Anionic Effects on Potassium Reactions in Variable-Charge Atlantic Coastal Plain Soils

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ABSTRACT

To better understand the role anions play in the rate of cation adsorption, the effect of anions on K mobility, retention, and rate of K reactions in two variable-charge Atlantic Coastal Plain soils was investigated. The soils studied were a Rumford loamy sand (coarse-loamy, siliceous, thermic Typic Hapludult) and a Kenansville loamy sand (loamy, siliceous, thermic Arenic Hapludult). The effects of ClO₄, Cl, SO₄, PO₄, and SiO₄ on the rate and magnitude of K adsorption on the two soils was investigated at pH 5 and 6 using a stirred-flow kinetic technique. The amount of K adsorbed. In general, the amount of K adsorbed in the presence of a particular accompanying anion was of the order SiO₄³⁻ > PO₄³⁻ > SO₄²⁻ > Cl > ClO₄. When SiO₄ was the accompanying anion in a 20 mg K L⁻¹ solution, K adsorption on the Rumford soil was as high as 358 mg K kg⁻¹, vs. a K adsorption maximum of only 58 mg K kg⁻¹ when ClO₄ was the accompanying anion. Likewise for the Kenansville soil, the SiO₄ maximum was 321 mg K kg⁻¹ while the ClO₄ maximum was only 89 mg K kg⁻¹. These studies demonstrate the role anions play in K retention and mobility, specifically on variable-charge Atlantic Coastal Plain soils.

In recent years there has been a voluminous amount of literature dealing with anion sorption on soils and soil constituents, particularly in Al and Fe oxides. This can be partly attributed to the increased attention given to better understanding variable-charge soils of tropical and temperate regions. These soils are often contain significant amounts of hydrous Al and Fe oxides, kaolins, and amorphous materials. At lower pH values, these variable-charge surfaces have net positive charge that is available for adsorption of anions. Anions can also be adsorbed on oxide surfaces through a ligand-exchange process involving H₂O or OH⁻ (Hsu, 1977). Depending on the type of anion involved, ligand exchange can occur on surfaces initially carrying a net negative, positive, or neutral charge.

Parfitt (1980) reported that the affinity of anions for hydrous Al and Fe oxides generally follows the order PO₄³⁻ > AsO₄³⁻ > SeO₄²⁻ = MoO₄²⁻ = F > SO₄²⁻ = SiO₄³⁻ > Cl > NO₃⁻ > ClO₄. Hsu (1979) arranged anions in a series according to their effectiveness in inhibiting the crystallization of Al hydroxide: PO₄³⁻ > SiO₄³⁻ > SO₄²⁻ > Cl > NO₃⁻ > ClO₄. Adsorption occurs at Fe,Al-OH or Fe,Al-OH₃ sites, and the amount adsorbed depends on the number of such sites, the pH, and the electrolyte concentration of the solution (Parfitt, 1978). Thus, acid soils with large amounts of high-surface-area hydrous Al and Fe oxides will be the most reactive towards most anions (Gallez et al., 1977).

Hingston et al. (1967) studied the adsorption of several anions on goethite at different pH values and defined the relationship between the adsorption plateau and pH as the adsorption envelope. Hingston et al. (1972, 1974) determined adsorption envelopes for SiO₄ on goethite and gibbsite and concluded that the results were consistent with ligand exchange. Reactions involving H₄SiO₄ adsorption on amorphous hydroxides also revealed ligand-exchange mechanisms (Hingston and Raupach, 1967). Studies of anion reactions on soils and soil constituents suggest the occurrence of three types of adsorption: (i) nonspecific adsorption, which is characteristic of NO₃, Cl, and ClO₄. These anions can only be adsorbed by positively charged surfaces and are held loosely in the outer diffuse layer of the double layer; (ii) specific adsorption of anions of completely dissociated acids, which is characteristic of SO₄ and F. These anions are chemically adsorbed, involving a ligand exchange with surface H₂O; and (iii) specific adsorption of anions of incompletely dissociated acids, which is characteristic of PO₄, SiO₄, MoO₄, AsO₄, SeO₃, B(OH)₄, and other tetrahedral-forming anions. This adsorption involves an exchange with ligand hydroxyls. The requirement for such adsorption is the presence of both a proton donor and a proton acceptor.

