Distribution Patterns of Native Sulfate Displaced by Respective Pore Volumes of Oxalic Acid in Cecil Bt Soil

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ABSTRACT : In this investigation we tried to investigate the effect of oxalic acid on the fate of native sulfate in Bt soil that contained a high kaolinitic clay by observing the distribution of two anions using soil column under the given competitive adsorption between displaced and displacing anions. To do this, the soil columns uniformly packed to a bulk density of 1.25 g/cm^3 with Cecil Bt soil were disected and analyzed the amounts of sulfate and oxalic acid both in solution and solid phases after flowing the designated pore volumes of oxalic acid. The results showed that two sets of curves-nonlinear (> 10^{-3} M) and linear (< 10^{-3} M) curves where the solution of oxalic acid was not adjusted, while the approaches to the plateau were slow when pH of oxalic acid was adjusted to 5. The cumulative amount of sulfate desorbed by successive addition of oxalic acid was nonlinearly approached to the plateau at the concentration of 10^{-3} M or greater, indicating that the number of addition of oxalic acid increased with decreasing order of oxalic acid. However, the plateau did not obtain where the concentration of oxalic acid were less than 10^{-4} M, showing a linear increase. Therefore, we may conclude that the rate-limited desorption was involved as the concentration of oxalic acid decreased.

Key words: Bt soil, oxalic acid, pore volume, sulfate.

INTRODUCTION

The fate of anion species in solution and solid phase in soils and other reactive porous materials is strongly influenced by the adsorption-desorption of these species between the solution and solid phases. In order to describe and predict fate of anions and their transports, it is necessary to quantify the individual species through the soil with different rates analogous to those described in chromatography, because multiple species of anions mutually compete for exchange sites during convective-dispersive-adsorptive transport of ions through soils. The transport of two ions-displaced and displacing-in an exchanger material postulated by Cho[1] indicated that the concentration distributions of displacing and displaced ions within a soil column can be related to the selectivity coefficient of ion exchange reaction, exchange capacity, and the concentration of displacing ions.

The probable adsorption mechanism of organic anions proposed by Hingston et al.,[2,3] is that organic anions are adsorbed by ligand exchange (specific adsorption) or anion exchange on the soil surfaces. Evidence that organic anions can modify the sorption of inorganic phosphate by soils showed that the presence of certain organic anions not only reduced greatly the amount of phosphate adsorbed but also were effective in preventing phosphate precipitation by iron and aluminum and in liberating fixed phosphate from the basic phosphate of these elements at very low pH values[4]

In soil with significant anion exchange capacity (kaolinitic clays, low pH, and high sesquioxide contents), determining the effects of other anions on the retention and movement of sulfate is quite challenging. The transport of sulfate through the rhizosphere would be small although many soils have a tremendous capacity adsorbing anions - inorganic or organic anions - even when the soil sulfate content is already high. Sulfate reaction through the non-

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specific and specific adsorption mechanism on the soil surface undergoes a variety of reactions in the soil system during adsorption, subsequent desorption by the counter anions presented in solution and movement within the soil profile. In addition to this, the presence of organic anions competing for the common sorption sites may play an important role in sulfate sorption and transport in soils, because of their position within the lyotropic series and because of their continuous production within the soil-root system.

The objectives of this study are i) to investigate the effect of oxalic acid on the fate of native sulfate in soil, ii) to observe the distribution of these anions using soil column under the competitive anions presented.

MATERIALS AND METHODS

Soil samples of Cecil Bt horizon (clayey, kaolinitic, thermic, Kandiudults) collected at the Simpson Experimental Station near Clemson, South Carolina, were used in this study. Soils were air-dried and ground to pass 2 mm-sieve.

