

ZINC ADSORPTION BY TWO ALKALINE SOILS¹

S. KUO² AND D. S. MIKKELSEN

University of California, Davis

Received for publication November 13, 1978; revised March 9, 1979

ABSTRACT

Zinc adsorption by two alkaline soils, Mormon clay loam and Willows clay, both deficient in zinc for rice culture, was examined over a wide range of zinc solution concentrations. At zinc equilibrium concentrations (0.1 ppm zinc for Willows clay and 0.23 ppm for Mormon clay loam), zinc adsorption at 25°C can be described by either the Langmuir or the Freundlich adsorption isotherm. The exponent of concentration of the Freundlich equation is about 1.0. At higher zinc concentrations, however, zinc adsorption can be described only by the Freundlich equation, with the exponent of concentration being 0.31. Zinc adsorption by Mormon clay loam and Willows clay is an endothermic reaction. The rate of zinc adsorption can be described by a multiple-order kinetic equation. The activation energy of adsorption is 43.1 kilocalories per mole for Mormon clay loam and 31.4 kilocalories per mole for Willows clay. Because of the high activation energy, the adsorption is considered to be chemisorption rather than due to the electrostatic attraction forces between zinc ions and the surfaces of colloidal particles. The greater stability of adsorbed zinc may result from dehydration during the aging of zinc adsorbed on the surface of clay minerals.

INTRODUCTION

Zinc deficiency is the most common micronutrient problem in calcareous and alkaline soils used for rice production. It may be a result of low availability of soil zinc, a short interval of availability as a consequence of various soil adsorptive or chemisorptive mechanisms, or possibly ionic antagonisms that interfere with plant absorption and translocation of zinc. The ionic interactions involved and environmental effects have been reviewed by the authors (Mikkelsen and Kuo 1977). Because soils with zinc deficiency generally have a high pH, are high in sodium or calcium carbonate, have a high organic matter content, and interact with metal oxide fractions under anoxic soil conditions, these soil characteristics have received considerable attention in respect to plant availability and uptake. Already reported have been the adsorption of zinc by calcite and dolomite (Jurinak and Bauer 1956) by metal oxides (Kinni-

burgh and Jackson 1974; Shuman 1975; Loganathan et al. 1977) and by organic matter (DeMumbrum and Jackson 1956; Randhawa and Broadbent 1965). The formation of zinc phosphate in upland soils and zinc sulfide in flooded soils have also been considered factors in zinc availability to plants (Hossner and Blanchar 1969; Kittrick 1976). In general, zinc adsorption is found to be pH-dependent (Shuman 1975), related to soil CEC (Shuman 1975; Udo et al. 1970), and modified by bicarbonate antagonism (Forno et al. 1975).

Zinc adsorption by various surface phenomena is known to be influenced by temperature. Although the adsorption of zinc by calcite is an exothermic reaction, indicating that adsorption decreases with increasing temperature, zinc adsorption by dolomite and calcium magnesite is an endothermic reaction, increasing with temperature (Jurinak and Bauer 1956). Exothermic reactions of zinc adsorption by soil have also been reported (Sidhu et al. 1977). None of the published reports, however, give much information on the kinetics of zinc adsorption by soils. This research was conducted to determine the characteristics of zinc adsorption by two alkaline soils, the rate of zinc adsorption, and the associated energetics.

¹ Contribution from Department of Agronomy and Range Science, University of California, Davis, California.

² Present address: Western Washington Research and Extension Center, Washington State University, Puyallup, Washington.

