

Anion Exchange Chemistry of Middle Atlantic Soils: Charge Properties and Nitrate Retention Kinetics

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ABSTRACT

The negative impact of nitrate (NO_3) on groundwater supplies has sparked a great deal of interest and concern in recent years, particularly in areas where coarse-textured soils abound. In light of this concern, the anion exchange chemistry of eight soils from the Middle Atlantic region was studied with particular emphasis on NO_3 retention and kinetics. The soils were chosen to encompass a range of physicochemical and mineralogical properties and were extensively characterized. Anion exchange capacity (AEC) was determined on Cl-saturated samples by desorption of Cl with SO_4 . Anion exchange capacity ranged from 0 to $1.35 \text{ cmol}_c \text{ kg}^{-1}$ for the eight soils and was found to parallel increases in clay and Fe oxide contents in the soil profiles. Point of zero salt effect (PZSE) values were determined by potentiometric titration with 0.001, 0.01, and 0.1 M NaCl as the indifferent electrolyte. These were of little value in predicting the development of AEC for the soils. The kinetics of NO_3 adsorption and desorption were studied using a stirred-flow reaction chamber and a first-order reaction best described the data. Nitrate adsorption was found to be completely reversible, indicating a simple electrostatic retention mechanism. The effect of pH and NO_3 concentration on cumulative NO_3 adsorbed (CNA) and on NO_3 adsorption kinetics was also studied. The CNA was found to increase with a decrease in pH below 5.5 and to increase with increasing NO_3 concentration. The latter indicated an increase in competitiveness by NO_3 for positively charged sites.

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IN RESPONSE TO the growing alarm about ground and surface water degradation, there has been increased concern about NO_3 mobility and retention in soils. Excess applied N from various sources has been shown to negatively impact ground water under sandy soils of the Delmarva (Delaware-Maryland-Virginia) Peninsula (Liebhart et al., 1979; Ritter and Chirnside, 1982; Robertson, 1977a,b). At present, however, little attention has been focused on anion exchange chemistry and, in particular, on the retention of NO_3 in soils of the eastern USA.

Nitrate is usually assumed to be weakly held by soils and would not be extensively retained in the root zone. Recently, some researchers have reported retention of NO_3 in Middle Atlantic soils in quantities worthy of consideration when formulating N-fertilizer recommendations. Meisinger et al. (1982, 1983) found large quantities of NO_3 from fertilizer applied the previous year remained in the root zone in spring, even though winter rainfall had been sufficient for percolation of NO_3 through the soil profile. The amount of residual NO_3 was influenced by the quantity of NO_3 fertilizer applied. No definitive mechanism was offered for the observed NO_3 retention. It could be ascribed to physical retention in occluded micropores or to chemical retention by adsorption. With the presence of variable-charged soil constituents, development of positive charge would be expected when the soil pH is less than the zero point of charge (ZPC) of the constituents due to protonation of surface functional groups. Negatively charged NO_3 should be adsorbed to these protonated sites provided it can com-

pete effectively with other anions present in the soil solution. The presence of variable-charged components such as Al and Fe oxides and clay minerals such as kaolinite in soils of the Middle Atlantic region has been well established (Elliott and Sparks, 1981).

Nitrate retention was observed in weathered tropical soils high in Al and Fe oxides from Chile, Mexico and Hawaii (Singh and Kanehiro, 1969; Kinjo and Pratt, 1971a,b; Kinjo et al., 1971; Espinozo et al., 1975). Retention of NO_3^- increased with decreasing pH, indicating pH-dependent variable charge was operative. Hingston et al. (1972) proposed that protonated surfaces of kaolinite and Al and Fe oxides were important sites for NO_3^- adsorption. Adsorption was considered electrostatic in nature and would therefore only occur at $\text{pH} < \text{ZPC}$. By determining the ZPC of a given soil as well as the native pH, one may be able to predict the sign of net surface charge and the likelihood of NO_3^- adsorption.

In this study, several common soil types, sampled from the Middle Atlantic region and representing a wide range of physicochemical and mineralogical properties, were characterized and their AEC and nitrate adsorption potential (NAP) determined at native pH. Point of zero salt effect was determined to assess its potential for predicting AEC. Cumulative nitrate adsorbed was determined as a function of pH and adsorptive solution concentration using a kinetic approach to further substantiate retention mechanisms involved. Any attempt to predict the fate of NO_3^- amendments should consider the rate and mechanism of adsorption.