Ion-exchange equilibria appear to be affected by the type of anion (Evangelou, 1986). Ayres and Hagiwara (1953) measured wide differences in K mobility in similar soils, depending on the K salt applied. Potassium added as KCl leached rapidly from the soil, compared with K supplied with SO₄ or PO₄. In studying Na–Ca exchange in soils, Babcock and Schulz (1963) found that, after leaching soils with SO₄ or Cl, exchangeable Na was higher when SO₄ was used. In various experiments, Sposito et al. (1981, 1983a,b,c) demonstrated that the type of anion present in a background ionic medium (Cl and NO₃ vs. ClO₄) used to carry out exchange studies has an effect on cation selectivity. However, Suarez and Zahow (1989) found that differences in Ca–Mg exchange behavior on Wyoming montmorillonite in Cl and ClO₄ background media were insignificant. Evangelou (1986) investigated the influence of anions on K quantity/intensity (Q/I) relationships. It was found that some Q/I parameters


were different between Cl and ClO₄ solutions. Specific SO₄ adsorption and competitive interactions between CaCl₂ and Ca, CaCl₂ and K, and KSO₄ and SO₄ on the solid phase appeared to be factors causing the differences.

Many questions remain unanswered concerning the effect of anions on the rate of cation adsorption. Previously conducted kinetic studies involving K have used Cl as the accompanying anion (Sparks, 1989). Our study examined the amount and rate of K adsorption as affected by five different anions. This work is important in ascertaining how anions affect K mobility, retention, and reaction rates in variable-charge Atlantic Coastal Plain soils since K leaching is often a problem in these soils.

**MATERIALS AND METHODS**

The soils in this study were sampled from field experiments conducted by Parker et al. (1989). These included a Rumford loamy sand and a Kenansville loamy sand, which are predominant soil types in the middle Atlantic Coastal Plain region.

The Ap horizons from each of the soils were sampled, air dried, and crushed to pass a 2-mm sieve in preparation for analyses. Soil pH was measured on a 1:1 soil/H₂O mixture, cation-exchange capacity (CEC) was determined by saturation of exchangeable K, Ca, Mg, and Al using methods outlined by Rhoades (1982) and Barnhisel and Bertsch (1982), and organic-matter content was determined by wet oxidation with K₂Cr₂O₇ (Nelson and Sommers, 1982). Particle-size distribution was determined by the pipet method (Gee and Bauder, 1986) and amorphous Al- and Fe-oxide content was determined by acid ammonium oxalate extraction (McKeague and Day, 1966).

The kinetic studies were carried out using the stirred-flow reaction chamber developed by Carski and Sparks (1985) and modified as in Toner et al. (1989). A magnetic stirring star and 1.0 g of pH-adjusted soil were placed in a chamber, complete with influent and effluent ports and a plunger base. A prefilter and filter were fitted just below the effluent port to retain the soil, a top was attached, and a known volume of deionized H₂O was injected into the chamber. The plunger base was then used to displace the excess air from the chamber, thus enabling precise control of the reaction volume. A LKB 2132 Microperpex peristaltic pump (LKB-Produktur AB, Bromma, Sweden) was used to maintain a constant adsorptive flow rate of 1.0 mL min⁻¹ and a LKB Ultronar II 2070 fraction collector was used to collect the chamber effluent at 4-min intervals. All treatments were duplicated. An adsorption run was conducted without soil to construct a dilution curve to distinguish the dilution effects from adsorption effects on effluent concentration for each run (Carski and Sparks, 1985).

