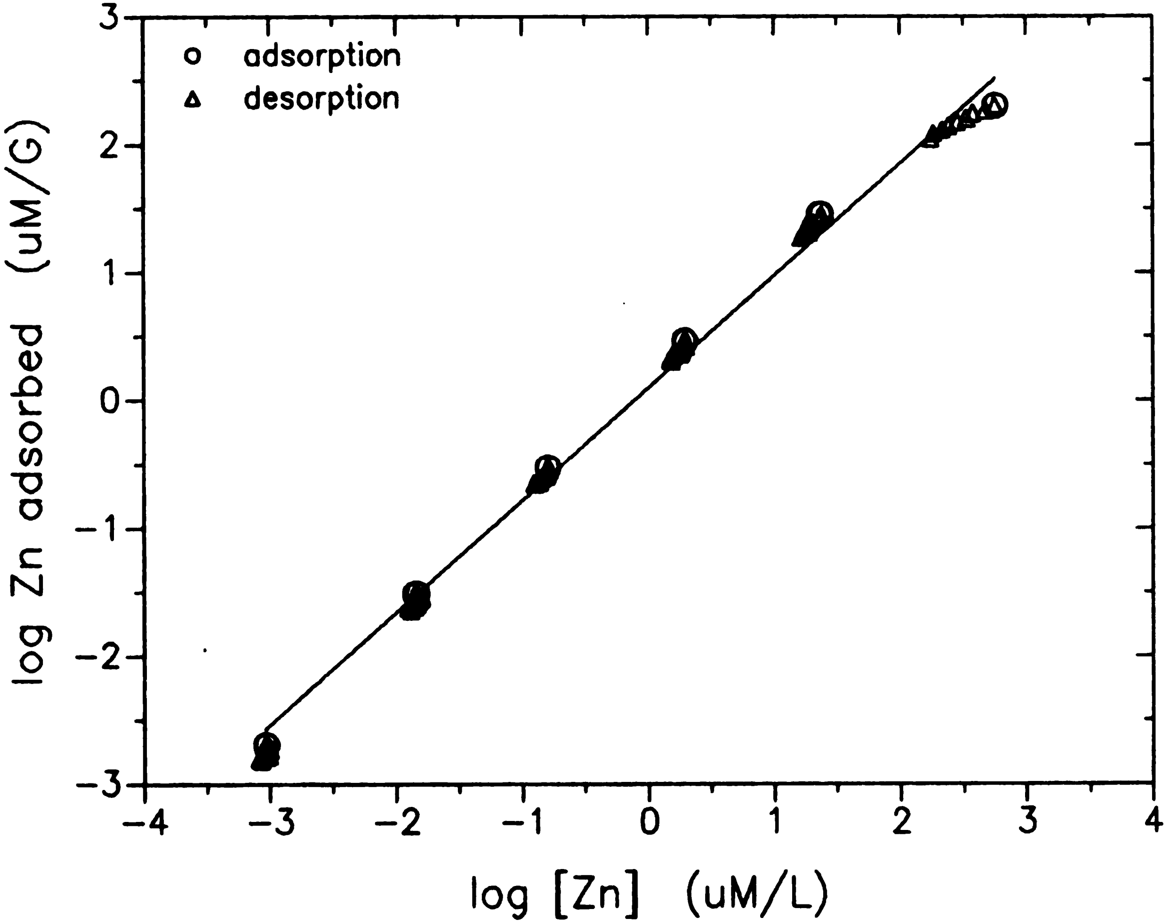

Figure 1. Adsorption and desorption of Zn by Na smectite.

adsorption on K smectite as well (Figure 2). Adsorption of Zn by Rb smectite obeyed the Freundlich equation to a degree, but more importantly, desorption hysteresis was observed at log (X/m) = 0 and below (Figure 3). At higher surface occupancies of Zn, adsorption appeared to be completely reversible as is expected in normal exchange reactions. For Cs smectite, desorption hysteresis was extreme throughout the entire adsorption range (Figure 4). Furthermore, the adsorption data did not conform to the Freundlich equation.

For Na, the desorption points are tightly grouped around the adsorption points, indicating that Na does not displace adsorbed Zn very effectively. As we proceed along the series Na, K, Rb, and Cs, there is a trend for the desorption points to spread out over a larger concentration range. This is an indication of the increasing ability of these cations to displace adsorbed Zn, and is in line with the free energy of adsorption of these cation on Wyoming montmorillonite as measured by Gast (1969). These observations are also in general agreement with data presented by Nelson and Melsted (1955), Garcia-Miragaya and Page (1977) and Shukla et al. (1980); (i.e that the smaller, more electropositive ion is adsorbed to a greater extent). That desorption hysteresis of Zn occurs on the smectites saturated with the smaller, more competative Rb and Cs ions seems to be a contradiction to the commonly observed lyotropic series. However, these observations can be explained from a kinetic viewpoint.

At the lowest Zn^{2+} level, adsorption as a function of time by the different clays follows the order Na > K > Rb > Cs (Figure 5). This order was observed at higher initial Zn^{2+} levels as well. Zn adsorption

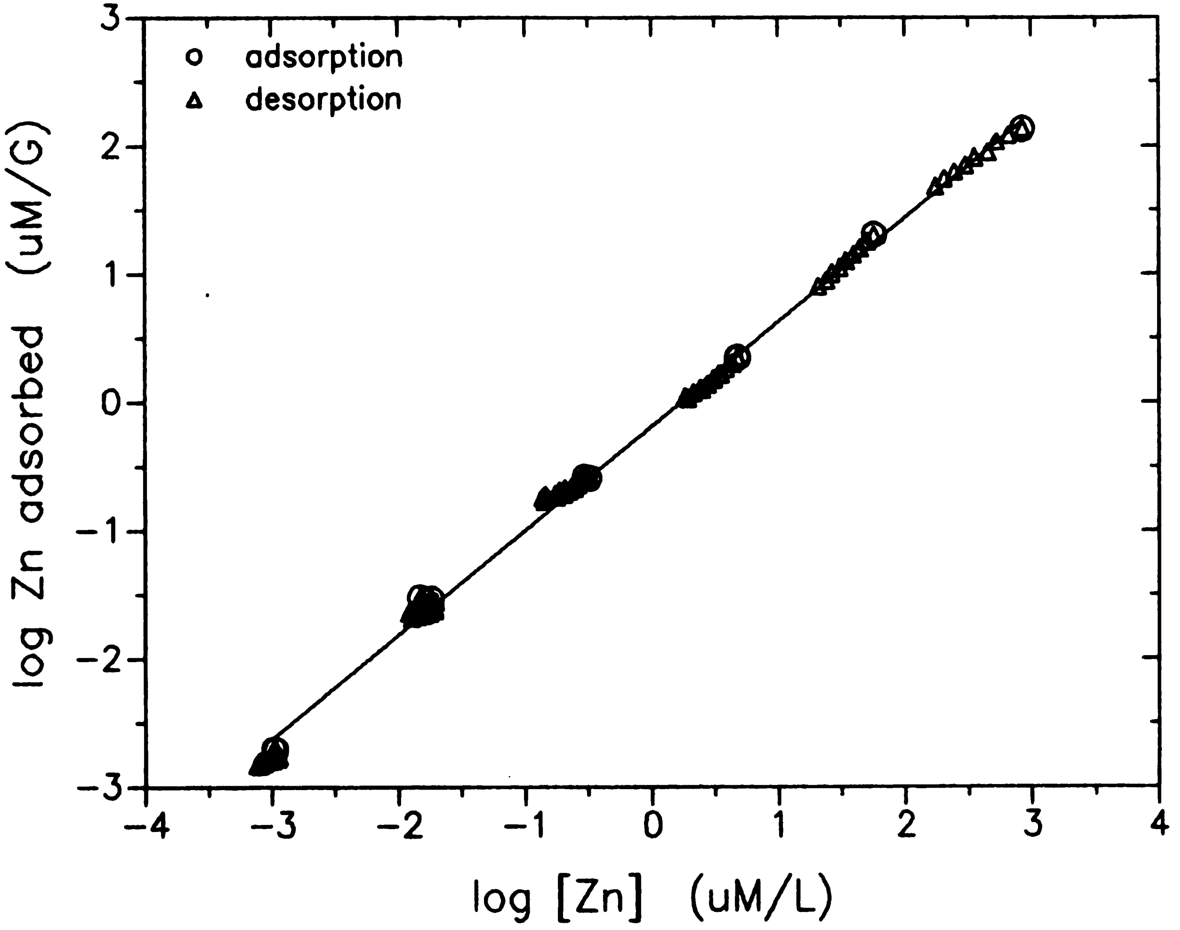

Figure 2. Adsorption and desorption of Zn by K smectite.

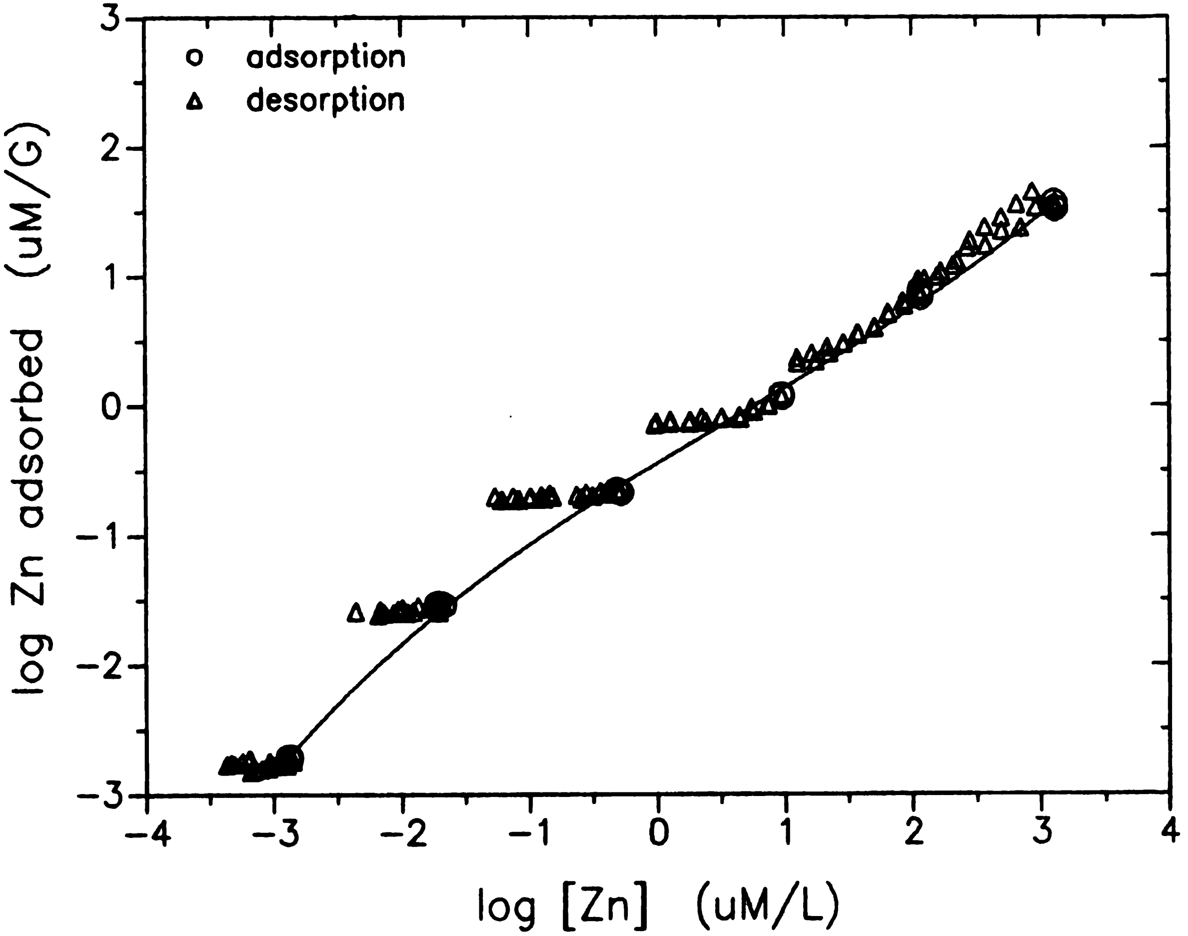

Figure 3. Adsorption and desorption of Zn by Rb smectite.