MATERIALS AND METHODS

Eight major soil types from the Middle Atlantic region were chosen for study. The soils were air dried, crushed and passed through a 1-mm mesh screen. Soil pH was determined in a water slurry (1:1 w/v) using an Orion 901 Ion-analyzer and an Orion combination electrode (Orion Research, Cambridge, MA). Organic matter was determined using a modified Walkley-Black procedure (Nelson and Sommers, 1982). Iron oxide content was determined using the Na-citrate-dithionite-bicarbonate extracting method (Mehra and Jackson, 1960). Amorphous Al oxides were measured using the NH_4 -oxalate extracting method (Iyengar et al., 1981). The mineralogy of the $< 2 \mu\text{m}$ clay fraction was determined by x-ray diffraction (XRD) using fractionation procedures outlined by Sparks and Jardine (1984). Particle size distribution was determined using the pipet method (Gee and Bauder, 1986).

Charge Analyses

Cation exchange capacity (CEC) was determined by compulsive exchange using 1 M NH_4OAc buffered at pH 5 (Thomas, 1982) or by Mg-Ca exchange (Okazaki et al., 1963). Anion exchange capacity was determined using the MgSO_4 -BaCl₂ method of Gillman (1979) as described by Rhoades (1982).

The potentiometric titration method of Parker et al. (1979) was employed for the determination of PZSE. Sodium chloride was used as the indifferent electrolyte to minimize specific adsorption. Four grams of NaCl-saturated soil were placed in 39 30-mL sample cups (three sets of 13 cups). Each set of cups was equilibrated at one of three different concentrations of NaCl: 0.1, 0.01, and 0.001 M. To each cup, 10 mL of the appropriate NaCl solution was added

followed by increasing amounts (0.5 mL increments) of 0.1 M HCl or NaOH. An appropriate volume of NaCl solution was then added to bring the total sample volume to 20 mL. This resulted in three sets of samples identical in acid/base additions and differing only in concentration of background electrolyte. Titration curves for the solution series minus the soil were constructed and used as blanks. The pH value for each sample cup was determined at 1 h and again at 48 h. The amount of H^+ or OH^- adsorbed by the soil at a given pH is equal to the amount of HCl or NaOH added to the sample minus the amount added to bring the blank to an equal pH. The amount of H^+ or OH^- added ($\text{cmol}_c \text{ kg}^{-1}$) is plotted vs. pH for each NaCl concentration series, and the intersection of the three curves indicates the PZSE.

Kinetic Studies

Kinetics of NO_3^- adsorption and desorption were studied using the stirred-flow reaction chamber developed by Carski and Sparks (1985). This apparatus consists of a chamber with influent and effluent ports, a magnetic stirring star, and adjustable plunger base. A 1.0-g sample of soil was placed in the chamber and retained therein using a Millipore AP prefilter (Millipore Corp., Bedford, MA) and a 0.8- μm Nuclepore Membrane filter (Nuclepore Corp., Pleasanton, CA) fitted just below the effluent port. A known volume of entrained fluid was injected into the chamber by syringe and any air trapped in the chamber was removed with the adjustable plunger base, thus allowing a known volume of solution to be diluted out. An LKB 2132 Microperplex peristaltic pump (Pharmacia LKB Biotechnology, Piscataway, NJ) was used to maintain a constant adsorptive solution flow velocity of 1 mL min^{-1} and an LKB Ultrac II 2070 fraction collector was employed to collect the chamber effluent in 2, 4, or 8 min increments.

Nitrate adsorption-desorption kinetics were studied at 2-min intervals on KCl- and KSO_4 -saturated samples from the Bt2 horizon of a Cecil soil (clayey, kaolinitic, thermic Typic Hapludult) using a 45 mg L^{-1} NO_3^- solution as KNO_3 , which is equivalent to the EPA safe drinking water standard for NO_3^- -N (Code of Federal Regulations, 1987). Desorption of NO_3^- from the KCl saturated soil was conducted using an equal molarity of Cl as KCl. Chloride, SO_4 and NO_3^- concentrations were determined using a Waters 430/501 ion chromatography system (Waters Div. of Millipore Corp., Milford, MA) with acetonitrile-glycerol-borate buffer as the mobile phase.

Cumulative NO_3^- adsorbed and NO_3^- -adsorption kinetics as a function of pH were studied at pH levels of 4.0, 5.5, and 7.0 ± 0.1 on four soils, the Cecil, Dothan (fine-loamy, siliceous, thermic Plinthic Paleudult), Matapeake (fine-silty, mixed, mesic Typic Hapludult), and Evesboro (mesic, coated Typic Quartzipsamment). These four soils were chosen to give a range in clay and Al and Fe oxide contents (Table 1). The horizon with the highest AEC was chosen from each soil. All soils were presaturated with KCl prior to pH adjustment. Each was adjusted to the desired pH by shaking 4.0 g soil for 24 h with 50 mL of 0.015 M KCl brought to the desired pH by additions of either HCl or

Table 1. Classification and chemical, physical, and mineralogical properties of Middle Atlantic region soils.