The Rumford and Kenansville soils contain variable-charge colloids, thus negative or positive charge can be created depending on pH. Therefore, the pH of the adsorbents and adsorptives was studied at pH levels of 5 and 6 ± 0.1 to avoid the confounding effects of variable pH on K adsorption (Toner et al., 1989). These pH values were chosen because they are in the typical range for Atlantic Coastal Plain soils. For the kinetic studies, adsorbents included the Ap horizons of the Rumford and Kenansville soils. The soils were adjusted to the desired pH by shaking 3.0 g of soil for 24 h with 0.01 M HNO₃ (for pH 5) or 0.01 M NaOH (for pH 6) brought to the desired pH by additions of either NaOH or HCl. The samples were then centrifuged for 10 min at 1747 g after which a pH reading was taken. This process was repeated until the desired pH of the supernatant was reached. After pH adjustment, the samples were filtered and the retained soil was air dried. Adsorptives included K solutions as ClO₄, Cl, SO₄, PO₄, and SiO₃. Adsorptive concentrations of 20 and 50 mg K L⁻¹ in a background electrolyte solution of 0.01 M NaCl were used. The pH of the K solutions was brought to either 5 or 6 ± 0.1 by adjusting the pH of the 0.01 M NaCl matrix with additions of either NaOH or HCl. All treatments were duplicated. To maintain SiO₃ stability, SiO₃ solutions were kept in polyethylene bottles and test tubes as recommended by Beckwith and Reeve (1963).

The K concentration in the effluent samples was measured using atomic adsorption spectrophotometry. The quantity of adsorbed K at each time increment was calculated using the relationship (Schnabel and Fitting, 1988)

\[
q(t) = \frac{[2(c_{0} - c(t))] \Delta t + [C(t) - C(t_{i})]V}{m}, \quad [1]
\]

where,

- \( q(t) \) = retention when both effluent fraction and chamber concentrations of K are considered,
- \( c \) = concentration of K in fraction collected,
- \( C \) = solute concentration of K in chamber,
- \( t_{i} \) = time at end of sample collection period \( i \),
- \( \Delta t \) = length of collection period,
- \( V \) = flow rate,
- \( V \) = volume of solution in chamber,
- \( m \) = mass of soil in chamber,

and subscript \( s \) denotes soil in the chamber.

The rate data were applied to several kinetic equations including zero-, first-, and second-order equations. The first-order equation seemed to describe the data satisfactorily, as it had been previously observed for K adsorption on clays and soils (Jardine and Sparks, 1984; Sparks, 1989). We are not implying that first-order kinetics is the best or only model to describe the rate of K adsorption on these soils. From first-order relationships, apparent adsorption rate coefficients (\( k_{1} \)) were determined so that the trends in K adsorption rate as affected by different anions could be assessed.

**RESULTS AND DISCUSSION**

Some basic properties of the soils studied are given in Table 1. The pH of the soils was moderately acidic. They contained a large proportion of sand, low organic-matter contents, and had low CEC, which is typical for most Atlantic Coastal Plain soils (Sparks, 1980). They had small, but measurable, quantities of amorphous Fe and Al oxides. The mineralogy of the <2-μm clay fraction, as determined by x-ray diffraction and differential scanning calorimetry analyses, was dominated by kaolinite and chloritized vermiculite.

The amount of K adsorbed on the soils as affected by anion at pH 5 and 6 was generally of the order SiO₃ > PO₄ > SO₄ > Cl > ClO₄, as shown for the Kenansville loamy sand (Fig. 1 and 2, Table 2). Although not as consistent, the same trend was noted for the Rumford loamy sand (Table 2). Adsorption of anions like PO₄ is known to create negative charge or to impart CEC to soil colloids. This phenomenon accounts for the greater K adsorption that was observed with anions such as SiO₃ and PO₄ (Uehara and Gillman, 1981).