MATERIALS AND METHODS

Two alkaline, rice-production soils were used in this study: Mormon clay loam (an overwashed Sacramento series soil) and Willows clay. Mormon clay loam is a montmorillonitic, thermic vertic Haplaquall, and Willows clay is a montmorillonitic thermic typic Pelloxerertt. The soils were collected from the plow layer (0 to 20 cm), air-dried, and crushed to pass a 2-mm sieve before analysis. Soil organic matter was determined by the method of Walkley and Black (1934), percent clay by the method of Jackson (1956), calcium carbonate by that of Williams (1949), and pH was determined on a 1:2 soil:water suspension. Total zinc was determined after HClO_4 digestion. Some physical and chemical properties of these two soils are shown in Table 1. For the equilibrium adsorption studies, 1 g of air-dried soil was treated with 20 ml of zinc solution with concentrations varying from 4 to 200 ppm Zn in 0.016 *M* CaCl_2 solution and shaken at three temperatures (10, 25, and 35°C) for 4 days. At the end of the 4-day reaction time, the soil suspension was centrifuged at 1355 g for 20 min at room temperature. The concentration of zinc in the supernatant solution was determined by atomic absorption spectrometry. The amount of zinc adsorbed was calculated from the difference between the initial and final zinc solution concentrations.

Rates of zinc adsorption were determined by the same procedures described above: 1 g of air-dried soil was treated with 20 ml of 16 ppm Zn in 0.016 *M* CaCl_2 solution and shaken at three temperatures (10, 25, and 35°C) for different periods. At the end of the reaction time, the suspensions were filtered immediately through Whatman 42 filter paper. The filtrate was used for Zn determination by atomic absorption spectrometry.

To determine the effect of ionic interference on zinc adsorption in these soils, 0.2 g of soil was

treated with 16 ppm Zn (2.5×10^{-4} mol/liter) containing 5×10^{-4} mol/liter each of Mn^{2+} , Fe^{2+} , Cu^{2+} , and Hg^{2+} cations in solution. The pH of the solutions ranged from 5.5 to 6.1. The soil suspensions were shaken for 1 h at 25°C and filtered immediately through Whatman 42 filter paper under vacuum. The zinc concentration of the filtrate was determined by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Figure 1 shows zinc adsorption by Willows clay and Mormon clay loam plotted on a logarithmic scale according to the Freundlich adsorption isotherm (Eq. (1):

$$X = K_1 C^{1/n} \quad (1)$$

For both soils, the Freundlich plot could be drawn as two linear plots, the concentration exponent ($1/n$) of the Freundlich equation being about 1.0 for the initial linear curve for both soils, but decreasing to 0.31 for the linear portion at the higher concentrations. The zinc concentration at which the two lines of the linear Freundlich's plot meet appears to be influenced by the zinc adsorption capability of the soils. Willows clay soil, with a high zinc adsorptive capacity, had a lower threshold zinc concentration, at which the slope of the two linear Freundlich plots separate, than that of Mormon clay loam. In both soils, when the adsorptive capacity increased, e.g., at an elevated temperature (35°C), the concentration of zinc in solution, at which the two straight lines deviated, was decreased.

Zinc adsorption at low zinc concentrations, where the exponent of concentration of the Freundlich equation is 1.0, can be described also by the Langmuir adsorption isotherm (Eq. (2)):

$$\frac{C}{X} = \frac{1}{K_2 M} + \frac{C}{M} \quad (2)$$

Plotting zinc concentration in solution over the amount of zinc adsorbed in micrograms per gram of soil as a function of equilibrium zinc concentration in solution gives a straight line (Fig. 2). This monolayer type adsorption capacity (M), as calculated from the slope of the straight line, is 618 $\mu\text{g/g}$ for Mormon clay loam and 1600 $\mu\text{g/g}$ for Willows clay. The higher clay content and pH of Willows clay soil (Table 1) is likely responsible for its higher zinc adsorption capability.