Soil type	Classification
Cecil clay	clayey, kaolinitic, thermic Typic Hapludults
Dothan loamy sand	fine-loamy, siliceous, thermic Plinthic Paleudults
Kenansville loamy sand	loamy, siliceous, thermic Arenic Hapludults
Matapeake silt loam	fine-silty, mixed, mesic Typic Hapludults
Sassafras sandy loam	fine-loamy, siliceous, mesic Typic Hapludults
Evesboro loamy sand	mesic, coated Typic Quartzipsamments
Leon loamy sand	sandy, siliceous, thermic Aeric Haplaquods

KOH. The samples were then centrifuged and the pH recorded. This process was repeated until the desired pH of the supernatant was reached and maintained after a 24 h equilibration period. After pH adjustments, the soil suspension was filtered and the recovered soil was air dried and crushed to pass a 1-mm mesh screen. One gram of pH-adjusted soil was then placed in the stirred-flow reaction chamber with a known volume of deionized water adjusted to the desired pH with HCl or KOH. The soil was then flushed free of excess Cl with pH-adjusted deionized water until effluent Cl content, determined by ion chromatography analyses, was equal to that of the influent. Nitrate adsorptive solutions of 10 mg L⁻¹ N as KNO₃, adjusted to the desired pH with HNO₃ or KOH, were then pumped through the chamber at a flow rate of 1.0 mL min⁻¹. The NO₃ added in pH adjustment using HNO₃ was accounted for in the total concentration of the adsorptive solution. The effluent was collected in appropriate time increments (2 min for low-adsorption-capacity soils such as the Matapeake at pH 5.5 to as much as 8 min for high-adsorption-capacity soils such as the Cecil) until an apparent equilibrium was reached. An adsorption run was conducted without soil to construct a dilution curve to separate the dilution effects from the effect of adsorption on effluent concentration for each run (Carski and Sparks, 1985). All phases of the kinetic experiments were conducted in duplicate. Nitrate adsorbed with time was evaluated using the relationship (Seyfried et al., 1989)

$$q(t_i) = \left[\frac{\sum(C_{ns_i} - C_s) J \Delta t}{[c(t_i)_{ns} - c(t_i)_s] V} \right] m \quad [1]$$

where:

- q* = quantity of NO₃ adsorbed
- C* = the concentration of the effluent at time *t*
- c* = the solution concentration in the chamber
- V* = the volume of solution in the chamber
- J* = the flow velocity
- t_i* = time at the end of effluent collection period *i*
- Δt* = length of collection period
- m* = mass of soil in the chamber

The subscripts *ns* and *s* represent no soil and soil in the chamber, respectively.

Nitrate adsorptive solutions of 45, 90, and 165 mg L⁻¹ were used to evaluate the effect of initial NO₃ concentration on the kinetics and magnitude of NO₃ adsorption at pH 4.0 on the Cecil Bt2 soil using the above procedure. The 165 mg L⁻¹ NO₃ solution was chosen to approximate soil solution NO₃ levels resulting from N-fertilizer applications of 0.336 Mg ha⁻¹, based on the water-holding capacity of a typical Middle Atlantic soil. Applications of N-fertilizers at this level are not uncommon in this region.

RESULTS AND DISCUSSION

The soils examined in this study had diverse physicochemical properties (Table 1). The Cecil and Do-

than soils were characterized by high clay and oxide contents while the Evesboro soil was extremely sandy. Kaolinite and Al and Fe oxides were present throughout all the soil profiles that were studied. These soil constituents exhibit variable charge and thus can develop positive charge. Their presence is an indicator that anions, perhaps even NO₃, could be adsorbed.

Charge Properties

The PZSE and water pH for the Cecil, Dothan, and Matapeake soil profiles are presented in Table 2. The pH corresponding to PZSE for all horizons tested was consistently lower than the water pH, which would suggest negative charge development and repulsion of NO₃ anions. However, the soils possessed significant AEC in some cases (Tables 1 and 2). The interaction between permanent negative charge and variable positive charge is a function of the physical nature of the variable charge component. If variable charge sesquioxides occur as coatings on minerals with permanent negative charge then the permanent negative charge may be obscured and the variable charge components may exert an increased electrochemical influence relative to their mass. Under these conditions, the ZPC of the whole soil would be similar to that of the oxide coatings themselves (Elliott and Sparks, 1981). If, however, the oxides occur as discrete particles along with the permanent charge components,

Table 2. Water pH, PZSE, and AEC for three selected soil profiles.