On variable-charge soils such as those studied, the overall charge on the soils is pH dependent. Sparks (1986) emphasized that Al and Fe oxides and hydrous
oxides are important sources of pH-dependent charge, they are rarely >5% by weight in soils, and their characteristically high surface area, combined with their frequent occurrence as grain coatings, results in a relatively high activity. Depending on the particular anions present in a soil, some types are more apt to be adsorbed than others. Silicate and PO$_4$ are specifically adsorbed in an exchange with ligand hydroxyls, which are components of oxide surfaces. Kingston et al. (1972) defined a relationship where, at different pH levels, there is a limit to the amount of negative charge contributed by adsorbed anions, which decreases with increasing pH due to the occupation of sites by OH. The protons accompanying the anions react with surface OH to form surface H$_2$O ligands. This relationship would be expected for all anions only if their full charge was developed in the layer of the coordinated ligands. Silicate and PO$_4$ are two such anions that exhibit this behavior and, hence, react with oxide surfaces. Silicate and PO$_4$ are able to adsorb onto oxides when the surface charge is zero or even negative. At least for PO$_4$, anion coordination with surface metal ions occurs and H$_2$O and OH ions bonded to the metal ions are replaced by PO$_4$ (Uehara and Gillman, 1981). Therefore, variable-charge soils exhibit a greater affinity for SiO$_3$ and PO$_4$ than for Cl or ClO$_4$ (Hingston and Raupach, 1967; Hingston et al., 1967, 1972, 1974). In this study, the large affinity for SiO$_3$ by these variable-charge soils is evidenced by adsorption of large quantities of K (Table 2).

Phosphate adsorption in soils is influenced by the presence of other anions, especially SiO$_3$ and organic anions (Parfitt, 1978). Even though PO$_4$ and SiO$_3$ can behave similarly, in this study in two instances it was observed that more K was adsorbed when SiO$_3$ was the accompanying anion than when any other anion was present (Table 2). McKeague and Cline (1963a,b) demonstrated an inverse relationship between pH and the SiO$_3$ concentration of soil solutions where the magnitude of SiO$_3$ adsorption was greatest between pH 7 and 9 and rapidly decreased at higher and lower values. Beckwith and Reeve (1963) found that the resid-

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**Table 1.** Physicochemical and mineralogical properties of soils studied.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>pH</th>
<th>Cation-exchange capacity (cmol kg$^{-1}$)</th>
<th>Organic matter (g kg$^{-1}$)</th>
<th>Particle-size analysis</th>
<th>Mineralogy of &lt;2-μm clay fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>K = CV = Q &gt; C &gt; M</td>
</tr>
<tr>
<td>Rumford loamy sand</td>
<td>Ap</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>K &gt; Q &gt; CV &gt; C &gt; M</td>
</tr>
<tr>
<td></td>
<td>0-25</td>
<td>5.4</td>
<td>1.7</td>
<td>10.0</td>
<td>80.6</td>
<td></td>
</tr>
<tr>
<td>Kenansville loamy sand</td>
<td>Ap</td>
<td></td>
<td></td>
<td></td>
<td>83.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0-23</td>
<td>5.2</td>
<td>3.6</td>
<td>13.0</td>
<td>89</td>
<td></td>
</tr>
</tbody>
</table>

† K = kaolinite; CV = chloritized vermiculite; Q = quartz; C = chlorite; M = mica.

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**Table 2.** Effect of anion and pH on K adsorption on soils studied.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Cumulative K adsorbed (mg kg$^{-1}$)</th>
<th>pH 5</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Rumford loamy sand</td>
<td>58º°°</td>
<td>346</td>
<td>335</td>
<td>350</td>
<td>358</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(90º°°) (118)</td>
<td>(106)</td>
<td>(98)</td>
<td>(38)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kenansville loamy sand</td>
<td>74º°°</td>
<td>137</td>
<td>169</td>
<td>268</td>
<td>255</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(86) (98)</td>
<td>(118)</td>
<td>(98)</td>
<td>(38)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rumford loamy sand</td>
<td>158º°°</td>
<td>167</td>
<td>269</td>
<td>375</td>
<td>249</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(78) (78)</td>
<td>(66)</td>
<td>(78)</td>
<td>(38)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kenansville loamy sand</td>
<td>89º°°</td>
<td>100</td>
<td>202</td>
<td>240</td>
<td>321</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(42) (40)</td>
<td>(54)</td>
<td>(94)</td>
<td>(38)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Adsorptive concentration was 20 mg K L$^{-1}$.
° Number in parentheses represents time in minutes when an apparent equilibrium in adsorption for anions was attained, except for SiO$_3$, where the number represents the time at which the experiment had to be stopped.