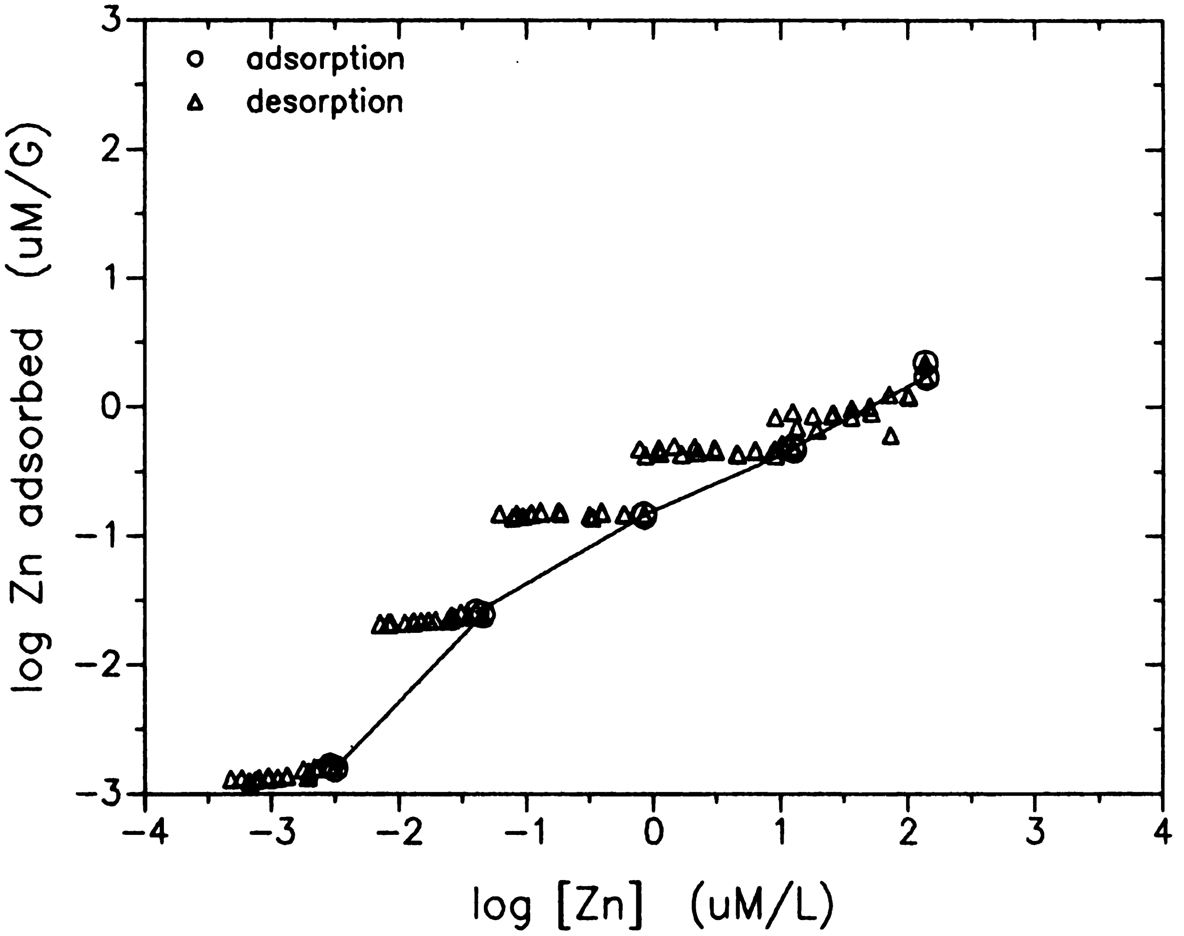

Figure 4. Adsorption and desorption of Zn by Cs smectite.

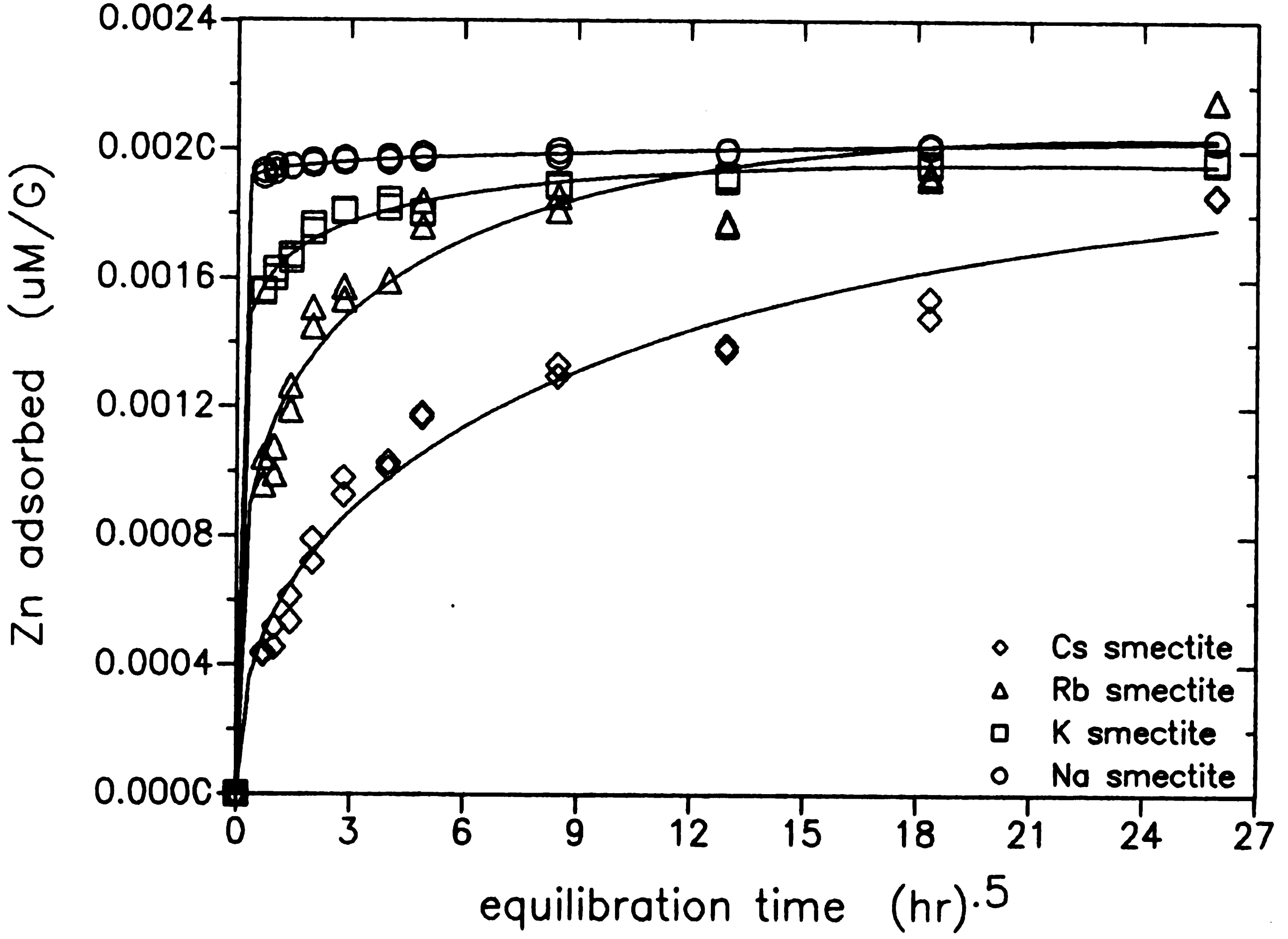

Figure 5. **Adsorption of Zn by alkali metal saturated smectites as a function of time.**

by Na (Figure 6) and K smectite (Figure 7) was > 99% complete in less than 24 hrs. This rapid equilibrium is characteristic of an ion exchange reaction (Helfferich, 1962). Adsorption equilibria of Zn for Rb (Figure 8) and Cs smectites (Figure 9) was not attained even after 672 hrs.

The different adsorption rates of Zn can be attributed to the hydrated nature of the individual alkali metal ions and their effect on the basal spacings of smectites (Wyoming montmorillonite) in H_2O (Table 2). Sodium and K spacings were large and indeterminate, and while data were not available for Rb, the value is expected to be slightly higher than that reported for Cs.

Table 2. Effect of interlayer cation on basal d(001) spacings of Wyoming montmorillonite immersed in water.

Interlayer cation	d(001) spacing[1]
	10^{-8} m
Na	>>
K	>>
Rb	--
Cs	12.5
Mg	19.5
Ca	19.0
Sr	19.0
Ba	18.8