For SO_4 extraction studies, 5 g of air-dried soil samples were equilibrated with PO_4 (as KH_2PO_4) solutions of known concentration ranging from 40 to 400 $\mu g/mL$. The clear supernatant centrifuged for 15 min. at 1750 rpm after 8 hours shaking was used for the analysis of phosphate and sulfate in solution. And the soil samples were washed with double-ionized water twice to remove the PO_4 and SO_4 remained as a soil solution phase. After this, the soil samples were centrifuged again to remove the excessive water still remained in soil samples. The soil samples were weighed in order to get the calculation of soil and the correction of concentration of PO_4 and SO_4. These procedures were repeated until SO_4 was not recovered in solution. The same procedure was used for the oxalic acid extraction under the two pH conditions of unadjusted and pH 5. At this time, 0.1 N KOH or 0.1 N HCl was used to adjust the solution pH of oxalic acid to pH 5.

For displacement experiments, the columns (20 cm long and 5.0 cm diameter) were uniformly packed to a bulk density of 1.25 g/cm^3 with Cecil Bt soil up to 10 cm soil depth from the bottom of column. The pore volume was calculated on the basis of bulk density, volume of soil occupied, and porosity. Apart from this pore volume calculation, the actual pore volume were obtained by measurement differences between the weights of wet and oven-dry soil. The error between the calculate and the actual were less than 1% in pore volume.

An oxalic acid solution was introduced into the column at a constant flow rate using a Cassette pump (Monostat, New York) until desired pore volumes of effluent were collected in a fraction collector. Effluent, collected in a conical tubes every hour, were used to determine the amount of sulfate and oxalic acid. Then the soil samples from soil columns were removed and sampled immediately at 0.5 cm intervals from the inflow position. These samples were used to determine the amounts of sulfate and oxalic acid in solution and solid phase. Separation of solution phase was done with a sectioned soil samples immediately by water extraction for the analysis of anions in solution phase. Then, these samples were centrifuged to remove the excessive water remained in soil samples. For an accurate analysis of anions in solid phase. The soil samples, after decanting supernatant, reweighed for the measurement of solution remained from water extraction, used for correction of anions in solid phase. The concentrations of anions in the extract were analyzed using a Dionex 200 ion chromatograph.

RESULTS AND DISCUSSION

Prior to this investigation, we studied the single and binary adsorption isotherms of oxalic acid and SO_4 for adsorption sites in Cecil Bt soil. Batch adsorption experiments indicated that the soils have the capacity to adsorb an additional 170 $\mu g/g$ SO_4 in addition to 510 $\mu g/g$ of indigenous SO_4 in soil, while the maximum amount of oxalic acid adsorbed at pH 5 and unadjusted solution pH were 59 $\mu g/g$ and 68 $\mu g/g$ soil. This indicated that Cecil Bt soil had a tremendous capacity adsorbing anions - inorganic or organic anions - even when the soil SO_4 content is already high. For binary adsorption, adsorption of SO_4 was drastically reduced in the presence of oxalic acid when the concentration of oxalic acid was greater than 10^{-3} M.

In order to observe the effects of indigenous pH and concentration of oxalic acid on the adsorption of oxalic acid and the desorption of native SO_4 from Cecil Bt soil, repetitive additions of six different concentrations of oxalic acid was studied under two pH conditions such as pH 5 and as unadjusted (Fig. 1 and Fig. 2).

From this observation we found that the adsorption reaction of oxalic acid rapidly approached to the first apparent equilibrium status with the charged surfaces and exchange process with the certain amount of SO_4 adsorbed in the soil particle surfaces. The following equilibrium status was then obtained with the changes of concentration

continuously introduced in the system. Therefore, the approach to the maximum adsorption of oxalic acid would be obtained later under a given concentration of oxalic acid until the available adsorption sites were occupied by oxalic acid anions, that makes the possibility of oxalic acid transport with water-flow in the system.