Depth	Horizon	pH	PZSE†	AEC†
m				
cmol _c kg ⁻¹				
Cecil clay				
0-0.03	A	4.37	3.00	0
0.03-0.20	E	4.58	4.35	0
0.20-0.60	Bt1	4.65	4.00	0.67
0.60-1.63	Bt2	5.07	4.25	1.35
1.63-1.96	C	4.32	3.85	0.39
Dothan loamy sand				
0-0.23	A	5.74	3.50	0
0.23-0.38	E	6.25	3.50	0
0.38-0.76	Bt1	4.87	3.50	0.11
0.76-0.97	Bt2	4.56	3.75	0.41
0.97-1.52	Btv1	4.33	4.25	0.88
Matapeake silt loam				
0-0.25	Ap	5.77	3.50	0
0.25-0.53	Bt1	4.58	3.60	0.08
0.53-0.66	2Bt1	4.54	3.40	0.12
0.66-0.79	2Bt2	4.65	3.65	0.16
0.79-1.14	2Bt3	4.57	3.72	0.06

† PZSE = point of zero salt effect value, AEC = anion exchange capacity

Table 1. (cont.)

Horizon	Depth	pH	CEC†	AEC†	OM†	Particle size analysis			Fe oxide	Al oxide	Mineralogy‡
						Sand	Silt	Clay			
						%					
						cmol _c kg ⁻¹			%		
Bt2	0.60-1.63	5.1	3.97	1.35	0.27	31.2	23.8	45.0	2.70	0.11	K ₁ , CV ₂ , G ₃
Btv1	0.96-1.52	4.3	7.80	0.88	0.16	42.8	10.9	46.3	3.60	0.14	K ₁ , CV ₂ , G ₃ , Q ₄
C	0.56-1.52	7.1	3.58	0.11	0	89.5	8.2	2.3	0.13	0.07	K ₁ , Q ₂ , CV ₃ , M ₄
Bt1	0.28-0.53	4.6	9.37	0.08	0.35	25.2	50.2	23.8	0.85	0.24	CV ₁ , K ₂ =Q ₃ , M ₄
BC	0.66-0.84	5.0	6.89	0.44	0.10	76.3	7.5	16.2	2.60	0.13	K ₁ , Q ₂ , G ₃ , M ₄
B	0.68-1.65	5.0	0.14	0.02	0.18	95.4	3.2	1.4	0.04	0.02	K ₁ , CV ₂ , M ₃ , Q ₄
Bh2	0.33-0.48	4.3	1.07	0	3.20	88.2	8.9	2.9	0.04	0.68	Q ₁ , K ₂ , CV ₃ , M ₄

† CEC = cation exchange capacity, AEC = anion exchange capacity, OM = organic matter

‡ K = kaolinite, CV = chloritized vermiculite, Q = quartz, M = mica, G = gibbsite; 1 = most abundant, 4 = least abundant

their influence is greatly diminished, and the ZPC of the whole soil will be depressed to a more acid pH (Uehara and Gillman, 1980a). Little if any correlation of PZSE with AEC was found for the soils tested (Table 2) and PZSE was therefore a poor indicator of AEC. The low PZSEs for the whole soils would seem to suggest that the oxides present in these soils occur predominantly as discrete particles and positive charge contributions required to satisfy the permanent negative charge component deflate PZSE to an exaggeratedly low pH. As positively and negatively charged particles usually coexist in a soil sample, AEC and CEC are not mutually exclusive and regions of anion adsorption may occur despite an ostensibly negatively charged soil sample.

For the Cecil, Dothan, and Matapeake soils, AEC increased with depth, paralleling accumulation of clay and Al and Fe oxides (Table 2). Field studies conducted on Middle Atlantic soils have also shown an increase in NO_3 retention with depth (Meisinger et al., 1982, 1983). In view of these findings, our data indicate that chemical retention may be a significant factor in the accumulation of NO_3 throughout soil profiles. However, this does not preclude concurrent physical retention in occluded soil micropores. A stepwise multiple linear regression analysis was conducted relating development of AEC to organic matter, Al oxides, Fe oxides, and clay content for the complete profiles of the soils listed in Table 1. The best model describing development of AEC was a simple correlation with Fe oxide as the independent variable ($\text{AEC} = 0.38 + 27.46 F$, where F is Fe oxide content in g kg^{-1}) with a multiple correlation coefficient (R^2) of 0.861 and a probability of $>99.9\%$. Although the correlation was not as significant, AEC development was also adequately described by the one-variable clay model ($\text{AEC} = 8.98 + 368.77 C$, where C is clay content in g kg^{-1}) with a multiple correlation coefficient of 0.762 and a probability of $>99.9\%$.