[1] MacEwan and Wilson (1980) p. 203

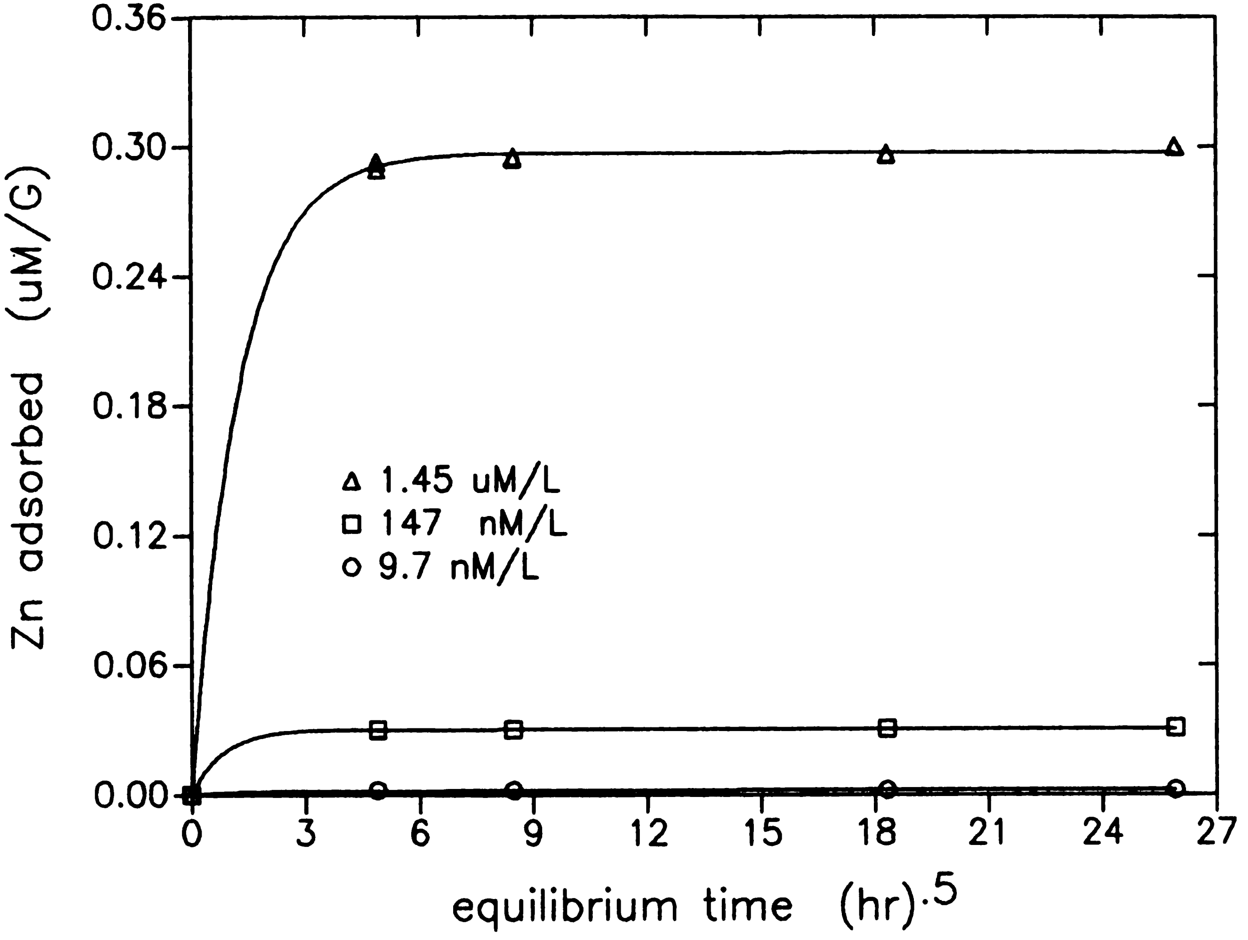

Figure 6. **Effect of time on the adsorption of Zn by Na smectite at three initial Zn levels.**

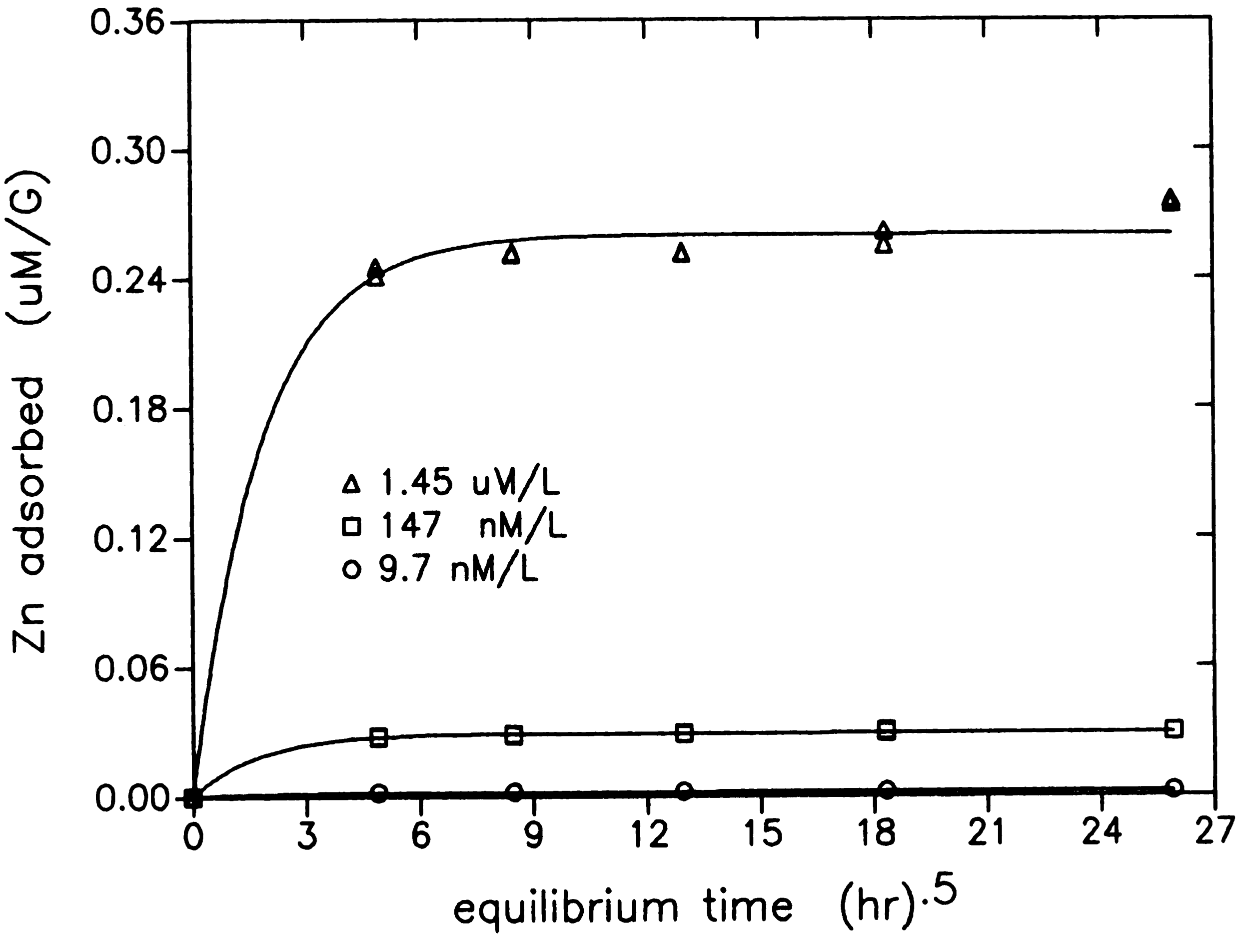

Figure 7. **Effect of time on the adsorption of Zn by K smectite at three initial Zn levels.**

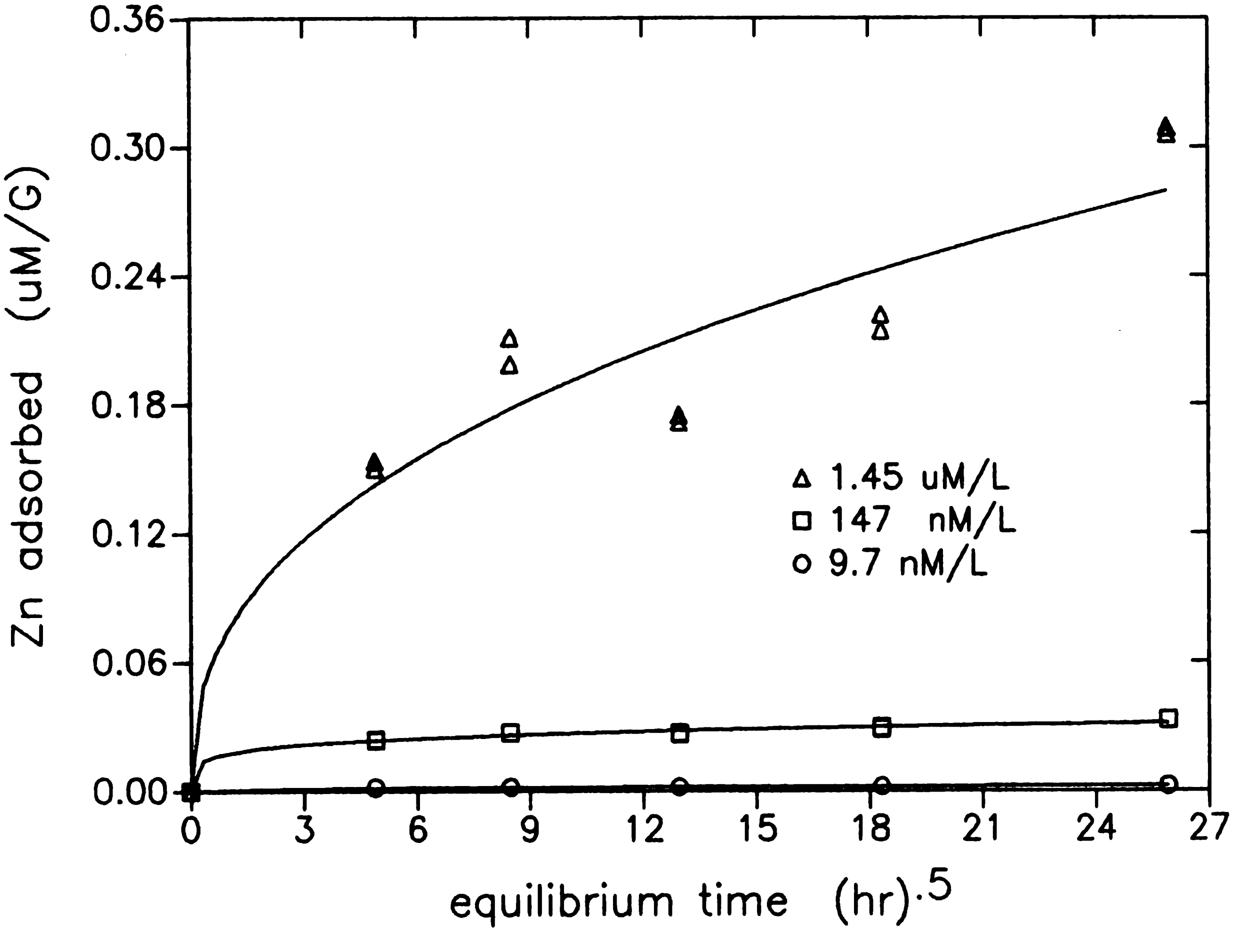

Figure 8. Effect of time on the adsorption of Zn by Rb smectite at three initial Zn levels.

