

ASPECTS OF NITROGEN KINETICS IN MID-ATLANTIC SOILS

By

**Theodore H. Carski**

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By

Theodore H. Carski

Approved: \_\_\_\_\_

Donald L. Sparks, Ph.D.

Professor in charge of dissertation on behalf of the Advisory  
Committee

Approved: \_\_\_\_\_

A. L. Morehart, Ph.D.

Chairman of the Department of Plant Science

Approved: \_\_\_\_\_

R. B. Murray, Ph.D.

Associate Provost for Graduate Studies

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## ABSTRACT

The use of miscible displacement techniques to study kinetics of ion exchange on clay minerals and soils is increasing. A device that ensures constant dilution volumes, regardless of adsorbent, was developed to differentiate the adsorption and desorption processes from the dilution process. This device, the stirred-flow reaction chamber, was employed to kinetically study nitrate retention and differentiation of soil N fractions.

Anion adsorption-desorption kinetics for systems including Cl, NO<sub>3</sub>, and SO<sub>4</sub> were studied using soils of the Mid-Atlantic region. Nitrate-Cl exchange was nearly 100% reversible, stoichiometric, and very rapid, indicating simple electrostatic exchange. Total amounts of NO<sub>3</sub> or Cl adsorbed accounted for only 11% of the anion exchange capacity (AEC) when soils were pre-saturated at very low opposing anion concentrations (0.7 mM (-) charge). Total NO<sub>3</sub> or Cl adsorption accounted for 90% of the AEC when the pre-saturating concentration equalled 0.2 M (-) charge. This may indicate the need for differentiation of *total* and *effective* AEC.

The chemically induced release of NH<sub>4</sub> from four Delaware soils was monitored over time using the stirred-flow system. The extractants used



were 0.02 M  $\text{KMnO}_4$  - 0.5 M  $\text{H}_2\text{SO}_4$  at 297 K, and 0.01 M  $\text{CaCl}_2$  at 368 K. The kinetic approach presented does allow direct differentiation of two  $\text{NH}_4$  releasing reactions. The reactions were considered to represent the release of  $\text{NH}_4$  from an inorganic and an organic source. Using this approach, estimates of these pools were made and compared with estimates based on traditional batch techniques. Neither extractant gives direct evidence for the existence of a chemically active pool, however, there is indirect evidence for such a pool.

## INTRODUCTION

The use of nitrogen (N) fertilizers in crop production has changed dramatically since the 1940's. Not only has the total use increased by a factor of twenty, but its use is becoming increasingly concentrated in corn and wheat production (USDA, 1977). Before commercial N fertilizer became the dominant N source for crop production, N requirements were primarily met by inputs from traditional sources such as soil N, manure N, and  $N_2$  fixation. The increased use of N fertilizer has been accompanied by increased research into efficient fertilizer N use.

Research efforts concerned with efficient N use have waxed and waned over the past 30 years, often being influenced by projected N fertilizer prices. Research seeking to maximize N efficiency was given less emphasis during periods of low-cost N fertilizer (Keeney, 1982; Olsen and Kurtz, 1982; Stanford, 1982). In recent years however, as energy and therefore N prices climbed, interest in improving N use efficiency has redeveloped. Further impetus to increase N fertilizer efficiency has resulted from environmental concerns, especially, minimizing surface and ground water pollution (Keeney, 1982; Stanford, 1982). Nitrate leaching, and its subsequent entrance into

groundwater supplies, is of particular importance in Delaware (Ritter and Chirnside, 1982).

Maximizing N efficiency usually requires an evaluation of soil N availability so that a sufficient amount of fertilizer N can be added to supplement that supplied by the soil. Thus evaluation of the soil N supply should be a major component in any fertilizer management scheme aimed at improving N use efficiency. Nitrogen efficiency research has used many approaches, including yield response studies, N budget studies, and studies attempting to index soil nitrogen availability (Legg and Meisinger, 1982; Olsen and Kurtz, 1982; Stanford, 1982). These approaches have been complicated by the fact that soil N includes many chemical species co-existing in dynamic equilibrium (Harris, 1982).