On the other hand, the cumulative adsorption by the repetitive additions of the respective oxalic acids showed that the adsorption was drastically increased with increasing number of additions when the concentrations of added oxalic acid were greater than 5×10^{-3} M for indigenous pH and adjusted pH 5 of the solutions, respectively, whereas the adsorption of oxalic acid with 10^{-4} M or lower concentration were linearly increased with increasing concentrations, at least within the number of additions in this study. We assumed that the prominent adsorption was caused by the its concentration of oxalic acid as well as low pH by deprotonation from carboxyl groups.

The subsequent desorption of SO_4 as a function of number of additions of oxalic acid represented that the magnitude of SO_4 desorbed for each addition of oxalic acid decreased with increasing number of additions of oxalic

acid. For example, three additions of 1×10^{-2} M of pH adjusted oxalic acid to the soil sample removed more than 95% of the native SO_4 in Cecil Bt soil, whereas the desorption of SO_4 at unadjusted pH condition took approximately 11 additions of 0.01 M oxalic acid (Fig. 1b and Fig. 2b). Under the less than 1×10^{-4} M of oxalic acid added, the amount of desorbed SO_4 ranged from 0.65 to 0.95 μ eq/g soil, that were slightly higher than that of water-soluble. From this results, the nonlinear desorption curves of native SO_4 at 5×10^{-3} M of oxalic acid or greater could be interpreted by rate-limited, that is, chemical reaction, and hydroxyl ions at pH 5 may be involved significantly on the displacement of native SO_4 bound to the surface sites.

As shown in Fig. 3, the exchange ratios between SO_4 desorbed and oxalic acid adsorbed were increased with decreasing concentration of the oxalic acid. This results could be interpreted as the dissociated H^+ from carboxyl groups of oxalic acid influenced the amount of adsorption capacity exceeding the amount of adsorption capacity as observed from the batch method. And the adsorption increment of the oxalic acid for the each addition drasti-
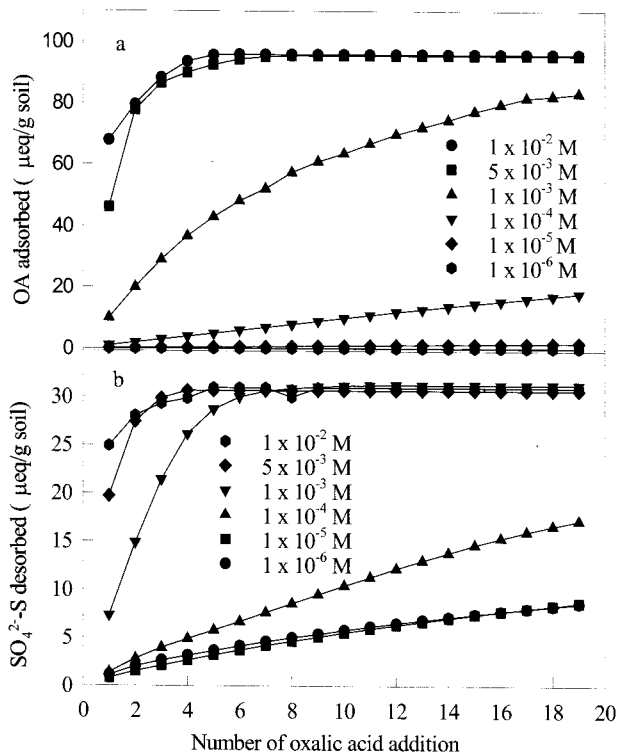

