DIVISION S-2—SOIL CHEMISTRY

Zinc Adsorption by a Lateritic Soil in the Presence of Organic Ligands

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ABSTRACT

Soluble Zn in soils and its availability to plants may be influenced by the presence of organic ligands, particularly in the rhizosphere, where soluble organic matter may be present in high concentrations. Zinc adsorption by a lateritic podzolic soil was measured in the presence of 0 to 3 mmol L^{-1} of acetate, oxalate, citrate, tricarballylate, salicylate, or catechol, or 0 to 3 $mmol_c$ L^{-1} of humate. Zinc remaining in solution was measured by atomic absorption spectrometry after shaking the soil for 17 h at a soil/liquid ratio of 1:5 in a 0.003 mol L^{-1} KCl solution containing 0 to 500 μmol L^{-1} Zn and the ligands. In the absence of organic ligands, more than 95% of the zinc was adsorbed. The amount of adsorption was linearly correlated with pH and the concentration of $ZnOH^+$ in solution after shaking (r^2 = 0.98; multiple regression). Zinc adsorption and pH decreased in the presence of each of the ligands except catechol. Seventy four percent of the variation in adsorption was accounted for by the combined effects of the concentration of zinc–ligand complex (Zn–*L*) and the concentration of $ZnOH^+$ that were present in solution after adsorption. However, other factors such as changes in the number of sites available for adsorption, the point of zero salt effect (pzse) of the soil, and the charge of zinc species also contributed to the magnitude of zinc adsorption.

In soils containing concentrations of plant-available Zn that are marginal for adequate plant growth, the presence of organic ligands in the rhizosphere may influence the concentration of Zn in solution and thereby its availability to plants (Norvell, 1972). The soil solution can contain many kinds of organic ligands (Stevenson and Ardakani, 1972; Tiller, 1983), which may have originated from plant exudates, decaying organic matter, or as the product of microbial activities. Concentrations of organic ligands found in the rhizosphere are usually higher than in the bulk soil solution. Generally, the ligand has a short existence, because microorganisms themselves can also use these ligands as their substrates (Lindsay, 1972). Stevenson and Ardakani (1972) reviewed the types of organic ligands in soils and divided them into two broad groups. The first group consists of defined biochemical compounds produced by root exudation and microorganisms, whereas the other group is made up of less-defined molecules usually referred to as humic and fulvic acids. The latter type are the product of the microbial breakdown of dead plant and animal debris (Stevenson and Ardakani, 1972). The importance of these ligands, however, is that they are able to form complexes with micronutrients; and the complexes are more soluble than the free ion (Broadbent and Ott, 1957; Hodgson et al., 1965, 1966; Norvell, 1972; Prasad et al., 1976). Some ligands, particularly those defined as humic acid, form strong complexes with metal ions and become insoluble.

Adsorption is a major contributing factor to low concentrations of Zn in solution in Zn-deficient soils (Ellis and Knezek, 1972). Soil pH has been shown to affect Zn adsorption, either by changing the number of sites available for adsorption or by changing the concentration of the Zn species that is preferentially adsorbed (Barrow, 1986). Soluble organic ligands may also influence Zn adsorption by these two mechanisms. Adsorption of organic anions can increase the negative charge on surfaces (Parfitt and Russell, 1977; Barrow, 1985) and hence increase Zn adsorption. On the other hand, the presence of organic ligands in solution may decrease Zn adsorption by competing with the surface for the Zn. Indeed, Zn adsorption onto clays and hydrous oxides has been shown to increase (Pickering, 1980) or decrease (Kinniburgh and Jackson, 1974) in the presence of organic ligands. However, these studies were conducted at high Zn concentrations and ionic strengths, which are not normally found in unpolluted and nonsaline soils. The variable effect of ligands on Zn adsorption will also depend on pH, concentration of ligand and metal, the pzse of soil, the formation constant of the complex, and the ionic strength of the soil solution.

The objective of this study was to examine the effect of three concentrations of seven organic ligands on Zn adsorption by a lateritic soil from Western Australia where Zn concentrations and ionic strengths are low (Robson and Gilkes, 1981; Dolling and Ritchie, 1985).