The subject of soil N is extremely diverse, it includes the distribution and transformation of organic and inorganic N forms as well as their atmospheric and biospheric interrelations (Stevenson, 1982). This complex collection of reaction pathways is often depicted as the N cycle (Fig. 1). Soil N can be broadly classified into four groups; i) available inorganic N, including exchangeable  $\text{NH}_4$ , and soluble  $\text{NO}_2$  and  $\text{NO}_3$ , ii) fixed or nonexchangeable  $\text{NH}_4$ , iii) easily mineralizable N, and iv) stable organic N associated with the organic matter pool. These classes are useful as an aid in understanding the broad spectrum of soil N, but are difficult to quantify in terms of plant availability (Keeney, 1982; Stanford, 1982).



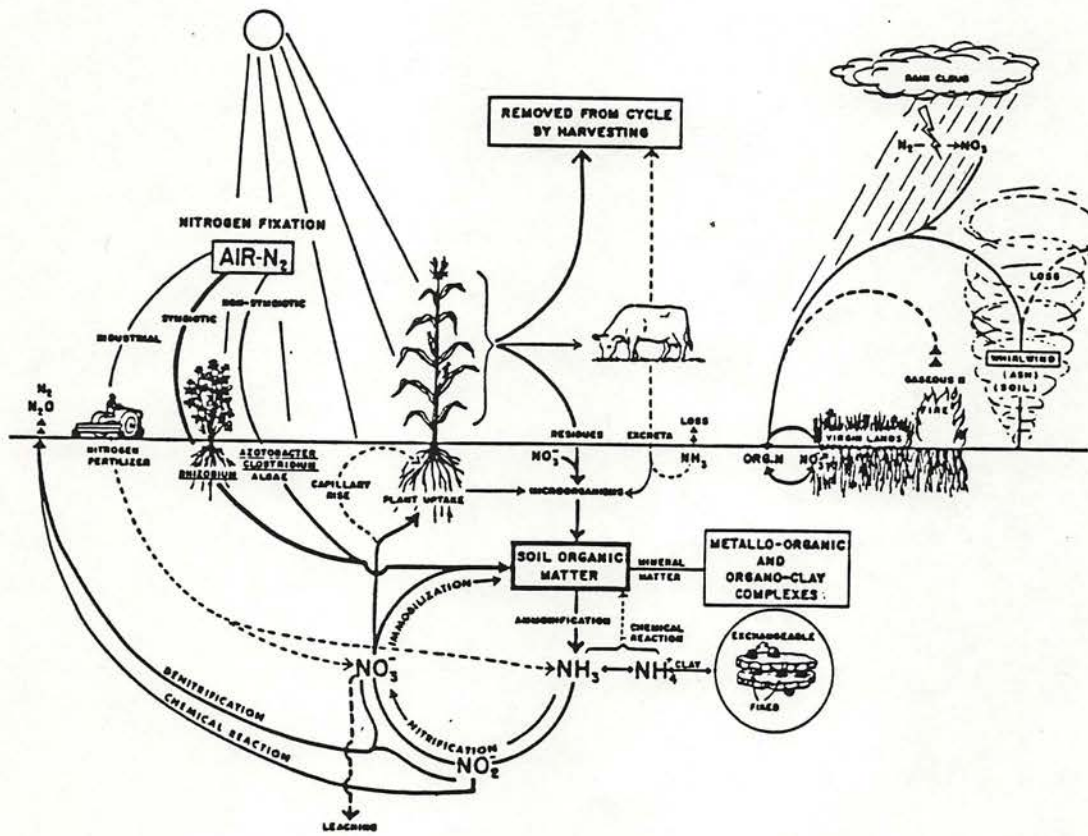


Figure 1: The nitrogen cycle in soil.



Inorganic N is the exchangeable  $\text{NH}_4$  and the soluble  $\text{NO}_2$  and  $\text{NO}_3$  present in the soil at a given point in time. It is usually estimated by extraction with a salt solution, e.g., 2 M KCl, followed by the analytical determination of the inorganic N species in the extract (Bremner, 1965; Keeney and Nelson, 1982). This fraction is readily available to plants, and is usually considered to be the equivalent of N fertilizer. The amount found in the soil can vary due to fertilizer, management, and environmental factors. Excess inorganic N may be carried forward to the next crop depending on the climatic conditions between crops, particularly the amount of rainfall (Keeney, 1982; Stanford, 1982).

The second group, nonexchangeable  $\text{NH}_4$ , is  $\text{NH}_4$  which is fixed within the interlayers of specific 2:1 silicate clays such as vermiculite and *illite* (Nommik, 1965; Young and Aldag, 1982; Nommik and Vahtras, 1982). Once entrapped within the interlayer it is only slowly released to field crops (Axley and Legg, 1960; Keeney and Bremner, 1964; Keeney and Bremner, 1966). Nonexchangeable N can therefore usually be disregarded as a significant N source for annual crops.