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**Fig. 1.** Effect of anion and time on K adsorption of Kenansville loamy sand at pH 5 using 20 mg K L$^{-1}$ adsorptives.

**Fig. 2.** Effect of anion and time on K adsorption on Kenansville loamy sand at pH 6 using 20 mg K L$^{-1}$ adsorptives.
nal solution SiO$_3$ concentration of soils shaken with H$_2$SiO$_3$ was controlled by an adsorption equilibrium, which was dependent on pH. Below pH 8 to 9, the residual solution SiO$_3$ concentration in soil suspensions steadily increased. Subsequently, Beckwith and Reeve (1964) concluded that pH rather than the presence of competing anions was responsible for the release of SiO$_3$ into solution. Specific sorption of silica compounds was responsible for controlling solution SiO$_3$ levels.

Although pH can affect SiO$_3$ behavior, there was not a consistent pattern between amounts of K adsorbed at pH 5 vs. 6 (Table 2). For some anions, more K was adsorbed at pH 5 and for others, more K was adsorbed at pH 6, regardless of the soil type or anion present. With increasing acidity, in general, more positive charge is created and anion adsorption can increase; however, little effect of lowering the pH by one unit was observed for adsorption of the cation K.

Figure 3 shows the effect of K concentration on K adsorption kinetics. Here SiO$_3$ was the accompanying anion and it is evident that more K was adsorbed at the higher adsorptive concentration. This same effect was observed when other anionic forms of K salts were used; however, the overall trend in K adsorption with time was similar for both adsorptive concentrations. Also notable is the greater adsorption of K on the Rumford loamy sand than on the Kenansville loamy sand (Fig. 3). This may be due to the higher clay content of the Rumford soil (Table 1), which contains a high quantity of chloritized vermiculite. It is well known that vermiculitic-type clays have a strong affinity for K ions (Jardine and Sparks, 1984).

The kinetic studies with SiO$_3$ had to be stopped after a period of only 38 min but, at this relatively short time, there was considerable K adsorption with SiO$_3$ In some cases, more K was adsorbed when the accompanying anion was SiO$_3$ than what was observed with some of the other anions at longer time periods (Table 2). The experiments with SiO$_3$ stopped prematurely due to increased pressure in the stirred-flow reaction chamber. A physical alteration inside the chamber, such as flocculation, was suspected, since polymerization of SiO$_3$ was thought not to have occurred (Roberts, 1987, personal communication). Iler (1979) reported that SiO$_3$ in the form of monomers and low-molecular-weight polymers polymerizes as pH increases. Brown and Mahler (1987) maintain that, as the pH of the system is raised by acid consumption or by leaching of soil solutions to greater depths, SiO$_3$ could polymerize and precipitate onto soil surfaces. Evidently, an increased pH, the soil solution SiO$_3$ not in contact with adsorption surface area can be concentrated to the point where polymerization occurs in solution (Chadwick et al., 1987). Concurrently, if a soil dries, the ionic strength of the soil solution increases and thus enhances the formation of polymers. Thus, the factors of low pH and a system where the soil was saturated with SiO$_3$, as seen in our study, would not be conducive to polymerization. Hence, polymerization was probably not a factor since: (i) the concentration of the adsorptive SiO$_3$ solutions did not change with time; (ii) increasing the K concentration from 20 to 50 mg L$^{-1}$ and thus the amount of SiO$_3$ in solution did not affect the time at which the clogging problem started; and (iii) there were not large pH fluctuations in the initial SiO$_3$ adsorptive solutions and the collected SiO$_3$ fractions, compared with the other anions, which would have been the case if only SiO$_3$ was polymerizing. To examine the possibility of a physical alteration other than polymerization, turbidity measurements of the SiO$_3$ solution could be taken over time to see if the SiO$_3$ was indeed flocculating and therefore clogging the chamber (Roberts, 1987, personal communication).

Even though the amount of K adsorbed differed with anion type, the rate of K reactions in the soils as indicated by the magnitude of apparent adsorption rate coefficients ($k_2$) (Table 3) was not greatly affected. Additionally, for a particular anion, pH had little effect on the $k_2$ values for a given soil.

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