It is not surprising that clay and oxide contents are correlated to AEC in these soils. The predominant clay mineral in the soils is kaolinite (Table 1) which

has an average ZPC of 6.0 (Bohn et al., 1985) and would therefore exhibit positive charge below this pH. Iron oxides have a ZPC ranging from 6.7 to 9.0, while Al oxides exhibit a ZPC of 7.5 to 9.2 (White and Zelazny, 1986). Both Al and Fe oxides were present in all of the soils we studied (Table 1). If the pH of the soil solution were below these values, the oxides would be positively charged. Iron oxides were found in copious quantities in the Cecil, Dothan, and Sasfras (fine-loamy, siliceous, mesic Typic Hapludult) soil horizons and these soils also had the highest AEC values. Contrastingly, the Evesboro and Leon (sandy, siliceous, thermic Aeric Haplaquod) soil horizons had the lowest AEC and Fe oxide content (Table 1).

Although not shown, organic matter content was highest in the surface horizons and decreased precipitously with depth in the soils listed in Table 1. In the Leon soil, however, organic matter content did not decrease substantially with depth. The fact that no horizon with higher organic matter content exhibited significant AEC (Table 2) implies that organic matter was not important in retaining NO_3 in any of the soils.

Nitrate Retention and Kinetic Studies

Kinetic studies conducted on samples from the Cecil Bt2 horizon with NO_3 and Cl adsorptive solutions indicate that NO_3 adsorption is both rapid and reversible, which is characteristic of electrostatic exchange (Fig. 1). Adsorption and desorption of NO_3 were essentially equal ($1.51 \text{ cmol kg}^{-1} \text{ NO}_3$ adsorbed, $1.56 \text{ cmol kg}^{-1} \text{ NO}_3$ desorbed). The slight excess in desorbed NO_3 is attributable to the cumulative margin of error associated with successive measurements of NO_3 by ion chromatography in determining CNA. A preference for Cl was evident in that NO_3 adsorption was complete after 106 min while Cl adsorption (NO_3 desorption) was complete in 26 min.

Adsorption and desorption of NO_3 on Cl-saturated soil samples conformed to first-order kinetics (Fig. 2). Coefficients of simple determination (r^2) for first-order regressions were typically 0.90 or higher. An electrostatic or outer-sphere complexation mechanism for NO_3 retention on Middle Atlantic soils agrees with

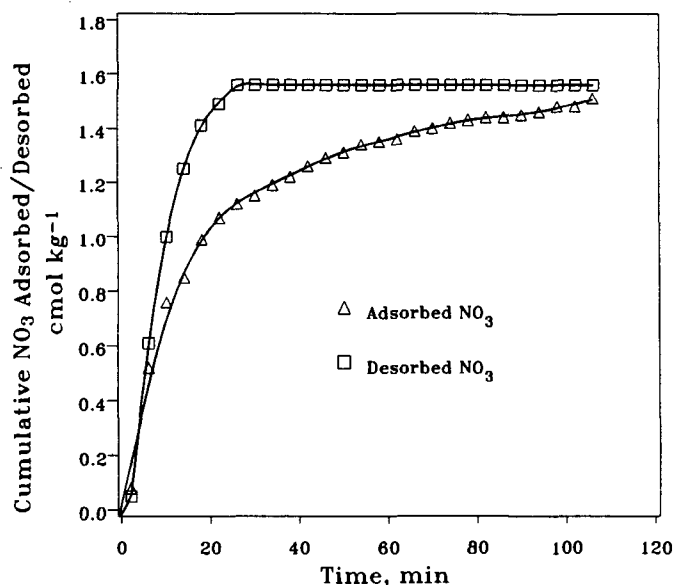


Fig. 1. Reversibility of NO_3 adsorption on the Cecil Bt2 horizon at pH 4.0 and a NO_3 solution concentration of 90 mg L^{-1} .

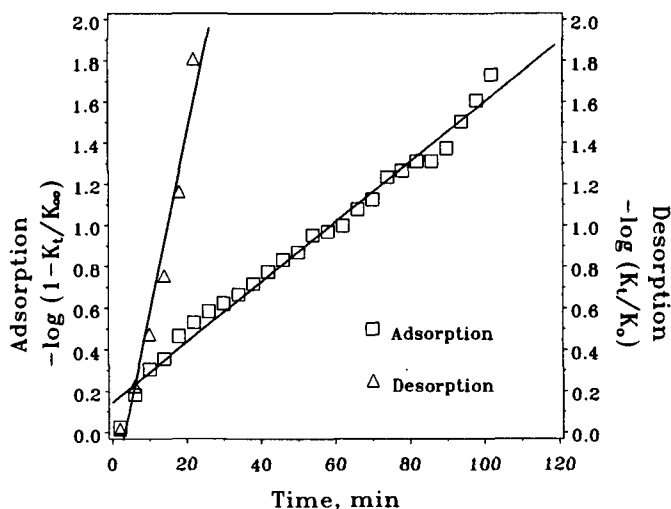


Fig. 2. First-order kinetics of NO_3 adsorption/desorption on the Cecil Bt2 horizon at pH 4.0 and a NO_3 solution concentration of 90 mg L^{-1} .