Fig. 1. Cumulative adsorption of oxalic acid (a) and the relative desorption of sulfate (b) by the repetitive addition of various concentrations of oxalic acid in Cecil Bt soil. Solution pH was adjusted to 5.
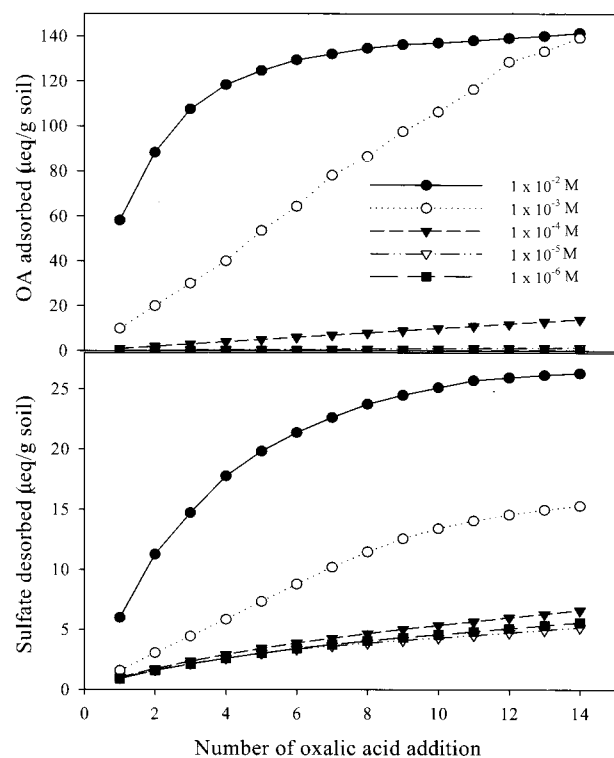

Fig. 2. Cumulative adsorption of oxalic acid (a) and the relative desorption (b) of sulfate by repetitive addition of various concentrations of oxalic acid in Cecil Bt soil. Solution pH of the oxalic acid was not adjusted.

cally reduced after three additions at 5 x 10³ M or greater as shown in Fig. 4.

A number of authors have investigated the effects of organic acids on metal dissolution from well characterized silicate minerals[5,6], and the chelating effects of organic acid on precipitation products of aluminum hydroxides and iron oxides[4,7-9].

In this experiment, the analysis of equilibrium solution for the sequential addition of the oxalic acid (< 5 x 10³ M) showed that the dissolution of aluminum and iron increased with increasing number of additions of oxalic acid until a sharp drop was observed from the four addition of oxalic acid, resulting in that the subsequent dissolution of metal ions can attribute precipitation products of metal-hydroxides by chelating effects of oxalic acid at the low pH.

In Fig. 5, the distribution patterns of SO_4 displaced and oxalic acid as the solution phase of a soil column packed with the Cecil Bt soil, performed at unsaturated and indigenous pH of 0.01 M oxalic acid, were plotted versus depth. The flux after 9 pore volumes of oxalic acid passed through the column was reduced to approximately 0.4 of initial flux as of 1 cm/h, resulting in the possible changes of instantaneous reaction to kinetic because of a limited rates of supply of solutes through solution to the sites.

Many researchers reported that variations of pore water velocity at different rates at the reaction sites changed the position and the shape of the solute distribution[10-12]. However, we neglected the velocity variation because it was very difficult to separate the physical and chemical measurement. The distribution of displaced SO_4 in solution clearly showed that the oxalic acid had a marked influence on the mobility and resulting distribution of displaced SO_4 in solution phase, and that the distribution of the displaced SO_4 in solution upon addition of oxalic acid solution were very much governed by pore volumes applied.

The movement of dissolved SO_4 to the deeper depth was accelerated as the number of pore volumes of 0.01 M oxalic acid increased from 0 to 9, with decreasing the
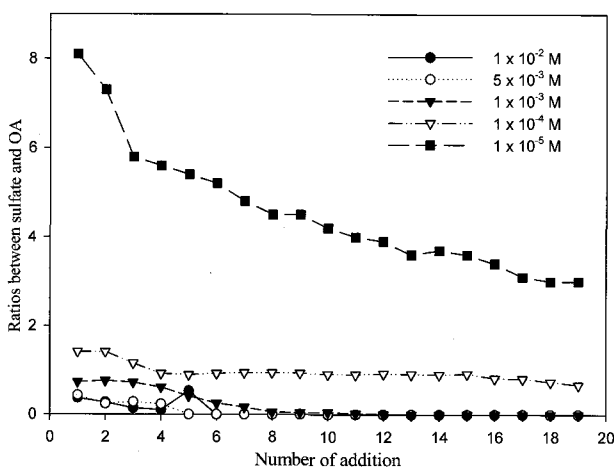