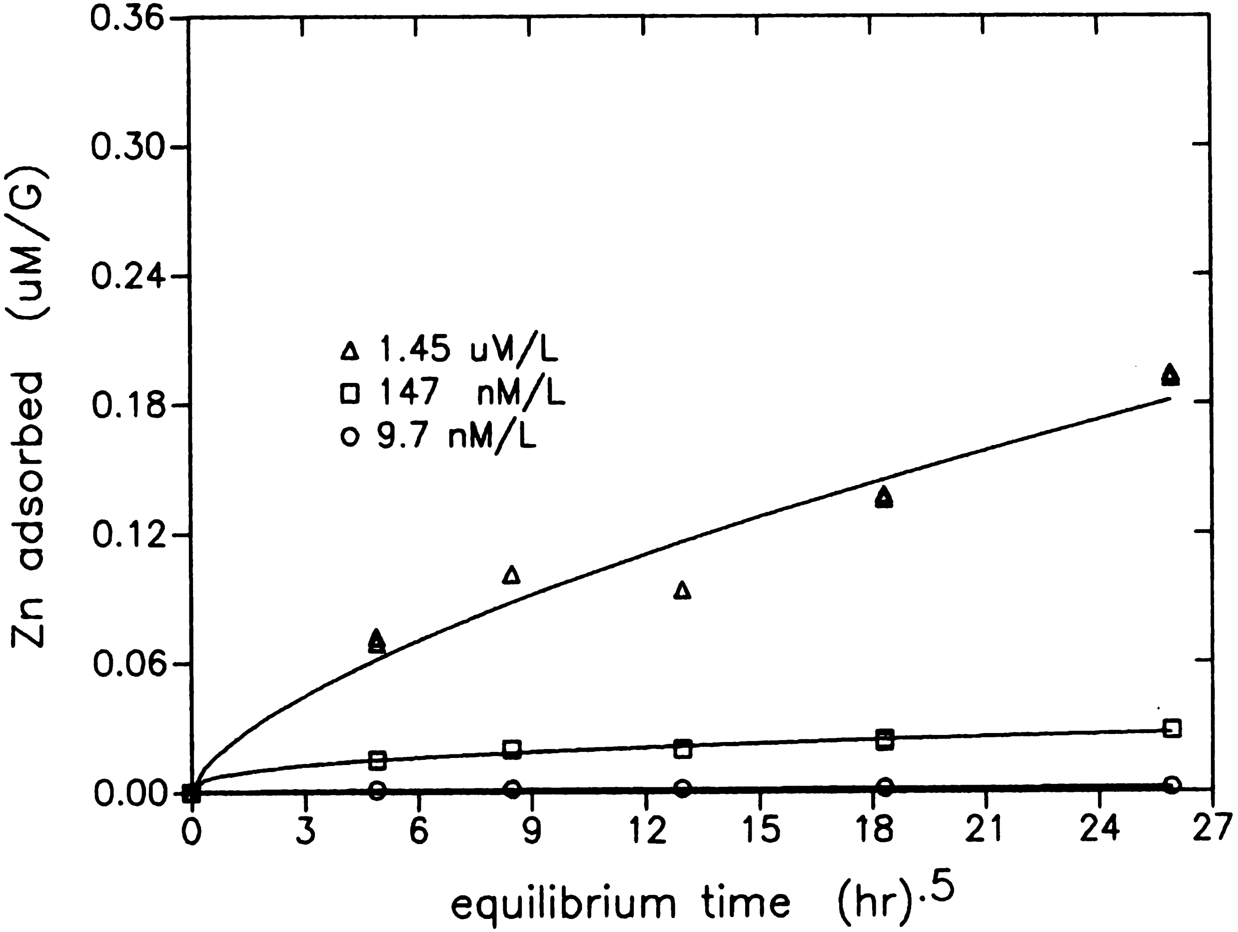

Figure 9. Effect of time on the adsorption of Zn by Cs smectite at three initial Zn Levels.

Interestingly, the values reported for alkaline earth ions are relatively constant. The value for Zn is expected to be very similar since its crystal radii and aqueous chemistry is similar to that for Mg (Cotton and Wilkinson, 1980). This would account for the fact that equilibrium was attained quite rapidly for Ca-Zn exchange (Zielke, Chapter IV). Conversely, desorption hysteresis was shown to be concentration and pH dependent in these earlier studies, and was attributed to strong bonding, possibly at broken edge OH's. In the present study, similar hysteresis would be expected on Na (and K) smectites since these ions could not compete for specific adsorption sites in other studies (Harsh and Doner, 1984). One possible explaination for this behavior was that Zn remained fixed at broken edges when Ca-Zn clays were recycled for use in this experiment.

Regardless, migration of Zn into interlamelar exchange sites on Rb and Cs smectites appear to be sterically inhibited by the limited swelling as indicated by the nonattainment of equilibria. Similarly, once adsorbed at interlayer positions, migration into the bulk solution would be equally inhibited. As a result, the occurrence of hysteresis on Rb and Cs smectites appears to be a consequence of non equilibrium rather than strong irreversible bonding at specific adsorption sites. While this was a testable hypothesis, similar desorption kinetic experiments at the lowest Zn level failed to confirm this under these experimental conditions because the rate of adsorption proceeded faster than the rate of desorption even after 8 wks.

In summary, Zn adsorption by homoionic alkali metal smectites followed the order Na > K > Rb > Cs. Data obtained in kinetic experiments revealed that both adsorption and desorption of Zn was sterically inhibited by the limited swelling of Rb and Cs smectites. Desorption hysteresis was therefore attributed to nonattainment of equilibria rather than to specific bonding as was reported in earlier Ca-Zn adsorption-desorption experiments. Failure to consider the initial exchanger composition and its effect on the attainment of equilibrium, and the ability of some homoionic smectites (eg Cs) to produce nonlinear isotherms may result in erroneous conclusions as regards desorption hysteresis or adsorption at sites with different bonding energies.

Literature Cited

Cotton, F.A. and G. Wilkinsen. 1980. Advanced inorganic chemistry. (4th ed). Interscience Publishers. John Wiley & Sons. New York

Egozy, Y. 1980. Adsorption of cadimum and cobalt on montmorillonite as a function of solution composition. Clays and Clay Miner. 28:311-318.

Elrashidi, M.A., and G.A. O'Connor. 1982. Influence of solution composition on sorption of zinc by soils. Soil Sci. Soc. Am. J. 46:1153-1158.

Garcia-Miragaya, J., and A.L. Page. 1977. Influence of exchangeable cation on the adsorption of trace amounts of cadmium by montmorillonite. Soil Sci. Soc. Am. J. 41:718-721.

Gast, R.G. 1969. Standard free energies of exchange for alkali metal cations on Wyoming bentonite. Soil Sci.1 Soc. Am. Proc. 33:37-41.

Helfferich, F. 1962. Ion exchange. McGraw-Hill. New York.

Harsh, J.G. and H.E. Doner. 1984. Specific adsorption of copper on an hydroxy-aluminum-montmorillonite complex. Soil Sci. Soc. Am. J. 48:1034-1039.

MacEwan, D.M.C. and M.J. Wilson. 1980. Interlayer and intercalation complexes of clay minerals. p. 197-248. In G.W. Brindley and G. Brown (ed.). Crystal structures of clay minerals and other X-ray identification. Mineralogical Society Monograph No. 5. Miner. Soc., London.

Nelson, J.L., and S.W. Melsted. 1955. The chemistry of added zinc to soils and clays. Soil Sci. Soc. Am. J. 19:323-326.

Shukla, V.C., S.B. Mittal, and R.K. Gupta. 1980. Zinc adsorption in some soils as affected by exchangeable cations. Soil Sci. 129:366-370.

CHAPTER VI

SUMMARY AND CONCLUSIONS

A batch equilibrium technique based on principles of isotopic dilution and mass balance was developed to study adsorption and desorption of trace amounts of Zn by Ca smectite (montmorillonite # 25, Upton, Wyoming) The technique was tested by comparison with results obtained using conventional atomic adsorption for Zn analysis. Based on these comparisons it was concluded that ^{65}Zn in solution was in kinetic equilibrium with ^{65}Zn adsorbed on the surface of Ca smectite, and hence the technique was applicable to the study of desorption hysteresis in clay minerals. Desorption hysteresis occurred when <1% of the CEC was occupied by Zn but at higher occupancies Zn adsorption was completely reversible.

Three isotherms (Linear, Freundlich and Langmuir) were tested to determine their utility in characterizing desorption. Data were obtained for Zn adsorption-desorption with Ca smectite, Charity clay (aeric haplaquept), a strong acid cation exchange resin (Ca Dowex 50W-X8), and a weak acid cation exchange-chelating resin (Ca Chelex).

None of the equations could quantitatively describe Zn adsorption or desorption by and from Ca smectite or Charity clay since nonlinear isotherms were observed, but the Linear and Freundlich equations were better than the Langmuir. The Freundlich equation was a convenient method to view adsorption over several decades of Zn^{2+} activity, even though log-log plots tend to minimize data variability.

Adsorption of Zn by Ca Dowex was completely reversible and quantitatively described by the Freundlich equation. A two surface Freundlich isotherm was obtained for Chelex, and hysteresis was observed in the high affinity region. The "two surface" behavior was attributed to reduced selectivity of the resin for Zn in acid solutions. Hysteresis was attributed to strong bonding by the chelating resin.

Comparison of the behavior of the model ion exchangers with the smectite and Charity clay Freundlich isotherms allowed insight to the mechanisms operating in adsorption, desorption and hysteresis. For smectite the reaction was completely reversible at high surface occupancies, but hysteresis was observed at low surface occupancy. Reversibility was attributed to an ion exchange mechanism. For Charity clay, extreme hysteresis occurred at all Zn levels. Hysteresis on both materials resembled the behavior of the Chelex resin in the high affinity region. For smectite, hysteresis was attributed to strong bonding at broken edge OH's, while Zn retention on the Charity clay could be due to strong bonding on broken edges of clay minerals, Al and Fe oxides, free carbonates or organic matter.

There was a strong interaction between pH and hysteresis in Zn adsorption-desorption on Ca smectite. At pH 3.5, a linear Freundlich isotherm was observed and adsorption was reduced probably because of competition with Al^{3+} that resulted from acidic dissolution of the clay mineral. However, the reaction was completely reversible at all Zn levels. In general, as the pH increased, adsorption and hysteresis increased. At the highest initial Zn^{2+} level, adsorption was relatively constant at all pH's and was completely reversible. Furthermore, the ability of smectite clay to mask precipitation was observed since adsorption of large amounts of Zn was reversible even in alkaline solution. Thus hysteresis was shown to be pH dependent while adsorption in the higher end of the isotherm could be attributed to ion exchange on permanently charged sites. In combination these factors contributed to nonlinear Freundlich isotherms. The pH dependency of hysteresis must be attributed to strong bonding at broken edge OH sites since these sites are considered to be the only source of pH dependent charge in the system.

The effect of the initial exchange ion on Zn adsorption was also investigated using homoionic Na, K, Rb and Cs smectites. Hysteresis was not observed on Na an K smectites as was expected from the occurrence of hysteresis in previous Ca-Zn studies. This anomaly was attributed to incomplete removal of Zn from hysteretic sites because the smectites were prepared from clays recycled from previous Ca-Zn experiments. Regardless, the extent of Zn adsorption followed the lyotropic series Na > K > Rb > Cs. The ability of these ions to compete with Zn^{2+} for permanently charged exchange sites also followed this order and was observed as a spreading out of the desorption points along the lyotropic series.

Extreme hysteresis was observed for Rb and Cs smectites, and while this appeared to be contradictory to their highly competitive nature, kinetic studies revealed hysteresis was an artifact of nonequilibrium. Adsorption and desorption was sterically inhibited at interlayer exchange sites because Rb and Cs ions have a demonstrated ability to reduce swelling in smectite minerals thus reducing the rate of diffusion of Zn into and out of interlayer positions.