that proposed for NO_3 retention on tropical soils high in kaolinite and sesquioxides (Singh and Kanehiro, 1969; Kinjo and Pratt, 1971a,b; Kinjo et al., 1971; Espinoza et al., 1975).

Chloride adsorption and desorption on a NO_3 -saturated Cecil Bt2 soil also exhibited similar first-order behavior with nearly 100% reversibility. With the stirred-flow technique, it has been shown that K_{eq} values calculated using the relation $K_{\text{eq}} = k_a/k_d$, where k_a and k_d are the adsorption and desorption rate constants, respectively, compares well to the K_{eq} values determined using traditional thermodynamics of ion exchange theory (Carski and Sparks, 1986, unpublished data; Sparks, 1989). This would indicate that mass transfer phenomena are significantly reduced with this technique since, if diffusion were pronounced, the comparison between thermodynamic parameters calculated from a traditional equilibrium approach and from a kinetic approach would compare poorly (Ogwada and Sparks, 1986). Thus, the relationship $\Delta G^\circ = -RT \ln (k_a/k_d)$ is operational for the stirred-flow method. Accordingly, we calculated ΔG° values for NO_3 -Cl exchange on the Cecil soil. A ΔG° of $+3.81 \text{ kJ mol}^{-1}$ for NO_3 -Cl exchange indicated a small preference for the Cl ion.

Nitrate adsorption on the Cecil Bt2 horizon, as affected by a more strongly held anion such as SO_4 , was studied using a SO_4 -presaturated soil. Nitrate adsorption was dramatically reduced from approximately 50% of the AEC when Cl-saturated to approximately 15% of the AEC when SO_4 -saturated. As anticipated, SO_4 proved a more tenacious competitor for exchange sites than did NO_3 or Cl. If NAP is considered to be the amount of NO_3 retained when only electrostatically bound anions are present, then NAP would be equal to AEC and CNA would be substantial. As few native soil solutions would be dominated by weakly held Cl, it would appear that NAP in the presence of other more strongly held anions commonly encountered such as SO_4 , PO_4 , MoO_4 , and SeO_4 would not be as significant. Nonetheless, NO_3 does exhibit some

competitiveness for exchange sites with more strongly held anions such as SO_4 and retention could occur in soils, particularly at lower profile depths where clay and oxide contents are highest and concentrations of other anions such as PO_4 and SO_4 may be lower. The effect of competitive anions on NO_3 retention and kinetics of adsorption is further investigated in subsequent research.

Nitrate adsorption as a function of time at pH 4.0, 5.5, and 7.0 on the Cecil and Dothan soils, and at pH 4.0 for the Matapeake soil is shown in Fig. 3 to 5. Desorption of NO_3 from these soils using Cl as the desorptive ion was studied and reversibility was observed. The pH of each of the effluent solutions was recorded throughout the kinetic studies and remained essentially constant. The CNA vs. pH for the Cecil

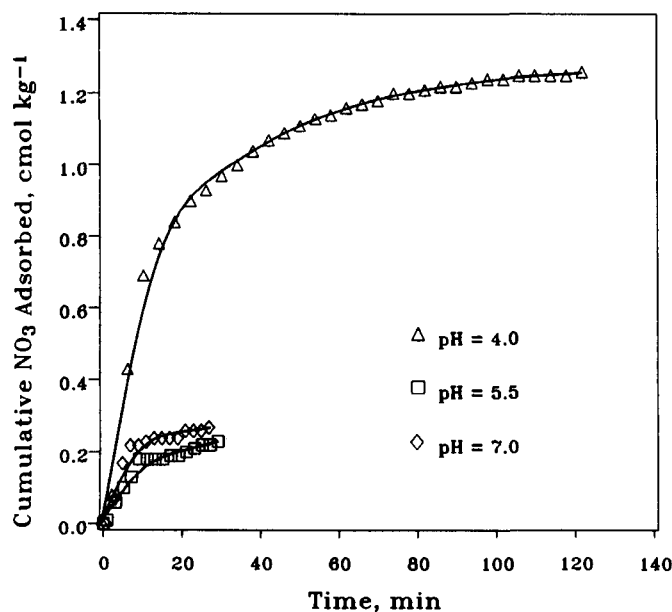


Fig. 3. Effect of pH on the kinetics and magnitude of NO_3 retention on a Cecil Bt2 horizon.