TABLE 1
Some physical and chemical properties of the experimental soils

Soil series	pH	Organic matter, %	CaCO_3 , %	Clay (<2), %	Total zinc, ppm
Mormon clay loam	7.7	0.6	1.0	9.2	75
Willows clay	8.5	1.0	1.2	49.0	50

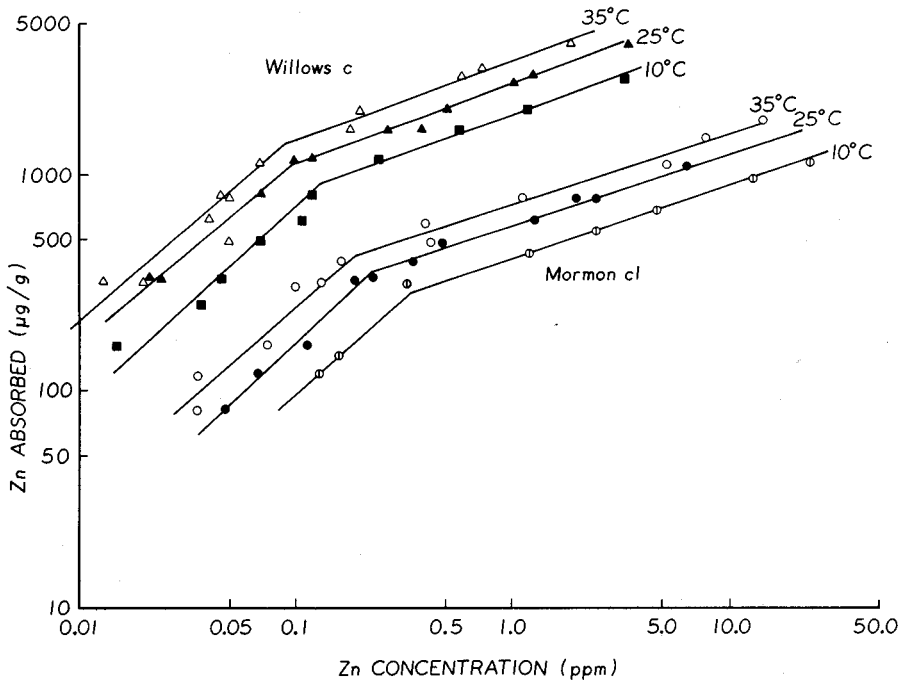


FIG. 1. Freundlich plot of zinc adsorption by Willows clay and Mormon clay loam at three temperatures, 10, 25, and 35°C on a logarithmic scale.

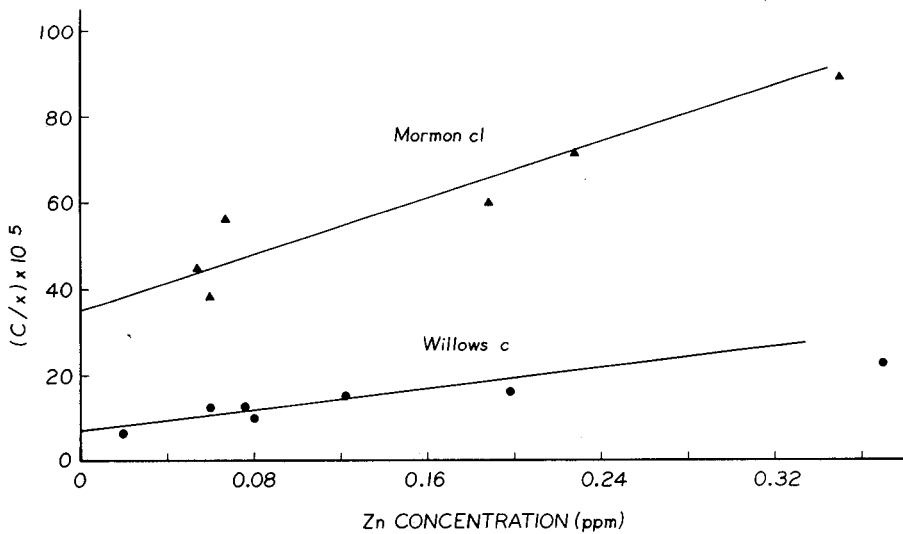


FIG. 2. Langmuir plot of zinc adsorption by Willows clay and Mormon clay loam. Equilibration time, 96 h at 25°C.