APPENDIX

APPENDIX

NUCALC

```
10 REM NUCALC.BAS CALCULATES PPM ZN IN SOLUTION FROM RADIACTIVE CPM AND
PRINCIPLES OF ISOTOPIC DILUTION VIA A MASS BALANCE APPROACH AND PRODUCES
A HARD COPY OF THE MODEL PARAMETERS AND INPUT AND OUTPUT FILES
20 REM NUCALC.BAS ALSO CALCULATES VALUES FOR CONSTRUCTION OF
GENERAL,FREUNDLICH AND LANGMUIR ISOTHERMS
30 REM NUCALC.BAS WAS WRITEN BY RICHARD CLEVELAND ZIELKE GRADUATE
ASSISTANT IN SOIL CHEMISTRY MICHIGAN STATE UNIVERSITY CROP AND SOIL
SCIENCES DEPARTMENT  JULY 23 1986
40 LPRINT CHR$(27) "N"CHR$(6)
50 LPRINT CHR$(27) "M";
60 LPRINT CHR$(27) "P" CHR$(15);
70 WIDTH "LPT1:",150
80 LPRINT CHR$(27) "1"CHR$(10);
90 LPRINT CHR$(27) "Q"CHR$(140);
100 DEFDBL Z,G,F,L
110 OPTION BASE 1
120 INPUT "WHAT IS THE NUMBER OF TREATMENTS?",N
130 INPUT "WHAT IS THE NUMBER OF ADSORPTION/DESORPTION CYCLES?",D
140 DIM CSTD(N,D),CSAM(N,D),ZI(N,D),ZF(N,D),ZREM(N,D)
150  DIM ZADS(N,D),ZINI(N,D),ZSOL(N,D),CORR(N,D)
160 DIM GX(N,D),GY(N,D),FX(N,D),FY(N,D),LX(N,D),LY(N,D)
170  REM CSTD-STANDARD CPM CORRECTED FOR COUNTING GEOMETRY  CSAM-SAMPLE
CPM       ZI-INITIAL PPM ZN  ZF-FINAL PPM ZN   ZREM-MG ZN REMAINING IN
SYSTEM AFTER EQUIL ZADS-MG ZN ADSORBED  ZINI-MG ZN IN SYSTEM BEFORE
EQUIL  ZSOL-MG ZN IN SOLUTION  AT EQUIL
180 REM CORR-SAMPLE COUNT ADJUSTED FOR COUNTING GEOMETRY
190 REM GX-ZN ACTIVITY (uM/L) GY-X/M (uM/G) FX-LOG [ZN] FY-LOG X/M LX-ZN
ACTIVITY LY-C/X/M (uM/L/uM/G)
200 INPUT "WHAT IS MESSAGE?",A$
210 INPUT "WHAT IS THE SAMPLE VOLUME IN MLS?",VS
220 INPUT "WHAT IS THE ANALYTE VOLUME IN MLS?",VA
230 INPUT "WHAT IS IONIC STRENGTH IN M/L?",U
240 INPUT "WHAT IS THE SAMPLE WEIGHT IN GRAMS? ",W
250 K-10^(-.5085*4*U^.5/(1+1.969*U^.5)) :REM EXTENDED DE BYE HUCKEL EQN
TO         CALCULATE ZN ACTIVITY COEFFICIENT
260 INPUT "WHAT IS THE AVERAGE BACKGROUND COUNT?",CBKGD
270 INPUT "WHAT IS THE AVERAGE STANDARD COUNT?",CSTD
280 STD-CSTD-CBKGD
290   LPRINT   "                   *************************PROGRAM   IS
NUCALC.BAS*************************         ":LPRINT "IDENTIFYING MESSAGE:
";:LPRINT A$
300 LPRINT "                         *****INPUT PARAMETERS FOR SPECIFIED
FILENAME*****"
```

```
310 LPRINT "SAMPLE VOLUME IN MLS=";VS
320 LPRINT "ANALYTE VOLUME IN MLS=";VA
330  LPRINT "IONIC STRENGTH=";U
340 LPRINT "ZN ACTIVITY COEFFICIENT= ";K
350  LPRINT "SAMPLE WEIGHT IN GRAMS=";W
360 LPRINT "BACKGROUND COUNT IN CPM=";CBKGD
370 LPRINT "UNCORRECTED STANDARD COUNT IN CPM=";CSTD
380 CLS:FILES "A:*.DAT"
390 INPUT "WHAT IS FILENAME CONTAINING CPM DATA (OMIT EXTENSION)?",F$
400 S$=F$+".DAT"
410 LPRINT "INPUT FILENAME=";S$:LPRINT
420 OPEN "I",#1,S$
430 FOR I=1 TO N:FOR J=1 TO D:INPUT#1,CSAM(I,J):NEXT:NEXT
440 LPRINT S$;:LPRINT "(UNCORRECTED FOR BACKGROUND CPM)"
450  FOR  I=1  TO  N:FOR  J=1  TO  D:LPRINT  CSAM(I,J);"  ";:NEXT:LPRINT,"
":NEXT:LPRINT
460 CLOSE #1
470 T$=F$+".COR"
480 FOR I=1 TO N:FOR J=1 TO D:CSAM(I,J)=CSAM(I,J)-CBKGD:NEXT:NEXT
490 OPEN "O",#2,T$
500  FOR  I=1  TO  N:FOR  J=1  TO  D:PRINT#2,CSAM(I,J);"  ";:NEXT:PRINT#2,"
":NEXT
510 LPRINT T$;:LPRINT "(CORRECTED FOR BACKGROUND CPM)"
520 FOR I=1 TO N:FOR J=1 TO D:LPRINT CSAM(I,J);" ";:NEXT:LPRINT," ":NEXT
530 LPRINT:
540 CLOSE #2
550 OPEN T$ FOR INPUT AS #3
560 FOR I=1 TO N:FOR J=1 TO D:INPUT#3,CSAM(I,J):NEXT:NEXT
570 LPRINT "INITIAL PPM ZN  FINAL PPM ZN    INITIAL MG ZN   MG ZN
REMAININ  MG ZN ADSORBED"
580               '*************************START             DATA
CALCULATIONS**************************
590 FOR I=1 TO N
600 FOR J=1 TO D
610 IF J=1 THEN CSTD(I,J)=STD*VS/VA
620 IF J>1 THEN CSTD(I,J)=CSTD(I,J-1)-CSAM(I,J-1)
630 CORR(I,J)=CSAM(I,J)*VS/VA
640 IF J=1 THEN INPUT "WHAT IS THE INITIAL PPM ZN?",ZI(I,J)
650 IF J>1 THEN ZI(I,J)=ZF(I,J-1)*(VS-VA)/VS
660 IF J=1 THEN ZINI(I,J)=ZI(I,J)*VS/1000
670  IF J>1 THEN ZINI(I,J)=ZREM(I,J-1)
680 ZSOL(I,J)=CORR(I,J)*ZINI(I,J)/CSTD(I,J)
690 ZF(I,J)=ZSOL(I,J)*1000/VS
700 ZREM(I,J)=ZINI(I,J)-ZF(I,J)*VA/1000
710 ZADS(I,J)=ZINI(I,J)-ZSOL(I,J)
720 GX(I,J)=ZF(I,J)*K/.06537
730 IF J=1 THEN GY(I,J)=(ZI(I,J)-ZF(I,J))*VS*1000/(65370!*W)
740 IF J>1 THEN GY(I,J)=GY(I,J-1)+(ZI(I,J)-ZF(I,J))*VS*1000/(65370!*W)
750 FY(I,J)=LOG(GY(I,J))/2.30256
760 FX(I,J)=LOG(ZF(I,J)/.06537)/2.30256
770 LX(I,J)=GX(I,J)
780 LY(I,J)=LX(I,J)/GY(I,J)
```

```
790   LPRINT  USING" ###.#########      ###.#########      ###.#########
###.#########
###.#########";ZI(I,J),ZF(I,J),ZINI(I,J),ZREM(I,J),ZADS(I,J)
800 NEXT J
810 LPRINT
820 NEXT I
830              '**************************END                 DATA
CALCULATIONS**************************
840 CLOSE #3
850 KILL T$
860  U$-F$+".OUT"
870  OPEN "O",#3,U$
880     FOR   I-1   TO   N:FOR   J-1   TO   D:PRINT#3,USING   "###.#######
";ZI(I,J);ZF(I,J);:NEXT:PRINT#3,:NEXT
890 LPRINT U$;:LPRINT "(ADJACENT COLUMNS ARE INITIAL AND FINAL ZN
REMAINING IN SOLUTION AT EQUILIBRIUM. THE # OF COLUMNS/2 -# OF
DESORPTION CYCLES. ADJACENT ROWS ARE REPS.)"
900 K$-"INI PPM ZN":L$-"FIN PPM ZN"
910 LPRINT USING "\         \";K$,L$
920     FOR   I-1   TO   N:FOR   J-1   TO   D:LPRINT   USING   "###.#######
";ZI(I,J);ZF(I,J);:NEXT:LPRINT:NEXT
930  CLOSE #3
940 GOSUB 1490
950 REM SUBROUTINE TO PRINT AND FILE GENERAL,FREUNDLICH AND LANGMUIR
ISOTHERMS
960 H$-"G"+F$+".SDF"
970 I$-"F"+F$+".SDF"
980 J$-"L"+F$+".SDF"
990 OPEN "O",#1,H$
1000 OPEN "O",#2,I$
1010 OPEN "O",#3,J$
1020   FOR   I-1   TO   N:FOR   J-1   TO   D:PRINT#1,USING   "####.#######
";GX(I,J);GY(I,J);:NEXT:PRINT#1,:NEXT
1030 LPRINT:LPRINT H$;:LPRINT "  GENERAL ADSORPTION ISOTHERM DATA"
1040 GOSUB 1250
1050 M$-"X(uM ZN/L)":N$-"Y(uM ZN/G)"
1060 LPRINT USING "\          \";M$,N$
1070   FOR   I-1   TO   N:FOR   J-1   TO   D:LPRINT   USING   "####.#######
";GX(I,J);GY(I,J);:NEXT:LPRINT:NEXT:LPRINT
1080   FOR   I-1   TO   N:FOR   J-1   TO   D:PRINT#2,USING   "##.#####
";FX(I,J);FY(I,J);:NEXT:PRINT#2,:NEXT
1090 LPRINT I$;:LPRINT "  FREUNDLICH ADSORPTION ISOTHERM DATA"
1100 GOSUB 1330
1110 O$-"X LOG[ZN]":P$-"Y LOG X/M"
1120 LPRINT USING "\         \";O$,P$
1130   FOR   I-1   TO   N:FOR   J-1   TO   D:LPRINT   USING   "##.#####
";FX(I,J);FY(I,J);:NEXT:LPRINT:NEXT:LPRINT
1140   FOR   I-1   TO   N:FOR   J-1   TO   D:PRINT#3,USING   "####.#######
";LX(I,J);LY(I,J);:NEXT:PRINT#3,:NEXT
1150 LPRINT J$;:LPRINT "  LANGMUIR ADSORPTION ISOTHERM DATA"
1160 GOSUB 1410
1170 Q$-"X(uM ZN/L)":R$-"Y(uM ZN/L/uM/G)"
1180 LPRINT USING "\            \";Q$,R$
```

```
1190 FOR I=1 TO N:FOR J=1 TO D:LPRINT USING "####.#######
";LX(I,J);LY(I,J);:NEXT:LPRINT:NEXT:LPRINT
1200 CLOSE #1:CLOSE #2: CLOSE #3
1210 LPRINT CHR$(27) "@"
1220 WIDTH "LPT1:",80
1230 END
1240 REM *****SUBROUTINE TO PRINT REGRESSION EQUATIONS
1250 LPRINT "FOR THE GENERAL ISOTHERM (ZN) VS  X/M "
1260 LPRINT "B=";B9;TAB(25),"A=";A3;TAB(45);"R^2=";R9
1270 Y5=B9*GX(1,1)+A3
1280 Y6=B9*GX(N,1)+A3
1290 LPRINT "X5=";GX(1,1);TAB(40),"Y5=";Y5
1300 LPRINT "X6=";GX(N,1);TAB(40),"Y6=";Y6
1310 LPRINT "Y=";B9;"X+";A3
1320 RETURN
1330 LPRINT "FOR THE FREUNDLICH EQUATION LOG [ZN] VS LOG X/M"
1340 LPRINT "B=";B3;TAB(25),"A=";A1;TAB(45);"R^2=";R3
1350 Y1=B3*FX(1,1)+A1
1360 Y2=B3*FX(N,1)+A1
1370 LPRINT "X1=";FX(1,1);TAB(40),"Y1=";Y1
1380 LPRINT "X2=";FX(N,1);TAB(40),"Y2=";Y2
1390 LPRINT "Y=";B3;"X+";A1
1400 RETURN
1410 LPRINT "FOR THE LANGMUIR ISOTHERM (ZN) VS  C/X/M"
1420 LPRINT "B=";B12;TAB(25),"A=";A4;TAB(45),"R^2=";R12
1430 Y7=B12*LX(1,1)+A4
1440 Y8=B12*LX(N,1)+A4
1450 LPRINT "X7=";LX(1,1);TAB(40),"Y7=";Y7
1460 LPRINT "X8=";LX(N,1);TAB(40),"Y8=";Y8
1470 LPRINT "Y=";B12;"X+";A4;TAB(40),"APPARENT ADSORPTION MAXIMUM=
";B14;" (uM Zn/G)"
1480 RETURN
1490 REM SUBROUTINE TO CALCULATE REGRESSION EQUATIONS
1500 LOXY=0
1510 PQXY=0
1520 PXXY=0
1530 XSUMLO=0
1540 YSUMLO=0
1550 XSUMPQ=0
1560 YSUMPQ=0
1570 XSUMPX=0
1580 YSUMPX=0
1590 XSSLO=0
1600 YSSLO=0
1610 XSSPQ=0
1620 YSSPQ=0
1630 XSSPX=0
1640 YSSPX=0
1650 FOR I=1 TO N
1660 REM *****GENERAL
1670 PXXY=PXXY+GX(I,1)*GY(I,1)
1680 XSUMPX=XSUMPX+GX(I,1)
1690 YSUMPX=YSUMPX+GY(I,1)
1700 XSSPX=XSSPX+GX(I,1)^2
```

```
1710 YSSPX=YSSPX+GY(I,1)^2
1720 REM *****FREUNDLICH
1730 LOXY=LOXY+FY(I,1)*FX(I,1)
1740 XSUMLO=XSUMLO+FX(I,1)
1750 YSUMLO=YSUMLO+FY(I,1)
1760 XSSLO=XSSLO+FX(I,1)^2
1770 YSSLO=YSSLO+FY(I,1)^2
1780 REM *****LANGMUIR
1790 PQXY=PQXY+LX(I,1)*LY(I,1)
1800 XSUMPQ=XSUMPQ+LX(I,1)
1810 YSUMPQ=YSUMPQ+LY(I,1)
1820 XSSPQ=XSSPQ+LX(I,1)^2
1830 YSSPQ=YSSPQ+LY(I,1)^2
1840 NEXT I
1850 REM *****TO CALCULATE GENERAL REGRESSION
1860 B7=PXXY-XSUMPX*YSUMPX/N
1870 B8=XSSPX-XSUMPX^2/N
1880 B9=B7/B8
1890 A3=YSUMPX/N-B9*XSUMPX/N
1900 R7=B7^2
1910 R8=B8*(YSSPX-YSUMPX^2/N)
1920 R9=R7/R8
1930 REM *****TO CALCULATE FREUNDLICH REGRESSION
1940 B1=LOXY-XSUMLO*YSUMLO/N
1950 B2=XSSLO-XSUMLO^2/N
1960 B3=B1/B2
1970 A1=YSUMLO/N-B3*XSUMLO/N
1980 R1=B1^2
1990 R2=B2*(YSSLO-YSUMLO^2/N)
2000 R3=R1/R2
2010 REM *****TO CALCULATE LANGMUIR REGRESSION
2020 B10=PQXY-XSUMPQ*YSUMPQ/N
2030 B11=XSSPQ-XSUMPQ^2/N
2040 B12=B10/B11
2050 A4=YSUMPQ/N-B12*XSUMPQ/N
2060 R10=B10^2
2070 R11=B11*(YSSPQ-YSUMPQ^2/N)
2080 R12=R10/R11
2090 B14=B11/B10
2100 RETURN
```