MATERIALS AND METHODS

Effect of pH on Zinc Adsorption in the Absence of Organic Ligands

The adsorption of Zn by a lateritic podzolic soil (Northcote classification: Dy 5.51; soil taxonomy: Entisol) was measured at four pH values and five concentrations of added Zn. The soil was chosen because of its relatively low sorption capacity (maximum Zn adsorption was 12 μmol g^{-1} soil). The soil contained 4 nmol g^{-1} of DTPA–extractable Zn, 3.1% of organic C, and 8.1 μg g^{-1} of $NaHCO_3$–extractable P. The cation-exchange capacity of the soil was 6.9 $cmol_c$ kg^{-1} and Ca and Al occupied 70 and 2% of the exchange sites, respectively. The soils were shaken with 3 mmol L^{-1} KCl solutions containing 100, 200, 300, 400, and 500 μmol L^{-1} $Zn(NO_3)_2$ at a soil/liquid ratio of 1:5. The concentrations were chosen because a preliminary experiment indicated that the Zn concentrations after adsorption spanned the range normally found in soils (Tiller et al., 1972; Pendias and Pendias, 1984). The pH of each sample was then adjusted by adding 0, 1, 1.5, and 2 mL of 0.1 mol L^{-1} HCl. The soil suspensions were shaken for 17 h, centrifuged at a relative

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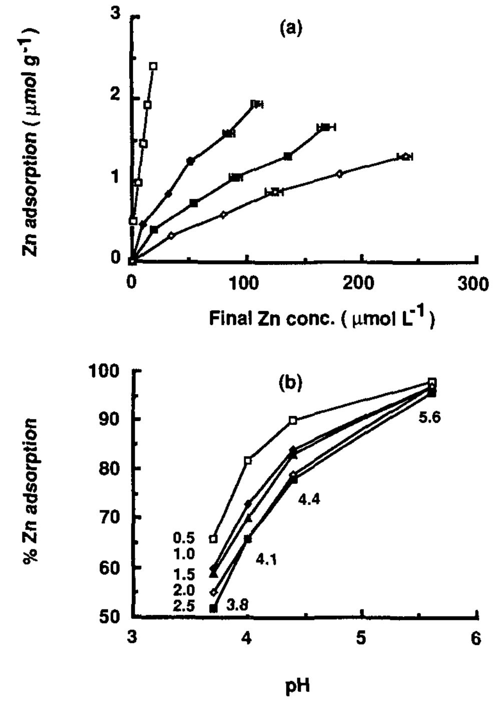

Fig. 1. Zinc adsorbed (a) as a function of Zn remaining in solution at pH 3.8 (◇), 4.1 (■), 4.4 (♦), and 5.6 (□) and (b) as a function of pH at 0.5 (□), 1.0 (♦), 1.5 (▲), 2.0 (◇) and 2.5 (■) µmol of added Zn per gram of soil.

Table 1. The type and amount (% of total soluble) of Zn complexed with the different ligands (*L*) before being added to the lateritic soil.

Ligand	Zn–*L* species	Total Zn as Zn–*L*
		%
Acetate	$Zn\text{–}L^+$	3–7
Oxalate	$Zn\text{–}L^0$	0
	$Zn\text{–}L_2^{2-}$	99
Tricarballylate	$Zn\text{–}L^-$	5–13
	$ZnHL^0$	20–27
	ZnH_2L^+	1–4
Citrate	$Zn\text{–}L^-$	93–99
Salicylate	$Zn\text{–}L^0$	<0.03
Catechol	$Zn\text{–}L^0$	<0.002
	$Zn\text{–}L_2^{2-}$	0
Humate	Unknown	Unknown

centrifugal force of 1000 *g* for 15 min, and filtered (<0.45 µm). Adsorption after 17 h was >98% of adsorption after 20 d.

The pH of filtrates was measured with a Beckman model Φ71 pH meter; the concentrations of Zn were determined by atomic absorption spectrometry. The amount of Zn that was adsorbed was estimated from the difference between the initial and the final concentrations. Zinc adsorption in the absence of the ligand, but at the same final pH as was observed in the presence of each concentration and type of ligand, was estimated by interpolation of five curves of Zn adsorbed in the absence of ligands vs. pH. The curves were constructed at constant final concentrations of 6, 8, 10, 12 and 14 µmol L^{-1} from equations fitted to the data in Fig. 1a.