The adsorption capacity calculated from the Langmuir plot, however, is lower than the amount of zinc adsorbed at the higher zinc concentrations used in these experiments (Fig. 1). This could indicate that the Langmuir isotherm

is not appropriate to describe the zinc adsorption by Mormon clay loam and Willows clay at high zinc concentrations. This could also be due in part to a different adsorption mechanism occurring at high zinc concentration with increasing

surface heterogeneity that affects the enthalpy of adsorption at higher surface coverage.

Figure 1 also shows the effect of temperature on zinc adsorption. Zinc adsorption increased with temperature over the range of zinc concentration investigated. This indicates that zinc adsorption by Mormon clay loam and Willows clay is an endothermic reaction. This endothermic reaction probably is attributed to the high enthalpy of adsorption as a consequence of dehydration of water molecules oriented on the zinc molecule (Jurinak and Bauer 1956).

The rate of zinc adsorption can be described by a multiple-order, kinetic equation

$$\frac{dC}{dt} = -k_1 C^n \quad (3)$$

where C is zinc concentration in solution, t is reaction time, and k and n are constants. Equation (3) implies that the reduction of zinc concentration in solution by surface adsorption is negatively proportional to the zinc concentration in solution raised to the power of n . Equation (3) is essentially the same kinetic equation used by Ferguson et al. (1973), Probert and Larsen (1972), and Barrow and Shaw (1975) in describing phosphorus adsorption and precipitation in soils. Integrating Eq. (3) gives Eq. (4)

$$\frac{1}{C^{n-1}} = \frac{1}{C_0^{n-1}} + (n-1)k_1 t \quad (4)$$

$$\log \frac{1}{C^{n-1}} = \log A + \log \left[1 + \frac{(n-1)}{A} k_1 t \right] \quad (5)$$

where $A = 1/C_0^{n-1}$. At time t , when $[(n-1)k_1 t/A] \gg 1$, Eq. (5) can be simplified as:

$$\log C = \frac{1}{1-n} \log(n-1)k_1 + \frac{1}{1-n} \log t \quad (6)$$

Thus, plotting zinc concentration as a function of time on a logarithmic scale according to Eq. (6) gives a straight line (Fig. 3). The order of reaction is about 4.1. The rate of zinc adsorption is seen to increase with increasing temperature. The activation energy of adsorption calculated from the Arrhenius plots is 43.1 kcal/mol for Mormon clay loam and 31.4 kcal/mol for Willows clay (Fig. 4). The high activation energy of adsorption indicates that diffusion is not a limiting factor controlling the rate of zinc adsorption. Consequently, adsorption of zinc by these two soils appears to occur by chemisorption.

Table 2 shows the influence of various biva-

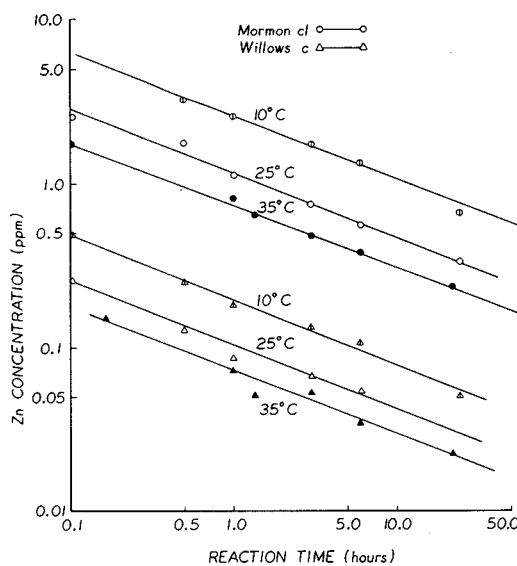


FIG. 3. Zinc adsorption by Willows clay and Mormon clay loam at 10, 25, and 35°C as a function of time plotted on a logarithmic scale.

lent cations on zinc adsorption by Mormon clay loam and Willows clay. For the four cations examined, the cationic interference on zinc adsorption is minimal with the Mn^{2+} , greatest with the Hg^{2+} , and intermediate with the Cu^{2+} and Fe^{2+} . It appears that the higher the atomic weight of the metal ion the greater the interference with zinc adsorption.