Fig. 3. Exchange ratios between the sulfate displaced by incoming oxalic acid as a solution by the respective addition for 5 different concentrations of oxalic acid.
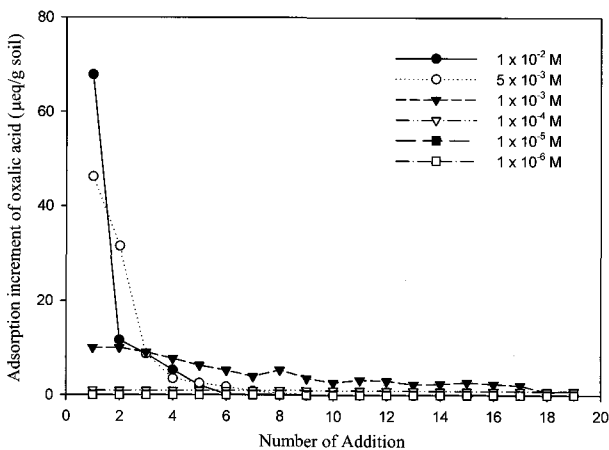

Fig. 4. Changes of increment of oxalic acid adsorbed by repetitive addition as influent at 5 different concentrations.
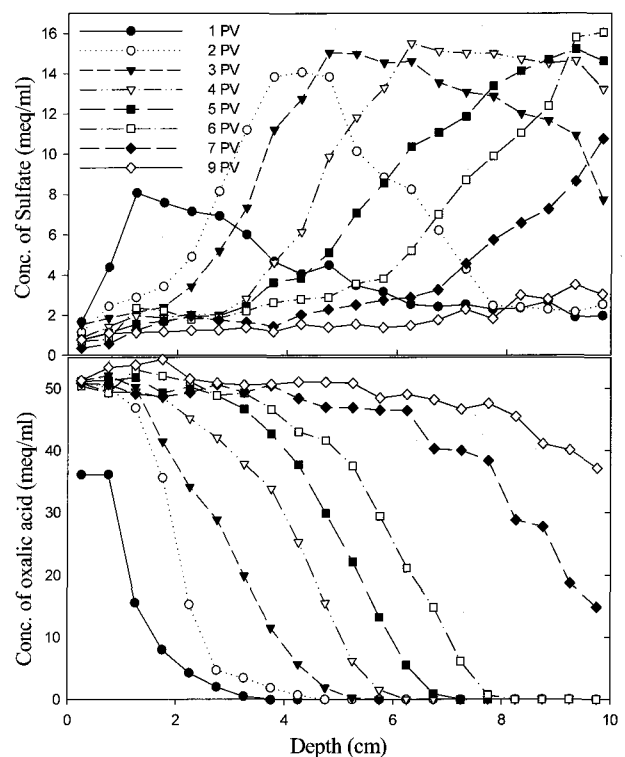

Fig. 5. Distributions of sulfate desorbed and oxalic acid as remained in a solution with depth for the respective addition of 10^{2} M oxalic acid.

amounts of SO_4 in solution near the inlet of the column. The amounts of SO_4 remained in solution phase were drastically decreased to less than 1.5 μeq/mL throughout the depths of column when 9 pore volumes of oxalic acid applied. This can be interpreted that the amounts of desorbed SO_4 were gradually decreased by migration with flowing solution due to the weak competition with oxalic acid for sorption sites, and the accumulation and mobility of SO_4 were influenced by the concentration of competing oxalic acid in solution. Therefore, the increasing amount of SO_4 in solution resulted in increasing competition between sulfate and oxalic acid for sorption sites or in suppressing the desorption of SO_4 as observed from the previous competitive adsorption experiment.