Zinc Adsorption in the Presence of Ligands

The adsorption of Zn by the same soil was measured at six Zn concentrations in the presence of three concentrations of each of seven organic ligands. The ligands varied in the number and type of functional groups and the ability to complex Zn (Table 1). The Zn concentrations were the same as in the pH experiment. The concentrations of the protonated ligands were 0, 1, and 3 mmol L^{-1} in 3 mmol L^{-1} KCl, except that for humic acid concentrations of 0, 1, and 3 $mmol_c$ L^{-1} were used, because its molecular weight is unknown. These concentrations were chosen so that after adsorption by the soil, the concentrations remaining in solution were similar to those reported in the literature as commonly found in most agricultural soils (Stevenson, 1982). Adsorption was measured as described in the pH experiment.

Ligand Adsorption

The adsorption of six organic ligands by the same soil was measured at five concentrations of each ligand.

Twenty milliliters each of salicylic, oxalic, and tricarballylic acids, at concentrations of 0, 1, 2, 5 and 10 mmol L^{-1} in 3 mmol L^{-1} KCl solution, were shaken with 4 g of soil for 17 h, centrifuged at relative centrifugal force of 1000 g for 15 min, and filtered (<0.45 µm). A known aliquot of each filtrate was taken and the pH adjusted to ≈3 with HCl. The solutions were backtitrated with KOH using an automated titrator (Radiometer). The concentrations of HCl and KOH used varied from one ligand to another. The equivalence point was taken as the point at which the greatest change in pH was observed. The concentration of the ligand left in the solution was estimated from the difference in the volume of alkali added to the blank filtrate (i.e., no ligand added) at the equivalence point and the volume of the alkali added to the filtrate from suspensions to which ligands had been added. An adsorption curve was then established by plotting the amount adsorbed (µmol g^{-1}) vs. final concentrations. The adsorption of citric and acetic acids were also determined by the same procedure, except that the concentrations used were 0, 0.5, 1, 2, and 5 mmol L^{-1} for citric acid and 0, 1.0, 2.1, 5.2, and 10.4 mmol L^{-1} for acetic acid. The adsorption of catechol was determined by the method of Beg et al. (1977).

Speciation of Zinc

The speciation of Zn in solutions before and after shaking with the soil was estimated using a chemical equilibrium program, TITRATOR (Cabaniss, 1987). The initial and final solution concentrations of Zn did not exceed the solubility product of any known Zn hydroxide or carbonate compound. Formation constants were taken from Lindsay (1979) and Martell and Smith (1977). The species considered were Zn^{2+}, $ZnOH^+$, $Zn(OH)_2^0$, $ZnCl^+$, and the organic complexes given in Table 1.

Determination of Point of Zero Salt Effect

The pzse (Sposito, 1981) of the soil was estimated from the mol g^{-1} of H^+ and OH^- consumed by the soil in the presence of nine amounts of 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} KOH at three ionic strengths. The amounts of 0.1 mol L^{-1} HCl used were 0, 0.5, 1, 1.5, 2, and 2.5 mL and the amounts of 0.1 mol L^{-1} KOH were 0.5, 1, and 1.5 mL; ionic strengths were adjusted by using KCl at the concentrations of 0.5, 0.05, and 0.005 mol L^{-1}.

Twenty milliliters of KCL (ionic strength = 0.5, 0.05, or 0.005 mol L^{-1}) and an aliquot of acid or alkali were added to 4 g soil, shaken for 17 h, centrifuged, and filtered (<0.45 µm). The pH of each filtrate was measured as described for the pH experiment.

The pzse was estimated from the crossover point of the three curves of mol g^{-1} H^+/OH^- added vs. pH at each ionic strength and was found to be at pH 3.9.

Table 2. Variation in the concentration of zinc species in solutions before being added to the lateritic soil.

	Zn_T = 100 µmol L^{-1}†			Zn_T = 500 µmol L^{-1}		
pH	Zn^{2+}	$ZnCl^+$	$ZnOH^+$	Zn^{2+}	$ZnCl^+$	$ZnOH^+$
	µmol L^{-1}		µmol L^{-1} × 10^{-2}‡	µmol L^{-1}		µmol L^{-1} × 10^{-2}‡
3.8	98.9	1.0	1.6	494.4	5.3	8.4
4.1	98.9	1.0	3.1	494.4	5.3	16.8
4.4	98.9	1.0	6.5	494.4	5.3	33.4
5.6	98.0	1.0	102.4	489.9	5.2	525.7

† Zn_T = total Zn concentration.