Over the years, some investigations have been made of the mechanism of zinc adsorption by layer silicates and metal oxides. The major studies were by DeMumbrum and Jackson (1956) and Stanton and Burger (1970). With both silicates and metal oxides, the hydroxyl group on the reaction surface is considered to be responsible for zinc adsorption. Because the Sp^3 hybrid orbital of zinc ion is vacant, zinc could possibly accept a pair of electrons from the oxygen of the surface hydroxyl group and form a chain of bonds with the mineral surface through the oxygen bridge. The high activation energy of adsorption indicates that zinc adsorption is a chemisorption phenomenon (Gadde and Laitinen 1974). Some polarization between surface hydroxyl groups and zinc molecules could also occur in the bonding formation. Therefore, Hg^{2+} , the largest cation used in these experiments, is the most effective in ionic competition with zinc adsorption (Table 2). The competition of the four bivalent cations on zinc adsorption is

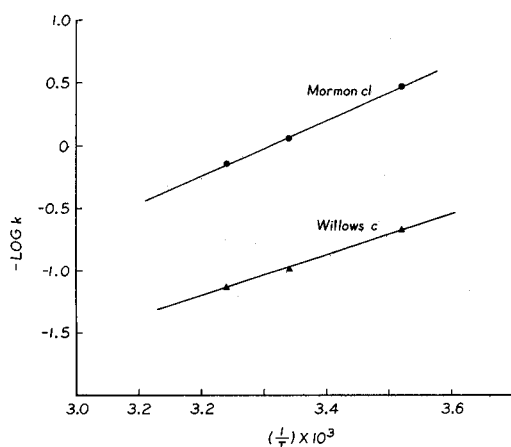


FIG. 4. Arrhenius plot of k_1 on a logarithmic scale against temperature.

TABLE 2

Effect of bivalent cations on zinc adsorption by soils

Ionic species	Initial Zn conc., ppm	Final Zn conc., ppm	
		Willows c	Mormon cl
Zn ²⁺	16.0	0.19	3.30
Zn ²⁺ + Mn ²⁺	16.0	0.26	4.75
Zn ²⁺ + Fe ²⁺	16.0	0.45	6.65
Zn ²⁺ + Cu ²⁺	16.0	0.30	7.61
Zn ²⁺ + Hg ²⁺	16.0	0.85	8.80

roughly in the order of $Hg^{2+} > Cu^{2+} > Fe^{2+} > Mn^{2+}$, which corresponds to the decrease in order of electronegativity. The contribution of electrostatic attraction forces on zinc adsorption appears to be very small, or otherwise the order of interference should be reversed, since the attraction force is inversely proportionate to the internuclear distance.

Surface zinc adsorption is an important process that regulates the zinc concentration in solution. The stability of the adsorbed zinc may change, however, over an extended period of reaction time. This is evident from the continuous decline of DTPA-extractable zinc with time (Kuo and Mikkelsen³), the decrease in readily exchangeable zinc (Nelson and Melsted 1955), and the decreased availability of residue zinc from applied zinc fertilizer (Brown et al. 1964). It is possible that the dehydration and recrystallization processes that occur on the surfaces of the colloidal particle will further enhance the stability of the adsorbed zinc.

³ S. Kuo and D. S. Mikkelsen, 1978, Kinetics of zinc desorption by some acid and alkaline soils, submitted.