With the same column we analyzed the distributions of SO_4 retained as a solid phase with respect to depth (Fig. 6). The results obtained from 1, 3, 5, 7, and 9 pore volumes of oxalic acid passed through the soil column showed that the SO_4 in soil exchanger was successively displaced until the exchange reaction stops as the displacing anion, oxalic acid, advanced, resulted in the depletion of SO_4 at that location.

The distribution pattern of SO_4 in solid phase displaced by the varying pore volumes of oxalic acid showed that the amounts of SO_4 remained in each location were less or slightly greater than the indigenous amount of SO_4 measured from the PO_4 extraction. Depth and degree of SO_4 displaced by oxalic acid increased as the pore volumes of oxalic acid passed through the column, showing that 1 pore volume of oxalic acid was effective on the displacement of SO_4 at the first 3 cm. The maximum concentration of SO_4 in solid phase occurred at 4 pore volumes of oxalic
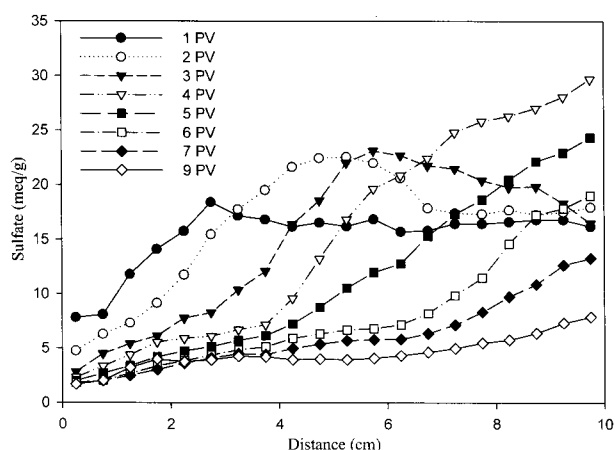
acid showed that the amount of SO_4 exceeded the indigenous amount of SO_4 as observed in batch method. This could be interpreted that the displaced SO_4 readsorbed in the lower locations of column followed by the maximum concentration of SO_4 in solution phase, where the concentration of oxalic acid in solution phase was low enough for the competitive adsorption of SO_4 simultaneously in the solution. The complete displacement of SO_4 by oxalic acid at the each location was, however, not obtained with the given pore volume condition until 9 pore volumes of oxalic acid passed through the column. From these findings we could assume that the rate of desorption of SO_4 influenced the distribution of SO_4 in solid phase throughout the competitive adsorption in the presence of oxalic acid.

On the other hand, we compared the ratios of SO_4 between the phases of solution and solid for the soil columns. As shown in Fig. 7, the location of ratio-peak moved toward the end of the soil column with decreasing peak ration after 3 pore volumes of oxalic acid passed. However all the peak ratios were less than 1, meant the amount of solid phase were greater than those of the solution phase. And the right-hand portion of each peak could be obtained by the invading oxalic acid front, whereas the left-hand part of the peak was obtained after a maximum concentration moved past a given soil location.

SUMMARY

The rate of desorption of SO_4 from soil surface may be determined by the exchange with oxalic acid entering to each location, resulted in the dominant factor on the distribution of SO_4 in solution and solid phase. And the relative

Fig. 6. Changes in sulfate remained as a solid phase displaced by steady state repetitive addition of 10^{-2} M oxalic acid.
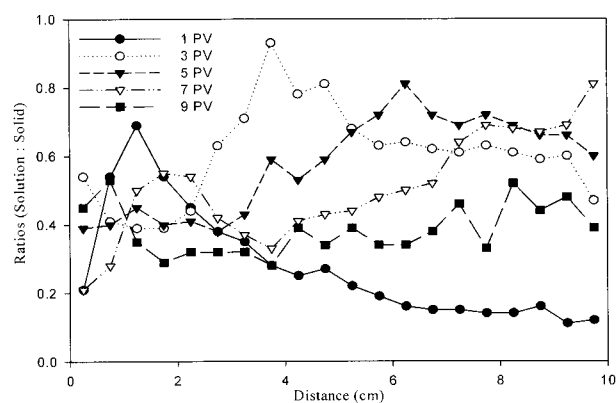