‡ Data presented have been multiplied by 10^2.

RESULTS

Effect of pH on Zinc Adsorption in the Absence of Organic Ligands

Zinc adsorption increased with increasing pH for each concentration of Zn added. At a constant pH, Zn adsorption increased with increasing concentration of added Zn. The final Zn concentration in solution decreased with increasing pH (Fig. 1a). At 2.5 µmol g^{-1} of added Zn, Zn concentration decreased from 238 to 19 µmol L^{-1} when the pH value of the solution was adjusted from 3.8 to pH 5.6. The magnitude of the decrease with increasing pH was smaller at the lower Zn additions. The rate of increase in % Zn adsorption with increasing pH was greatest at high Zn concentrations, with % Zn adsorption becoming similar (96–98%) at all initial Zn concentrations at pH 5.6 (Fig. 1b).

In the absence of organic ligands, the dominant Zn species in both final and initial solutions was Zn^{2+} (Table 2); $ZnCl^+$ formed ~1% of all Zn species present. The concentration of both species did not vary with pH. On the other hand, the concentration of $ZnOH^+$ increased nearly 100-fold when pH increased from 3.8 to 5.6, even though it represented a very small percentage of total Zn (<1%). Zinc adsorption was well correlated (r^2 = 0.90) with $ZnOH^+$ in the final soil solution (Fig. 2a), but was not correlated with any of the other species in a way that made adsorption independent of pH (e.g., $ZnCl^+$, Fig. 2b; $r^2 \leq 0.10$).

Multiple regression of Zn adsorbed with pH and each soluble Zn species in the final solution separately (Table 3) estimated that ≥97% of Zn adsorption could be accounted for by each pair of parameters. The standard partial regression coefficients indicated that both parameters in each regression had an equal effect on Zn adsorption except when the Zn species was $ZnOH^+$. In this case, $ZnOH^+$ apparently accounted for far more of the variation in Zn adsorption than pH.

Table 3. Multiple regression of Zn adsorption in the absence (−*L*) and presence (+*L*) of organic ligands.

Parameters of multiple regression with −log Zn adsorbed	r^2		Absolute standard partial regression coefficient	
	−*L*	+*L*	−*L*	+*L*
pH −log Zn_T†	0.98	0.38	1.6 1.62	0.36 0.69
pH −log Zn^{2+}	0.98	0.029	1.60 1.62	0.038 1.62
pH −log $ZnOH^+$	0.97	0.03	0.29 1.10	0.016 0.7
pH −log $ZnCl^+$	0.98	0.031	1.61 1.63	0.16 0.059

†Zn_T = total Zn concentration.

Zinc Adsorption in the Presence of Organic Ligands

Zinc adsorption and pH both decreased in the presence of each organic ligand except catechol (Fig. 3). The pH did not change significantly with the amount of Zn added, and therefore the mean value is given in Fig. 3. The extent to which the ligands decreased Zn adsorption was in the order of citrate ≥ oxalate > tricarballylate > humate > salicylate ≥ acetate > catechol = 0. The order of the extent to which the pH decreased was citrate > tricarballylate > oxalate > salicylate > humate > acetate > catechol.

Zinc adsorption in the presence of each ligand was then compared with Zn adsorption in the absence of the ligand but at the same final pH as observed in the presence of each concentration and type of ligand (Fig. 4). At a constant pH, the difference between Zn adsorption in the presence and in the absence of a ligand