REFERENCES

- Barrow, N. J., and T. C. Shaw. 1975. The slow reactions between soil and anions: 2. Effect of time and temperature on the decrease in phosphate concentration in the soil solution. *Soil Sci.* 119: 167-177.
- Brown, A. C., B. A. Krantz, and P. E. Martin. 1964. The residual effect of zinc applied to soils. *Soil Sci. Soc. Am. Proc.* 28: 236-238.
- DeMumbrum, L. G., and M. L. Jackson. 1957. Infrared adsorption evidence on exchange reaction mechanism of copper and zinc with layer silicate clay and peat. *Soil Sci. Soc. Am. Proc.* 28: 354-337.
- Forno, D. A., S. Yoshida, and C. J. Asher. 1975. Zinc deficiency in rice: 1. Soil factors associated with the deficiency. *Plant Soil* 42: 537-550.
- Ferguson, G. F., D. Jenkins, and J. Eastman. 1973. Calcium phosphate precipitation at slightly alkaline pH values. *J. Water Pollut. Control Fed.* 45: 620-631.
- Gadde, R. R., and H. A. Laitinen. 1974. Studies of heavy metal adsorption by hydrous iron and manganese oxides. *Anal. Chem.* 46: 2022-2026.
- Hossner, L. R., and R. W. Blanchar. 1969. The utilization of applied zinc as affected by pH and pyrophosphate content of ammonium phosphate. *Soil Sci. Soc. Am. Proc.* 33: 618-621.
- Jackson, M. L. 1956. Soil chemical analysis—advanced course. Published by the author, Department of Soil Science, University of Wisconsin, Madison.
- Jurinak, J. J., and N. Bauer. 1956. Thermodynamics of zinc adsorption in calcite, dolomite and magnesite-type minerals. *Soil Sci. Soc. Am. Proc.* 20: 466-471.
- Kittrick, J. A. 1976. Control of Zn⁺² in the soil solution by sphalerite. *Soil Sci. Soc. Am. J.* 40: 314-317.
- Kinniburgh, D. G., and M. L. Jackson. 1974. Zinc adsorption by iron hydroxy oxide soils. *Agronomy abstract*, p. 122.
- Loganathan, P., R. G. Burau, and D. W. Fuerstenau. 1977. Influence of pH on the sorption of Co²⁺, Zn²⁺ and Ca²⁺ by a hydrous manganese oxide. *Soil Sci. Soc. Am. J.* 41: 57-62.
- Mikkelsen, D. S., and S. Kuo. 1977. Zinc fertilization and behavior in flooded soil. Special publication No. 5. Commonwealth Bureau of Soils. Farnham Roy, England.
- Nelson, J. L., and S. W. Melsted. 1955. The chemistry of zinc added to soils and clays. *Soil Sci. Soc. Am. Proc.* 19: 439-443.
- Probert, M. E., and S. Larsen. 1972. The kinetics of heterogeneous isotopic exchange. *J. Soil Sci.* 23: 76-81.
- Randhawa, N. S., and F. E. Broadbent. 1965. Soil organic matter-metal complexes: 5. Reaction of zinc with model compounds and humic acid. *Soil Sci.* 99: 295-300.
- Shuman, L. M. 1975. The effect of soil properties in zinc adsorption by soils. *Soil Sci. Soc. Am. Proc.*

- 39: 454-458.
- Sidhu, A. S., N. S. Randhawa, and M. K. Sinha. 1977. Adsorption and desorption of zinc in different soils. *Soil Sci.* 124: 211-218.
- Stanton, D. A., and R. du T. Burger. 1970. Studies of zinc in selected Orange Free State soils: 5. Mechanism for the reaction of zinc with iron and aluminum oxides. *Agrochemophysica* 2: 65-75.
- Walkley, A., and I. A. Black. 1934. An examination of Degtjaroff method for determining soil organic matter and a proposed modification of the chromic and titration method. *Soil Sci.* 37: 29-38.
- Williams, D. E. 1949. A rapid manometric method for determination of carbonates in soils. *Soil Sci. Soc. Am. Proc.* 13: 127-129.
- Udo, E. J., H. L. Bohn, and T. C. Tucker. 1970. Zinc adsorption by calcareous soils. *Soil Sci. Soc. Am. Proc.* 34: 405-407.