ZNCALC

```
10 REM ZNCALC.BAS CALCULATES VALUES FOR CONSTRUCTION OF
GENERAL,FREUNDLICH AND LANGMUIR ISOTHERMS USING ZN(I,J) AND ZF(I,J) AS
MEASURED BY AA SPECTROSCOPY
20 REM ZNCALC.BAS WAS WRITEN BY RICHARD CLEVELAND ZIELKE GRADUATE
ASSISTANT IN SOIL CHEMISTRY MICHIGAN STATE UNIVERSITY CROP AND SOIL
SCIENCES DEPARTMENT  JULY 23 1986
30 LPRINT CHR$(27) "N"CHR$(6)
40 LPRINT CHR$(27) "M";
50 LPRINT CHR$(27) "P" CHR$(15);
```

```
60 WIDTH "LPT1:",150
70 LPRINT CHR$(27) "1"CHR$(10);
80 LPRINT CHR$(27) "Q"CHR$(140);
90 DEFDBL Z,G,F,L
100 OPTION BASE 1
110 INPUT "WHAT IS THE NUMBER OF TREATMENTS?",N
120 INPUT "WHAT IS THE NUMBER OF ADSORPTION/DESORPTION CYCLES?",D
130 DIM ZI(N,D),ZF(N,D),ZREM(N,D)
140 DIM ZADS(N,D),ZINI(N,D),ZSOL(N,D),ZDES(N,D)
150 DIM GX(N,D),GY(N,D),FX(N,D),FY(N,D),LX(N,D),LY(N,D)
160 ZI=INITIAL PPM ZN  ZF=FINAL PPM ZN   ZREM=MG ZN REMAINING IN SYSTEM
AFTER EQUIL ZADS=MG ZN ADSORBED  ZINI=MG ZN IN SYSTEM BEFORE EQUIL
ZSOL=MG ZN IN SOLUTION  AT EQUIL ZDES=MG ZN DESORBED
170 REM GX=ZN ACTIVITY (uM/L) GY=X/M (uM/G) FX=LOG [ZN] FY=LOG X/M LX=ZN
ACTIVITY LY=C/X/M (uM/L/uM/G)
180 INPUT "WHAT IS MESSAGE?",A$
190 INPUT "WHAT IS THE SAMPLE VOLUME IN MLS?",VS
200 INPUT "WHAT IS THE ANALYTE VOLUME IN MLS?",VA
210 INPUT "WHAT IS IONIC STRENGTH IN M/L?",U
220 INPUT "WHAT IS THE SAMPLE WEIGHT IN GRAMS? ",W
230 K=10^(-.5085*4*U^.5/(1+1.969*U^.5)) :REM EXTENDED DE BYE HUCKEL EQN
TO          CALCULATE ZN ACTIVITY COEFFICIENT
240   LPRINT   "                    *************************PROGRAM   IS
ZNCALC.BAS*************************       ":LPRINT "IDENTIFYING MESSAGE:
";:LPRINT A$
250 LPRINT "                        *****INPUT PARAMETERS FOR SPECIFIED
FILENAME*****"
260 LPRINT "SAMPLE VOLUME IN MLS=";VS
270 LPRINT "ANALYTE VOLUME IN MLS=";VA
280  LPRINT "IONIC STRENGTH=";U
290 LPRINT "ZN ACTIVITY COEFFICIENT= ";K
300  LPRINT "SAMPLE WEIGHT IN GRAMS=";W
310   INPUT   "WHAT   IS   FILENAME   CONTAINING   ZF(I,J)   DATA   (OMIT
EXTENSION)?",F$
320 S$=F$+".DAT"
330 LPRINT "INPUT FILENAME=";S$:LPRINT
340 OPEN "I",#1,S$
350 FOR I=1 TO N:FOR J=1 TO D:INPUT#1,ZF(I,J):NEXT:NEXT
360 LPRINT "INITIAL PPM ZN  FINAL PPM ZN     INITIAL MG ZN    MG ZN
REMAININ  MG ZN ADSORBED   MG ZN DESORBED"
370                '**************************START                 DATA
CALCULATIONS**************************
380 FOR I=1 TO N
390 FOR J=1 TO D
400 IF J=1 THEN INPUT "WHAT IS THE INITIAL PPM ZN?",ZI(I,J)
410 IF J>1 THEN ZI(I,J)=ZF(I,J-1)*(VS-VA)/VS
420 IF J=1 THEN ZINI(I,J)=ZI(I,J)*VS/1000
430  IF J>1 THEN ZINI(I,J)=ZREM(I,J-1)
440 ZSOL(I,J)=ZF(I,J)*VS/1000
450 ZREM(I,J)=ZINI(I,J)-ZF(I,J)*VA/1000
460 ZADS(I,J)=ZINI(I,J)-ZSOL(I,J)
470  IF J=1 THEN ZDES(I,J)=0 ELSE ZDES(I,J)=ZADS(I,J-I)-ZADS(I,J)
480 GX(I,J)=ZF(I,J)*K/.06537
490 IF J=1 THEN GY(I,J)=(ZI(I,J)-ZF(I,J))*VS*1000/(65370!*W)
```

```
500 IF J>1 THEN GY(I,J)-GY(I,J-1)+(ZI(I,J)-ZF(I,J))*VS*1000/(65370!*W)
510 FY(I,J)-LOG(GY(I,J))/2.30256
520 FX(I,J)-LOG(ZF(I,J)/.06537)/2.30256
530 LX(I,J)-GX(I,J)
540 LY(I,J)-LX(I,J)/GY(I,J)
550   LPRINT  USING"  ###.#########     ###.#########      ###.#########
###.#########                                            ###.#########
###.#########";ZI(I,J),ZF(I,J),ZINI(I,J),ZREM(I,J),ZADS(I,J),ZDES(I,J)
560 NEXT J
570 LPRINT
580 NEXT I
590                  '***************************END                DATA
CALCULATIONS***************************
600 CLOSE #1
610  U$-F$+".OUT"
620  OPEN "O",#3,U$
630     FOR  I-1  TO  N:FOR  J-1  TO  D:PRINT#3,USING  "###.#######
";ZI(I,J);ZF(I,J);:NEXT:PRINT#3,:NEXT
640 LPRINT U$;:LPRINT "(ADJACENT COLUMNS ARE INITIAL AND FINAL ZN
REMAINING IN SOLUTION AT EQUILIBRIUM. THE # OF COLUMNS/2 -# OF
DESORPTION CYCLES. ADJACENT ROWS ARE REPS.)"
650 K$-"INI PPM ZN":L$-"FIN PPM ZN"
660 LPRINT USING "\          \";K$,L$
670     FOR  I-1  TO  N:FOR  J-1  TO  D:LPRINT  USING  "###.#######
";ZI(I,J);ZF(I,J);:NEXT:LPRINT:NEXT
680  CLOSE #3
690 GOSUB 1220
700 REM SUBROUTINE TO PRINT AND FILE GENERAL,FREUNDLICH AND LANGMUIR
ISOTHERMS
710 H$-"G"+F$+".SDF"
720 I$-"F"+F$+".SDF"
730 J$-"L"+F$+".SDF"
740 OPEN "O",#1,H$
750 OPEN "O",#2,I$
760 OPEN "O",#3,J$
770   FOR  I-1  TO  N:FOR  J-1  TO  D:PRINT#1,USING  "####.#######
";GX(I,J);GY(I,J);:NEXT:PRINT#1,:NEXT
780 LPRINT:LPRINT H$;:LPRINT "  GENERAL ADSORPTION ISOTHERM DATA"
790 GOSUB 980
800 M$-"X(uM ZN/L)":N$-"Y(uM ZN/G)"
810 LPRINT USING "\           \";M$,N$
820   FOR  I-1  TO  N:FOR  J-1  TO  D:LPRINT  USING  "####.#######
";GX(I,J);GY(I,J);:NEXT:LPRINT:NEXT:LPRINT
830   FOR  I-1  TO  N:FOR  J-1  TO  D:PRINT#2,USING  "##.#####
";FX(I,J);FY(I,J);:NEXT:PRINT#2,:NEXT
840 LPRINT I$;:LPRINT "  FREUNDLICH ADSORPTION ISOTHERM DATA"
850 GOSUB 1060
860 O$-"X LOG[ZN]":P$-"Y LOG X/M"
870 LPRINT USING "\         \";O$,P$
880   FOR  I-1  TO  N:FOR  J-1  TO  D:LPRINT  USING  "##.#####
";FX(I,J);FY(I,J);:NEXT:LPRINT:NEXT:LPRINT
890   FOR  I-1  TO  N:FOR  J-1  TO  D:PRINT#3,USING  "####.#######
";LX(I,J);LY(I,J);:NEXT:PRINT#3,:NEXT
900 LPRINT J$;:LPRINT "  LANGMUIR ADSORPTION ISOTHERM DATA"
```

```
910 GOSUB 1140
920 Q$-"X(uM ZN/L)":R$-"Y(uM ZN/L/uM/G)"
930 LPRINT USING "\             \";Q$,R$
940  FOR  I-1  TO  N:FOR  J-1  TO  D:LPRINT  USING  "####.#######
";LX(I,J);LY(I,J);:NEXT:LPRINT:NEXT:LPRINT
950 CLOSE #1:CLOSE #2: CLOSE #3
960 END
970 REM *****SUBROUTINE TO PRINT REGRESSION EQUATIONS
980 LPRINT "FOR THE GENERAL ISOTHERM (ZN) VS  X/M "
990 LPRINT "B-";B9;TAB(25),"A-";A3;TAB(45);"R^2-";R9
1000 Y5-B9*GX(1,1)+A3
1010 Y6-B9*GX(N,1)+A3
1020 LPRINT "X5-";GX(1,1);TAB(40),"Y5-";Y5
1030 LPRINT "X6-";GX(N,1);TAB(40),"Y6-";Y6
1040 LPRINT "Y-";B9;"X+";A3
1050 RETURN
1060 LPRINT "FOR THE FREUNDLICH EQUATION LOG [ZN] VS LOG X/M"
1070 LPRINT "B-";B3;TAB(25),"A-";A1;TAB(45);"R^2-";R3
1080 Y1-B3*FX(1,1)+A1
1090 Y2-B3*FX(N,1)+A1
1100 LPRINT "X1-";FX(1,1);TAB(40),"Y1-";Y1
1110 LPRINT "X2-";FX(N,1);TAB(40),"Y2-";Y2
1120 LPRINT "Y-";B3;"X+";A1
1130 RETURN
1140 LPRINT "FOR THE LANGMUIR ISOTHERM (ZN) VS  C/X/M"
1150 LPRINT "B-";B12;TAB(25),"A-";A4;TAB(45),"R^2-";R12
1160 Y7-B12*LX(1,1)+A4
1170 Y8-B12*LX(N,1)+A4
1180 LPRINT "X7-";LX(1,1);TAB(40),"Y7-";Y7
1190 LPRINT "X8-";LX(N,1);TAB(40),"Y8-";Y8
1200  LPRINT  "Y-";B12;"X+";A4;TAB(40),"APPARENT  ADSORPTION  MAXIMUM-
";B14;" (uM Zn/G)"
1210 RETURN
1220 REM SUBROUTINE TO CALCULATE REGRESSION EQUATIONS
1230 LOXY-0
1240 PQXY-0
1250 PXXY-0
1260 XSUMLO-0
1270 YSUMLO-0
1280 XSUMPQ-0
1290 YSUMPQ-0
1300 XSUMPX-0
1310 YSUMPX-0
1320 XSSLO-0
1330 YSSLO-0
1340 XSSPQ-0
1350 YSSPQ-0
1360 XSSPX-0
1370 YSSPX-0
1380 FOR I-1 TO N
1390 REM *****GENERAL
1400 PXXY-PXXY+GX(I,1)*GY(I,1)
1410 XSUMPX-XSUMPX+GX(I,1)
1420 YSUMPX-YSUMPX+GY(I,1)
```

```
1430 XSSPX=XSSPX+GX(I,1)^2
1440 YSSPX=YSSPX+GY(I,1)^2
1450 REM *****FREUNDLICH
1460 LOXY=LOXY+FY(I,1)*FX(I,1)
1470 XSUMLO=XSUMLO+FX(I,1)
1480 YSUMLO=YSUMLO+FY(I,1)
1490 XSSLO=XSSLO+FX(I,1)^2
1500 YSSLO=YSSLO+FY(I,1)^2
1510 REM *****LANGMUIR
1520 PQXY=PQXY+LX(I,1)*LY(I,1)
1530 XSUMPQ=XSUMPQ+LX(I,1)
1540 YSUMPQ=YSUMPQ+LY(I,1)
1550 XSSPQ=XSSPQ+LX(I,1)^2
1560 YSSPQ=YSSPQ+LY(I,1)^2
1570 NEXT I
1580 REM *****TO CALCULATE GENERAL REGRESSION
1590 B7=PXXY-XSUMPX*YSUMPX/N
1600 B8=XSSPX-XSUMPX^2/N
1610 B9=B7/B8
1620 A3=YSUMPX/N-B9*XSUMPX/N
1630 R7=B7^2
1640 R8=B8*(YSSPX-YSUMPX^2/N)
1650 R9=R7/R8
1660 REM *****TO CALCULATE FREUNDLICH REGRESSION
1670 B1=LOXY-XSUMLO*YSUMLO/N
1680 B2=XSSLO-XSUMLO^2/N
1690 B3=B1/B2
1700 A1=YSUMLO/N-B3*XSUMLO/N
1710 R1=B1^2
1720 R2=B2*(YSSLO-YSUMLO^2/N)
1730 R3=R1/R2
1740 REM *****TO CALCULATE LANGMUIR REGRESSION
1750 B10=PQXY-XSUMPQ*YSUMPQ/N
1760 B11=XSSPQ-XSUMPQ^2/N
1770 B12=B10/B11
1780 A4=YSUMPQ/N-B12*XSUMPQ/N
1790 R10=B10^2
1800 R11=B11*(YSSPQ-YSUMPQ^2/N)
1810 R12=R10/R11
1820 B14=B11/B10
1830 RETURN
```