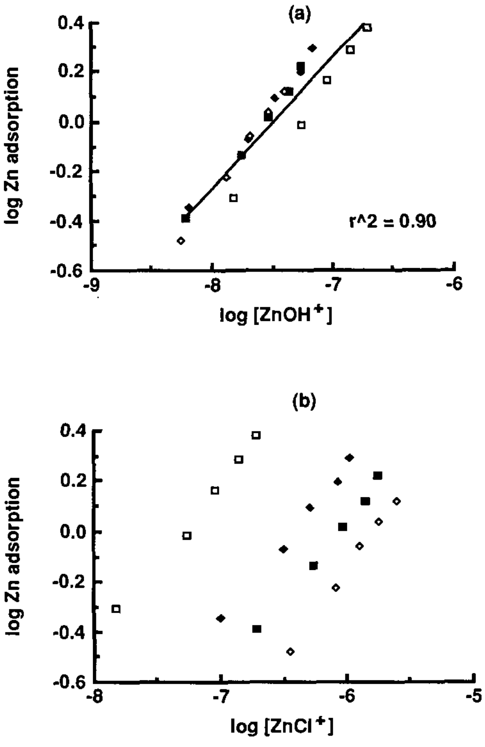

Fig. 2. The relationship between Zn adsorption and the concentration of (a) $ZnOH^+$ and (b) $ZnCl^+$ (mol L^{-1}) in the final soil solution at pH 3.8 (◇), 4.1 (■), 4.4 (◆), and 5.6 (□).

varied from one ligand to another. Adsorption was less in the presence than in the absence of citrate (at 1 mmol L^{-1} only), oxalate, tricarballylate (at 1 mmol L^{-1} only), acetate, or humate but was not affected by salicylate or catechol. When the initial ligand concentration was 1 mmol L^{-1}, the order in which the ligands decreased Zn adsorption was humate > oxalate > citrate > tricarballylate > acetate > salicylate = catechol = 0. However, when the initial concentration of the ligand was 3 mmol L^{-1}, citrate was less effective than acetate, and tricarballylate had a similar effect to acetate.

In the presence of organic ligands, Zn in the initial and final solutions was present as free Zn^{2+}, hydrolyzed Zn, and complexed forms. The percent Zn in complexed forms depended on the formation constant, pH, and the relative concentrations of Zn and the ligand. Oxalate and citrate complexed almost 100% of added Zn, whereas salicylate and catechol complexed very little (Table 1). Zinc adsorption in the presence of organic ligands was not correlated with either $ZnOH^+$ ($r^2 = 0.37$) or Zn-*L* ($r^2 = 0.06$) in the final solution. On the other hand, multiple regression of adsorption with the concentrations of both species gave a much better correlation ($r^2 = 0.74$). In the presence of ligands that complexed only a small proportion of total Zn (acetate, salicylate, and catechol), the correlation between Zn adsorption and $ZnOH^+$ concentration was good ($r^2 = 0.85$) Multiple regressions of Zn adsorbed with pH and each Zn species separately (Table 3) were not able to account for Zn adsorption adequately ($r^2 \leq 0.38$).

The decrease in Zn adsorption due to the presence of the organic ligands (estimated from the data in Fig. 4) increased linearly with the concentration of complex species in final solutions ($r^2 = 0.79$) except in the presence of 3 mmol L^{-1} of citrate (Fig. 5).