Fig. 7. Comparison of the sulfate between phases of solution and solid after treatment of the respective pore volume of 10^{-2} M oxalic acid.

distribution of SO_4 in solid phase at each location was influenced not only by the partition of displaced SO_4 between solid and solution phase, but by the competitive adsorption dependent upon the concentration of oxalic acid simultaneously present in solution. On the other hand, the results indicate that the presence of increasing amount of oxalic acid in solution enhance the competition for sorption sites with the displaced SO_4, resulting in the reduction of SO_4 adsorption.

Therefore, the depth of penetration of the displacing anion, oxalic acid, might occur behind the depth of displaced anions, SO_4 since the effectiveness of competitive adsorption capacity of oxalic acid was greater than that of SO_4 in this study. Thus, the transport behavior of displaced anion, SO_4, and displacing anion, oxalic acid, in this investigation could be much governed by the competitive adsorption characteristics and the relevant factors such as hydrodynamic dispersion coefficient and velocity in the system.

REFERENCES

1. Cho, C. M. (1985) Ionic transport in soil with ion-exchange reaction, Soil Sci. Soc. Am. J. 49, 1379-1386.

2. Hingston, F. J., Atkinson, R. J., Posner, A. M. and Quirk, J. P. (1968) Specific adsorption of anions on geothite, Trans, 9th. Int. Congr. Soil Sci. 1, 669-678.

3. Hingston, F. J., Posner, A M. and Quirk, J. P. (1972) Anion adsorption by geothite and gibbsite: 1. Role of the proton in determining adsorption envelop, J. Soil. Sci. 23, 177-192.

4. Li, N. C., Lidenbaum, A. and Parks, G. A. (1972) Some metal complexes of citric and tricarboxylic acids, J. Inorg. Nucl. Chem. 12, 122-128.

5. Huang, W. H. and Keller, W. D. (1971) Dissolution of clay minerals in dilute organic acid at room temperature, Am. Mineral. 56, 1082-1095.

6. Huang, W. H. and Keller, W. D. (1972) Organic acids as agents of chemical weathering of silicate minerals, Nature 239, 149-151.

7. Kwong, N., Kee, K. F. and Huang, P. M. (1977) Influence of citric acid on the hydrolytic reaction of aluminum, Soil. Sci. Soc. Am. J. 41, 692-697.

8. Kwong, N., Kee, K. F. and Huang, P. M. (1979) The relative interference of low-molecular weight complexing organic acids on the hydrolysis and precipitation of aluminum, Soil. Sci. 113, 337-342.

9. Kwong, N., Kee, K. F. and Huang, P. M. (1979) Surface reactivity of aluminum hydroxides precipitated in the presence of molecular weight organic acids, Soil. Sci. Soc. Am. J. 43. 1110-1113.

10. Cameron, D. R., and Klute, A. (1977) Convective-dispersive solute transport with combined equilibrium and kinetic adsorption model, Water Resour. Res. 13, 183-188.

11. Rao, P. S. S., Rolston, D. E., Jessup, R. E. and Davison, J. M. (1980) Solute transport in aggregated porous media: Theoretical and experimental evaluation, Soil Sci. Soc. Am. J. 44, 1139-1146.

12. van Genuchten, M. Th., Davison, J. M. and Wierenga, P. J. (1974) An evaluation of kinetic and equilibrium equations for the prediction of pesticide movement through porous media, Soil Sci. Soc. Am. Proc. 38, 29-35.