LIST OF REFERENCES

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Bar-Yosef, B. 1979. pH-dependent zinc adsorption by soils. Soil Sci. Soc. Am. J. 43:1095-1099.

Barney, G.S., 1984. Geochemical behavior of disposed radioactive waste. ACS Symposium Series No. 246:3-23. American Chemical Society. Washington D.C.

Bingham, F.T., A.L. Page, and J.R. Sims. 1964. Retention of Cu and Zn by H-montmorillonite. Soil Sci. Soc. Am. J. 28:351-354.

Borchardt, G.A., 1977. Montmorillonite and other smectite minerals. p. 293-330. J.B. Dixon, and S.B. Weed (ed.) In Minerals in soil environments. Soil Science Society of America. Madison, WI.

Bourg, A.C.M., and R.H. Filby. 1976. Isotopic exchange of Zn65 with stable Zn adsorbed on reference clay minerals. Geochim. Cosmochim. Acta. 40:1573-1574.

Bourg, A.C.M. , and R.H. Filby. 1974 Adsorption isotherms for the uptake of zinc by clay minerals in a freshwater medium. In Proceedings of the International Conference on Persistent Chem. Aquat. Ecosystems, Vol II. National Research Council of Canada. *Ottowa, Ont.

Boyd, G.E. J. Shubert, and A.W Adamson. 1947. The exchange adsorption of ions from aqueous solutions by organic zeolites I. Ion exchange equilibria. J. Am. Chem. Soc. 69:2818-2829.

Brummer, G., K.G. Tiller, V. Herms, and P.M. Clayton. 1983. Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils. Geoderma. 31:337-354.

Burkholder, H.C. 1976. Methods and data for predicting nuclide migration in geologic media. pp. 658-666. In Proc. Int. Symp. on Manage. of Wastes from LWR Fuel Cycle. Denver, Colo. 11-16 July 1976. CONF-760701. Natl. Tech. Information Serv., U.S. Dept. of Commerce, Springfield, Va.

Cavallaro, N., and M.B. McBride. 1984. Zinc and copper sorption and fixation by an acid soil clay: effect of selective dissolutions. Soil Sci. Soc. Am. J. 48:1050-1054.

Corey, R.B. 1981. Adsorption vs precipitation. p.161-182. In M.A. Anderson and A.J. Rubin (ed). Adsorption of inorganics at solid-liquid interfaces. Ann Arbor Science. Ann Arbor, Mich.

Cotton, F.A. and G. Wilkinson. 1980. Advanced inorganic chemistry. (4th ed) Interscience Publishers. John Wiley & Sons. New York.

DeMumbrum, L.E. , and M.L. Jackson. 1956. Infrared adsorption evidence on exchange reaction mechanism of copper and zinc with layer silicate clays and peats. Soil Sci. Soc. Am. J. 20:334-337.

Egozy, Y. 1980. Adsorption of cadmium and cobalt on montmorillonite as a function of solution composition. Clays and Clay Miner. 28:311-318.

Elgabaly, M.M. 1950. Mechanism of zinc fixation by colloidal clays and related minerals. Soil Sci. 69:167-174.

Elrashidi, M.A., and G.A. O'Connor. 1982. Influence of solution composition on sorption of zinc by soils. Soil Sci. Soc. Am. J. 46:1153-1158.

Farrah, H., and W.F. Pickering. 1976. The sorption of zinc species by clay minerals. Aust. J. Chem. 29:1649-1656.

Farrah, H., and W.F. Pickering. 1977. Influence of clay-solute interactions on aqueous heavy metal ion levels. Water, Air, Soil Pollut. 8:189-197.

Farrah, H., and W.F. Pickering. 1978. Extraction of heavy metal ion sorbed on clays. Water, Air, Soil Pollut. 9:491-498.

Freundlich, H. 1926. Colloid and capillary chemistry. Translated from the third German edition by H. Stafford Hatfield. Methven & Co. Ltd. London.

Frost, R.R., and R.A. Griffin. 1977. Effect of pH on adsorption of copper, zinc and cadmium from landfill leachate by clay minerals. J. Environ. Sci. Health, Part A. 12:139-156.

Fritz, J.S., and G.H Schenk. 1979. Quantitative analytical chemistry. Allyn an Bacon, Boston.

Gaines, G.L., and H.C. Thomas. 1953. Adsorption studies on clay minerals, II: A formulation of the thermodynamics of exchange adsorption. J. Chem. Phys. 21:714-718.