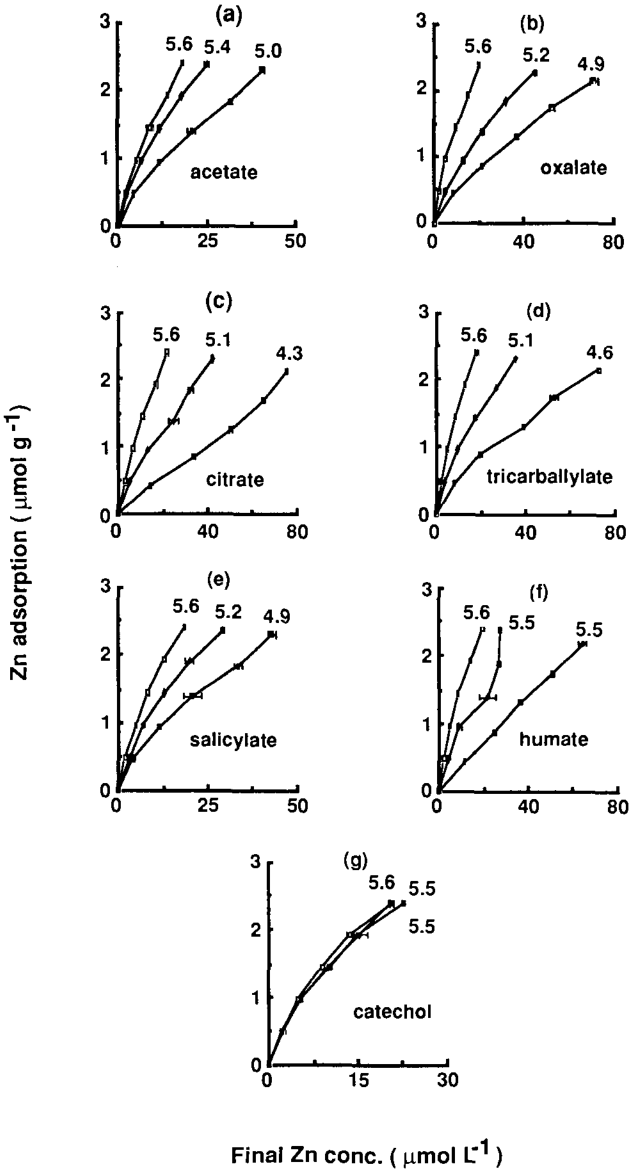

Fig. 3. Zinc adsorbed as a function of Zn remaining in solution in the presence of 0 (□), 1 (◆), and 3 (■) mmol L^{-1} of various organic ligands.

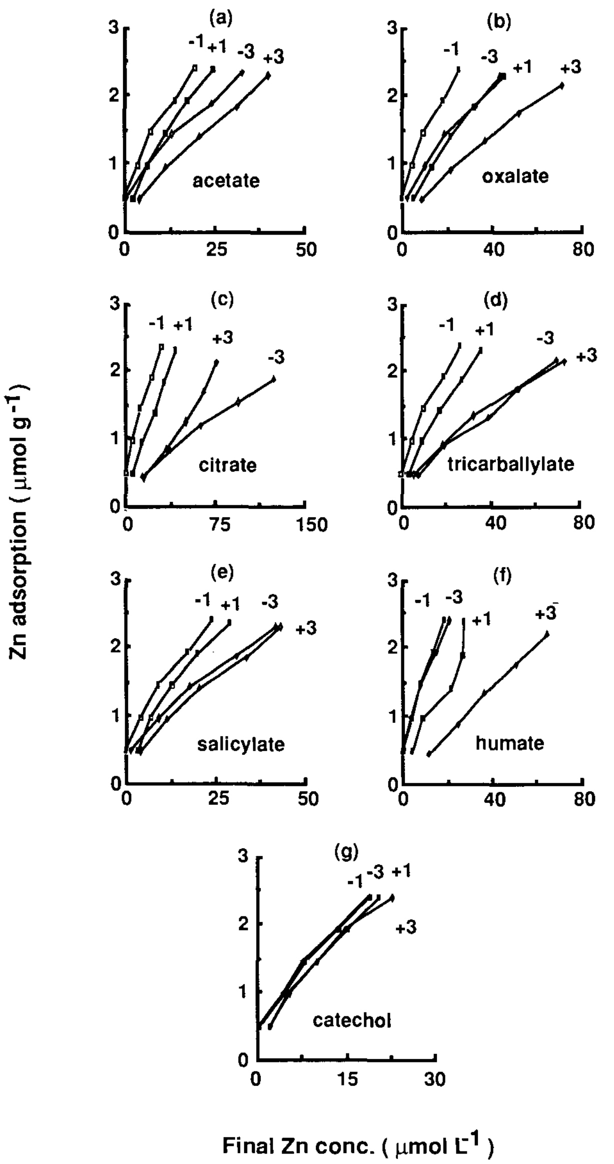

Fig. 4. Zinc adsorbed as a function of Zn remaining in solution at constant pH in the presence (+) and absence (−) of 1 or 3 mmol L^{-1} of various organic ligands.

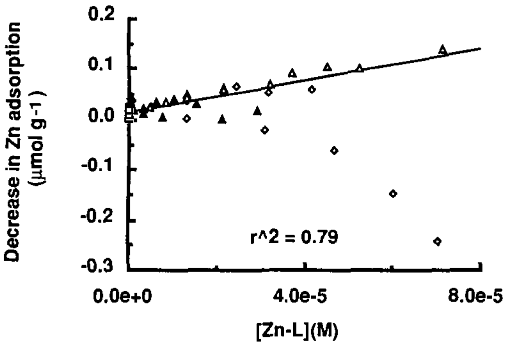

Fig. 5. The relationship between the decrease in zinc adsorption and the concentration of the Zn–ligand complex formed with acetate (♦), oxalate (△), citrate (◇), tricarballylate (▲), salicylate (■) and catechol (□).

Ligand Adsorption

Acetate, oxalate, and salicylate were moderately adsorbed, whereas catechol was adsorbed slightly at high rates of addition, and citrate and tricarballylate apparently were not adsorbed at all (Fig. 6).