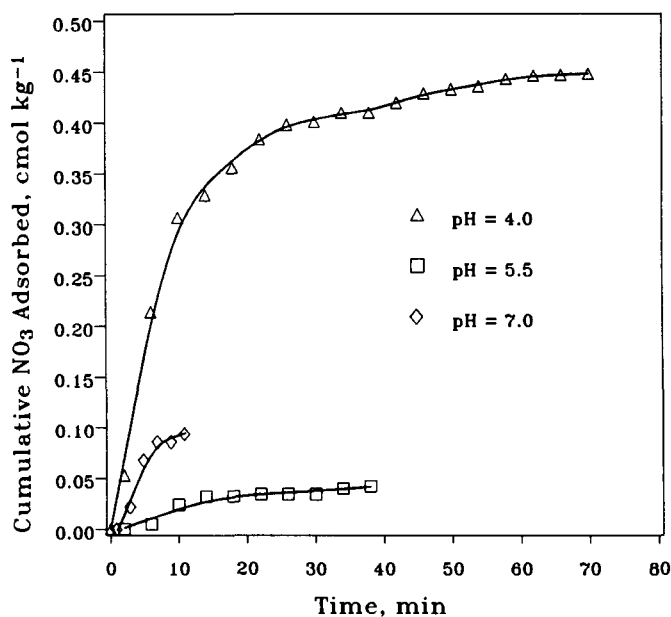


Fig. 4. Effect of pH on the kinetics and magnitude of NO_3 retention on a Dothan Bt1 horizon.

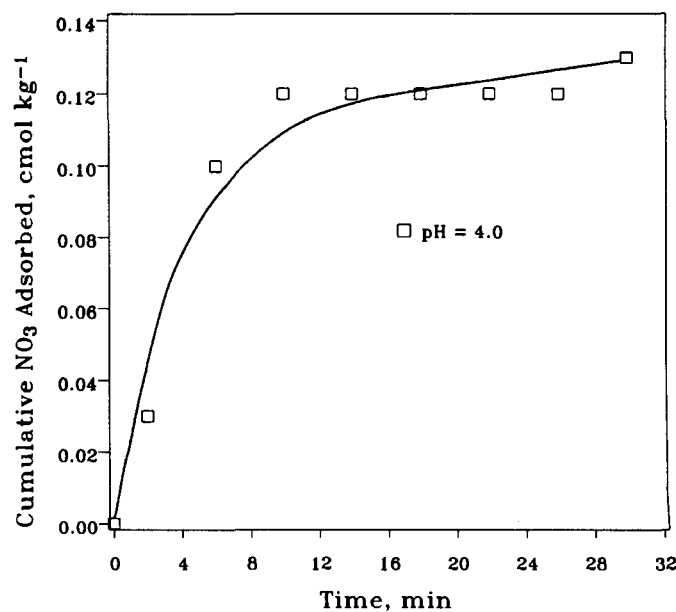


Fig. 5. Kinetics and magnitude of NO_3 retention on a Matapeake Bt1 horizon at pH 4.0.

Table 3. Adsorption rate constants (k_a) for NO_3 adsorption on selected soils as influenced by pH.

pH	CNA†	k_a
	cmol kg ⁻¹	
	Cecil Bt2	
4.0	1.26	0.017‡
5.5	0.23	0.058
7.0	0.27	0.056
	Dothan Btv1	
4.0	0.45	0.033
5.5	0.04	0.034
7.0	0.09	0.182
	Matapeake Bt1	
4.0	0.13	0.035
5.5	0.38	—
7.0	0.54	—

† CNA = cumulative NO_3 adsorbed

‡ The k_a values as a function of pH for the three soil horizons were determined at 45 mg L⁻¹ NO_3 .