Gamble, D.S., and M. Schnitzer. 1973. Trace metals and metal organic interactions in natural waters. Ann Arbor Science, Ann Arbor

Garcia-Miragaya, J., and A.L. Page. 1977. Influence of exchangeable cation on the adsorption of trace amounts of cadmium by montmorillonite. Soil Sci. Soc. Am. J. 41:718-721.

Gast, R.G. 1969. Standard free energies of exchange for alkali metal cations on Wyoming bentonite. Soil Sci. Soc. Am. Proc. 33:37-41.

Helfferich, F. 1962. Ion exchange. McGraw-Hill. New York.

Garcia-Miragaya, J., and A.L. Page. 1976. Influence of ionic strength and inorganic complex formation on the sorption of trace amounts of Cd by montmorillonite. Soil Sci. Soc. Am. J. 40:658-663.

Garcia-Miragaya, J., and A.L. Page. 1977. Influence of exchangeable cation on the adsorption of trace amounts of cadmium by montmorillonite. Soil Sci. Soc. Am. J. 41:718-721.

Griffin, R.A., and A.K. Au. 1977. Lead adsorption by montmorillonite using a competitive Langmuir equation. Soil Sci. Soc. Am. J. 41:880-882.

Grim, R.E. 1968. Clay mineralogy. 2nd ed. McGraw-Hill, New York.

Harsh, J.B, and H.E. Doner. 1984. Specific adsorption of copper on an hydroxy-aluminum-montmorillonite complex. Soil Sci. Soc. Am. J. 48:1034-1039.

Harsh, J.B. and H.E. Doner. 1984. Specific adsorption of copper on an hydroxy-aluminum-montmorillonite complex. Soil Sci. Soc. Am. J. 48:1034-1039.

Harter, R.D. 1983. Effect of soil pH on adsorption of lead, copper, zinc and nickel. Soil Sci. Soc. Am. J. 47:47-51.

Harter, R.D., and D.E. Baker. 1977. Application and misapplications of the Langmuir equation to soil adsorption phenomena. Soil Sci. Soc. Am. J. 41:1077-1080.

Helfferich, F. 1962. Ion exchange, McGraw-Hill. New York.

Hendrickson, L.L., and R.B. Corey. 1983. A chelating resin method for characterizing soluble metal complexes. Soil Sci. Soc. Am. J. 47:467-474.

Hendrickson, L.L., M.A. Turner, and R.B. Corey. 1982. Use of Chelex-100 to maintain constant metal activity and its application to characterization of metal complexation. Anal. Chem. 54:1633-1637.

Helfferich, F. 1962. Ion exchange, McGraw-Hill. New York.

Hingston, F.J., A.M. Posner, and J.P Quirk. 1972. Anion adsorption by goethite and gibbsite. I: The role of the proton in determining adsorption envelopes. J. Soil Sci. 23:177-192.

Hodgson, J.F., K.G. Tiller, and M. Fellows. 1964. The role of hydrolysis in the reaction of heavy metals with soil forming materials. Soil Sci. Soc. Am. J. 28:42-46.

Jackson, M.L., 1958. Soil chemical analysis. Prentice-Hall. New Jersy.

Jenny, H. 1961. Reflections on the soil acidity merry-go-round. Soil Sci. Soc. Am. J. 25:428-432.

Jurinak, J.J., and N. Bauer. 1956. Thermodynamics of zinc adsorption in calcite, dolomite and *manesite-type minerals. Soil Sci. Soc. Am. J. 20:466-471

Kalbasi, M., G.J. Racz and L.A. Bowen-Rudgers. 1978. Mechanism of zinc adsorption by iron and aluminum oxides. Soil Sci. 125:146-150.

Keren, R. 1980. Effects of hydroxy aluminum precipitation on the exchange capacity reduction and aggregate size distribution of montmorillonite hydroxy-aluminum complexes. Soil Sci. Soc. Am J. 44:1209-1212.

Kinniburgh, D.G., and M.L. Jackson. 1982. Concentration and pH dependence of calcium and zinc adsorption by iron hydrous oxide gel. Soil Sci. Soc. Am. J. 46:56-61.

Kittrick, J.A. 1976. Controls of Zn2+ in the soil solution by *sphalerite. Soil Sci. Soc. Am. J. 40:314-317.

Kuo, S., and A.S. Baker. 1980. Sorption of copper, zinc and cadmium by some acid soils. Soil Sci. Soc. Am. J. 44:969-974.

Kuo, S., and D.S. Mikkelsen. 1979. Zinc adsorption by two alkaline soils. Soil Sci. 128:274-279.

Kurdi, F., and Doner. 1983. Zinc and copper sorption and interaction in soils. Soil Sci. Soc. Am. J. 47:873-876.

Lai, S., J.J. Jurinak, and R.J. Wagenet. 1978. Multicomponent cation adsorption during convective-dispersive flow through soils: experimental study. Soil Sci. Soc. Am. J. 42:240-243.

Lamm, C.G., E.H. Hansen, and J.A. Jorgensen. 1963. Isotopic exchange in soil fertility studies. Soil Sci. 94:16-2Maes, A., and A. Cremers. 1975. Cation-exchange hysteresis in montmorillonite: a pH dependent effect. Soil Sci. 119:198-202.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40:1361-1403.

Lindsay, W.L. 1979. Chemical equilibria in soils. Wiley, New York.

Lindsay, W.L. 1972. Inorganic phase equilibria of micronutrients in soils. p.41-57. In J.J. Morvedt, P.M. Giordano, and W.L. Lindsay (ed.) Micronutrients in agriculture. Soil Science Society of America. Madison, WI.

Maes, A., and A. Cremers. 1975. Cation-exchange hysteresis in montmorillonite: a pH dependent effect. Soil Sci. 119:198-202.

Maquire, M., J. Slavek, I. Vimpany, F.R. Higginson, and W.F. Pickering. 1981. Influence of pH on copper and zinc uptake by soil clays. Aust. J. Soils Res. 19:217-229.

MacEwan, D.M.C. and M.J. Wilson. 1980. Interlayer and intercalation complexes of clay minerals. p. 197-248. In G.W. Brindley and G. Brown (ed.). Crystal structures of clay minerals and other X-ray identification. Mineralogical Society Monograph No. 5. Miner. Soc., London.

Marshall, C.E. 1964. The physical chemistry and mineralogy of soils. Wiley, New York.

Mattigod, S.V., A.S. Gibali, and A.L. Page. 1979. Effect of ionic strength and ion pair formation on the adsorption of nickel by kaolinite.

Mattigod, S.V., and G. Sposito. 1977. Estimated association constants for some complexes of trace metals with inorganic ligands. Soil Sci. Soc. Am. J. 41:1092-1097.

McBride, M.B., and J.J. Blasiak. 1979. Zinc and copper solubility as a function of pH in an acid soil. Soil Sci. Soc. Am. J. 43:866-870.

McBride, M.B., and M.M Mortland. 1974. Copper (II) interactions with montmorillonite: evidence from physical methods. Soil Sci. Soc. Am. J. 38:408-414.

McLaren, R.G., and J.G. Williams, and R.S. Swift. 1983. Some observations on the desorption and distribution behavior of copper with soil components. J. Soil Sci. 134:325-331.

Nelson, J.L., and S.W. Melsted. 1955. The chemistry of added zinc to soils and clays. Soil Sci. Soc. Am. J. 19:323-326.

Nicholas, D.J.D, and A.R. Egan. 1975. Trace elements in soil-plant-animal systems. Academic Press. New York.

Pionke, H.B. and R.B. Corey. 1967. Relations between acidic aluminum and soil pH, clay and organic matter. Soil Sci. Soc. Am. Proc. 31:749-752.

Posner, A.M, and J.W Bowden. 1980. Adsorption isotherms: should they be split? J. Soil Sci. 31:1-10.

Saeed, M., and R.F. Fox. 1977. Relations between suspension pH and zinc solubility in acid and calcareous soils. Soil Sci. 124:199-203.

Shukla, V.C., S.B. Mittal, and R.K. Gupta. 1980. Zinc adsorption in some soils as affected by exchangeable cations. Soil Sci. 129:366-370.

Shuman, L.M. 1980. Zinc in soils. p. In J. Nriagu (ed) Zinc in the environment. Part II. Wiley, New York.

Shuman, L.M. 1977. Adsorption of Zn by Fe and Al hydrous oxides as influenced by aging and pH. Soil Sci. Soc. Am. J. 41:703-706.

Shuman, L.M. 1976. Zinc adsorption isotherms for soil clays with and without iron oxides removed. Soil Sci. Soc. Am. J. 40:349-352.

Shuman, L.M. 1975. The effect of soil properties on zinc adsorption by soils. Soil Sci. Soc. Am. J. 39:454-458.

Singhal, J.P., and D. Kumar. 1977. Thermodynamics of exchange of zinc with Mg-bentonite and Mg-illite. Geoderma. 17:253-258.

Sposito, G. 1982 On the use of the Langmuir equation in the interpretation of "adsorption" phenomenon :II. The "two surface" Langmuir equation. Soil Sci. Soc. Am. J. 46:1147-1152.

Tabikh, A.A., I. Barshad, and R. Overstreet. 1960. Cation exchange hysteresis in clay minerals. Soil Sci. 104:219-226.

Tiller, K.G. 1967. Silicic acid and the reaction of zinc with clays. Nature. 214:852.

Tiller, K.G., and J.F. Hodgson. 1962. The specific adsorption of cobalt and zinc by layer silicates. p393-403. In Proceedings of the 9th (1960) National Conference on Clays and Clay Minerals. Pergamon Press. New York.

Tiller, K.G., an J.G. Pickering. 1974. The synthesis of zinc silicates at 200 C and atmospheric pressure. Clays Clay Miner. 22:409-416.

Tiller, K.G., J. Gerth, and G. Brummer. 1984. The relative affinities of Cd, Ni, and Zn for different soil clay fractions and goethite. Geoderma. 34:17-35.

Tiller, K.G., J.L. Honeysett, and M.P.C. de Vries. 1972. Soil zinc and its uptake by plants. I. Isotopic exchange equilibria and the application of tracer techniques. Aust. J. Soil Res. 10:151-164

Travis, C.C., and E.L. Etnier. 1981. A survey of sorption relationships for reactive solutes in soil. J. Environ. Qual. 10:8-17.

Turner, M.A., L.L. Hendrickson, and R.B. Corey. 1984. Use of chelating resins in metal adsorption studies. Soil Sci. Soc. Am. J. 48:763-769.

Tyler, L.D., and M.B. McBride. 1982. Mobility and extractability of cadmium, copper, nickel and zinc in organic and mineral soil columns. Soil Sci. 134:198-205.

Udo, E.T., H.L. Bohn, and T.C. Tucker. 1970. Zinc adsorption by calcareous soils. Soil Sci. Soc. Am. J. 34:405-407.

Vanselow, A.P. 1932. Equilibria of base exchange reactions of bentonites, permutites, soil colloids and zeolites. Soil Sci. 33:95-113.

Veith, J.A., and G.Sposito. 1977. On the use of the Langmuir equation in the interpretation of "adsorption" phenomenon. Soil Sci. Soc. Am. J. 41:697-702.

Van Bladel, R., and H. Laudelout. 1967. Apparent irreversibility of ion-exchange reactions in clay suspensions. Soil Sci 104:134-137.

Weigner, G. 1935. Ionen-umtausch und Struktur. Trans. 3rd Int. Congr. Soil Sci. Oxford.