DISCUSSION

Zinc adsorption by the lateritic soil at low Zn concentrations depended largely on the reactions of Zn in solution. Soil pH and competition between the soil surfaces and organic ligands were probably more important than changes in the number of sites available for adsorption. In the presence of organic ligands, the decrease in Zn adsorption was correlated with the extent of the formation of Zn complexes with organic ligands and the hydroxyl ion. In the absence of organic ligands, the adsorption was correlated with the concentration of $ZnOH^+$ in solution but neither the form of zinc being adsorbed nor the mechanism could be elucidated unequivocally.

The effect of pH on adsorption in the absence of ligands appeared to affect the forms being adsorbed and/or the mechanism of adsorption. Some possible models for adsorption are:

$$Zn^{2+} + S^{y-} = ZnS^{(2-y)+} \quad [1]$$

$$ZnOH^{+} + S^{y-} = ZnOHS^{(1-y)+} \quad [2]$$

where S is a surface site for adsorption and y is the charge on the surface site.

Adsorption may also result in the displacement of H^+ from a surface site or may be accompanied by the co-adsorption of OH^-. Both mechanisms would decrease solution pH. Equation 1 would cause some soluble $ZnOH^+$ to dissociate, and therefore would be accompanied by a rise in solution pH unless there was a concomitant displacement of H^+. Equation 2 would induce the hydrolysis of Zn^{2+}, and therefore solution pH would decrease. In our work, the pH change was negligible and the ratio of moles of H^+/OH^- produced to Zn adsorbed was < 0.1. However, it is difficult to deduce the mechanism of adsorption from pH changes, because other soil surface sites may have adsorbed H^+/OH^- released by Zn adsorption.

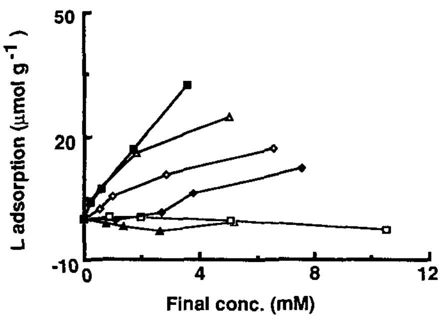

Fig. 6. The adsorption of catechol (♦), salicylate (■), acetate (△), oxalate (◇), tricarballylate (□), and citrate (▲) as a function of final solution concentration of each ligand.

The adsorption species and mechanisms cannot be elucidated from multiple regression because the logarithm of each Zn species and total Zn (Zn_T) concentration were linearly related to pH. $ZnOH^+$ was the only species that increased with pH and no other Zn species present in the final solution was linearly correlated with adsorption such that adsorption was independent of pH (Fig. 2).

The observation that pH and $ZnOH^+$ could account for slightly more of the variation in Zn adsorbed than $ZnOH^+$ alone might suggest that pH affected adsorption by more than just controlling the mechanism or the concentration of the adsorbing species (e.g., by changing the number of sites). However, the values of the absolute partial regression coefficients for each parameter indicated that the effect of $ZnOH^+$ on Zn adsorption was far greater than that of pH. A possible reason for the number of charged sites not having a greater effect on adsorption could be that the amount of Zn was too small to saturate the sites at any of the pH values investigated. Moreover, the low concentration of electrolyte may have restricted the increase in the number of adsorbed sites. Alternatively, pH may affect adsorption because the activities of the adsorbed species may be pH dependent.

Zinc adsorption has often been reported to increase markedly in the pH region that we investigated (Gadde and Laitinen, 1974; McKenzie, 1980). We did not observe such great changes in adsorption with pH. The differences between the results found here and those in previous studies could be due to the concentration of Zn used and the concentration of background electrolyte. In our study, the Zn concentrations (0–2.5 $\mu mol\ g^{-1}$) were similar to those found in agricultural soils, whereas concentrations used in other studies were probably too high ($>50\ \mu mol\ g^{-1}$) to exist in an unpolluted soil. McKenzie (1980) used 500 μmol Zn $g^{-1}\ MnO_2$ and Gadde and Laitinen used >4 mmol Zn $g^{-1}\ MnO_2$. The final solution concentrations of Zn were not supersaturated with respect to $ZnCO_3$ or ZnO at the pH values (<8) they investigated and assuming $\log pCO_2 = -2.5$.