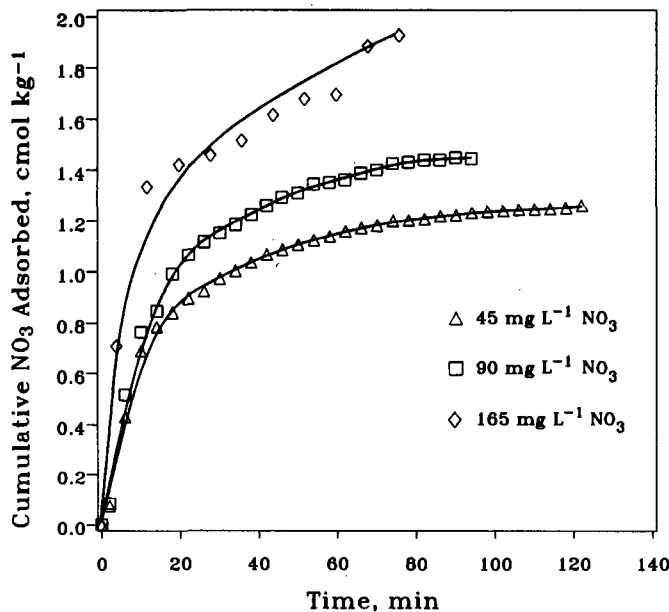


Fig. 6. Effect of initial adsorptive solution concentration on NO_3 adsorption on a Cecil Bt2 horizon at pH 4.0.

Bt2, Dothan Btv1 and Matapeake Bt1 horizons is shown in Table 3 along with the k_a values for each reaction. No kinetic data were obtainable at pH 5.5 and 7.0 for the Matapeake Bt1 due to the clogging of the stirred-flow reaction chamber, which prevented maintenance of a constant adsorptive solution flow velocity. For all three soil horizons, NO_3 adsorption at pH 4.0 was considerably greater than at pH 5.5 and 7.0 with little difference between the latter two pH levels. The observation of greater NO_3 adsorption at the lowest pH level is indicative of greater positive charge on the soils resulting from protonation of amphoteric functional groups on soil constituents, most notably Al and Fe oxides and the edges of kaolinite. Although not shown, even on the extremely sandy Evesboro B horizon (Table 1) at pH 4.0, 0.043 cmol kg⁻¹ NO_3 was retained, proof that NO_3 can be adsorbed to some extent on the coarsest Middle Atlantic soils.

Since no decrease in NO_3 adsorption was seen with

Table 4. Adsorption rate constants (k_a) for NO_3 adsorption on the Cecil Bt2 horizon as influenced by NO_3 adsorptive concentration.

NO_3 adsorptive concentration	CNA	k_a
	cmol kg ⁻¹	
mg L ⁻¹		min ⁻¹
45	1.26	0.017‡
90	1.51	0.015
165	1.93	0.016

† The k_a values as a function of NO_3 adsorptive concentration were determined at pH 4.0.

an increase in pH from 5.5 to 7.0 for any of the soils, it appears that a permanent positive charge component may be present as proposed by Uehara and Gillman (1980b). Unexpectedly, NO_3 adsorption was slightly greater at pH 7.0 than at pH 5.5. The slight increase in NO_3 adsorption at pH 7.0 vs. 5.5 could be due to the use of more-concentrated KOH solutions to adjust the soils to pH 7.0. This could cause mineral decomposition resulting in an increase in surface area with more sites for anion retention. It is also possible that the repeated washing with KOH removed a greater amount of specifically adsorbed anions such as phosphate from the variable charge components of the soil, resulting in an increase in ZPC. At any pH < ZPC, if the ZPC increases, AEC will also increase and NO_3 retention would therefore be greater. Furthermore, decomposition of Al- and Fe-containing minerals could result in dissolved Al and Fe, which would act as potential determining ions. This would again result in an increase in ZPC (Parker et al., 1979). Due to the strong buffering capabilities of the soils chosen, adjustment to pH beyond 7.0 was not possible without the use of extremely alkaline solutions which might drastically alter the chemical and physical properties of the soil samples. Consequently, further evidence for the existence of positive charge at pH > 7.0 was not obtainable.

The effect of adsorptive solution concentration on NO_3 retention on the Cecil Bt2 horizon at pH 4.0 is shown in Fig. 6. Cumulative NO_3 adsorbed ranged from 1.26 to 1.93 cmol kg⁻¹ with the 45 and 165 mg L⁻¹ NO_3 adsorptive solutions, respectively (Table 4). Increased NO_3 in solution clearly increases the effectiveness of NO_3 to compete for available positively charged sites. This substantiates the evidence of Meisinger et al. (1982, 1983) of increased NO_3 remaining in the root zone in spring following greater amounts of NO_3 applied as fertilizer for previous seasons' crops. Greater applications of NO_3 fertilizer would result in higher concentrations of NO_3 in the soil solution with a possible concomitant increase in retention of NO_3 .

Nitrate adsorption on all soils and at all levels of NO_3 concentration and pH conformed well to first-order kinetics based on r^2 and SE values. Furthermore, even as concentration was changed, the magnitude of the k_a values was relatively constant (Table 4) which further indicates that a first-order equation describes the data well (Sparks, 1989).

The k_a values generally increased with pH, indicating a higher rate of NO_3 adsorption. This would be expected, since fewer sites are available for NO_3 adsorption at the higher pH and CNA is lower.

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