In the presence of organic ligands, the speciation of Zn in solution was the major factor controlling Zn adsorption. Both hydroxyl ions and organic ligands were able to compete with the soil surfaces for Zn. Seventy four percent of the variation in Zn adsorption could be accounted for by the combined effect of the concentrations of $ZnOH^+$ and Zn–L in the final solution. Other factors that contributed to the extent of adsorption could have been precipitation, the charge of the complex, the difference between the pH of the soil and the pzse, and changes in the number of sites available for adsorption of positively charged Zn species with pH.

No change in Zn adsorption was observed in the presence of catechol, presumably because it does not form a complex with Zn at the pH studied. The effect of catechol would be expected to be greater at pH 9 ± 1 when it complexes a larger percentage of total soluble Zn.

Zinc adsorption in the presence of organic ligands that complexed $<1\%$ of total Zn (i.e., acetate, salicylate, and catechol) could be explained by the single effect of the concentration of $ZnOH^+$ in final solution ($r^2 = 0.85$). Zinc adsorption in the presence of salicylate was almost the same in both the presence and absence of the ligand at constant pH. The decrease in Zn adsorption observed in Fig. 4e was therefore, we concluded, due mainly to the drop in pH (which consequently decreased $ZnOH^+$ formation, as already discussed).

The differences that were demonstrated when Zn adsorption was compared at constant pH in the presence and absence of organic ligands (other than salicylate, acetate, and catechol) indicated that the decrease in pH (and hence changes in $ZnOH^+$) was not the only reason for the drop in Zn adsorption.

The decrease in Zn adsorption at a constant pH was also related to the concentration of Zn–complex species (Zn–L) in the final solution (Fig. 5). In the presence of all ligands, increasing the concentration of Zn–L lowered Zn adsorption. There were two exceptions: Zn adsorption was higher in the presence of 3 mmol L^{-1} of citrate than in its absence at a constant pH and the decrease in Zn adsorption due to tricarballylate was not as great as might be expected from the relationship in Fig. 5. The [$ZnOH^+$] was lower in the presence than in the absence of 3 mmol L^{-1} citrate, and therefore changes in $ZnOH^+$ concentration were unlikely to have been the cause of increased Zn adsorption. Precipitation of the Zn complexes could have been occurring, but no solubility data could be found to confirm or reject this hypothesis. However, other citrate salts are known to be quite insoluble (e.g., Ca citrate). Another possibility was that the formation of negatively charged complexes (rather than neutral or positive complexes) could have affected adsorption. Both tricarballylate and citrate form negatively charged complexes with Zn. In the presence of 3 mmol L^{-1} of citrate or tricarballylate, the pH of each system decreased to 4.3 and 4.6, respectively, which are both above the pzse of the soil (pH ~3.9). The increase in positive charge sites on the soil surfaces could have favored the adsorption of negatively charged complexes and thereby counterbalanced a decrease in adsorption due to complexing in solution.

Oxalate also forms a negatively charged complex. In this case, however, the pH of the soil (4.9–5.2) was well above the pzse and therefore the adsorption of the negatively charged complexes was possibly too small to counterbalance the decrease in Zn adsorption.

For humate, the amount of complexes formed could not be calculated because the equilibrium constant for the formation of a Zn-humate complex is not known. Nonetheless, the percentage decrease in Zn adsorption (49%) at constant pH was the largest observed for all the ligands. Comparison with the data of Zn adsorption in the presence of the other organic ligands suggests that most of the Zn was in a form complexed with humate.

The adsorption of the ligands may have increased the number of negatively charged sites (Barrow, 1985) and hence the adsorption of Zn. Such a mechanism does not appear to have been important in these experiments, presumably because the number of sites available were in excess in the natural soil for the low Zn concentrations that were used. Studies that have shown that the presence of acetate increased Zn adsorption (Bar-Yosef et al., 1975; Kinniburgh and Jackson, 1974) were carried out at much higher concentrations of Zn (10^{-3} mol L^{-1}) so that the number of negatively charged sites for adsorption may have been limiting in the absence of the ligands.

In conclusion, pH and the presence of organic ligands controlled the reactions of Zn in solution and thereby influenced the adsorption of Zn by the lateritic soil at low concentrations of Zn in solution.

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