The third group, easily mineralized N, is conceptually viewed as N held within an easily decomposed organic fraction. Jenkinson (1968) followed the movement of radioactively labeled carbon during decomposition, and found that differentiation of a highly labeled fraction was possible. He refers to this fraction as the biomass. Stanford defined a potentially mineralizable

fraction,  $N_o$ , as the amount of N mineralized by aerobic incubation at 308 K and field capacity water content according to first-order kinetics (Stanford and Smith, 1972; Stanford et al., 1974). Quantification of the easily mineralizable fraction has been the goal of both microbial incubation and chemical extraction techniques, however neither approach has been very successful since the amount of N actually mineralized in the field is dependent on microbial activity and environmental conditions.

The final class of soil N is organic N which is more resistant to decomposition. This is the largest fraction, usually accounting for about 95% of total soil N (Keeney, 1982; Stevenson, 1982). The size and composition of this pool is dependent upon environmental and management factors (Chichester, 1969; Campbell and Souster, 1982). Although N is only slowly mineralized from this pool, it has often been used as an index of a soil's N status.

A voluminous amount of research has been conducted on various aspects of soil nitrogen. However, a meager amount has appeared on the chemistry and kinetics of N in soil systems. To fully understand the fate of applied N in soils, one must understand the chemistry and kinetics involved. The objective of this dissertation is to kinetically describe  $\text{NO}_3$  retention and N mineralization in Mid-Atlantic Coastal Plain and Piedmont soils. The research will be divided into three parts; i) kinetic methodology development, ii) application of kinetics to  $\text{NO}_3$  retention, and iii) application of kinetics to

N mineralization.



# CHAPTER 1

## METHODOLOGY DEVELOPMENT

### 1.1 Literature Review

The study of ion exchange has seen the development and use of several methodologies. H. S. Thompson(1850) and J. T. Way(1850, 1852) conducted cation exchange experiments using columns of soil through which adsorbate solutions were leached. As the adsorbate solution passed through the soil it miscibly displaced the existing solution allowing the incoming cations to displace the existing cations on the colloid. The displaced cations were removed from the reaction site as the leachate was collected. However crude, the above experiments were likely the first examples of miscible displacement or flow techniques.

Way's work was criticized by the renowned chemist Liebig(Thomas, 1977; Ihde, 1984). Liebig believed that Way's exchange was simply due to cations being held within the capillaries of the soil column, much like water in a sponge. If true, this implied that the length and packing of the column



would affect the exchange capacity of the adsorbent. The realization that columns of the same soil did not always yield similar results lead soil scientists, including Way, to use digestion procedures(Kelley, 1948). These procedures involved placing known quantities of adsorbent and adsorbate in a closed vessel, and after time(digestion), analyzing the liquid, i.e., the beginning of the batch technique.

The above techniques were quite cumbersome, and thus did not enable soil scientists to accurately study the rates of the exchange reactions. When expanded over time these methodologies lead to the general acceptance of Way's conclusion: *exchange reactions were instantaneous*. Not until the work of Kelley(1948) was Way's conclusion about the kinetics of ion exchange seriously questioned. The methodologies that have evolved from these early authors, and are now used most often, are the column or flow technique and the closed vessel or batch technique.

The batch technique has been the most often used method to kinetically study ion exchange on soils and clay minerals(Sparks, 1985). This method still involves placement of adsorbate solution and adsorbent within a closed vessel, and allowing the reaction to take place. Agitation is often used to ensure adequate mixing of reacting species. The reaction is followed kinetically by preparing a vessel or tube for each time increment to be sampled. At the desired time the suspension is centrifuged to obtain a clear supernatant for subsequent analysis. Inherent in the batch methodology are

physical and theoretical problems. The separation of solution from soil by centrifugation usually requires several minutes, therefore rapid reactions can be completely missed (Zasoski and Burau, 1978; Sparks and Rechcigl, 1982; Sparks, 1985). The agitation needed to properly mix the reactants can be too vigorous, leading to surface chemistry changes of the adsorbent, or insufficient, leading to incomplete reactions or reduced rates (Barrow and Shaw, 1979). Therefore, the effect of agitation on adsorbent surface chemistry must be determined for each system studied.

Theoretically, as the exchange process takes place, the adsorbate concentration will decrease and the concentration of the exchanged species will increase. This means that the reactant and product concentrations are constantly changing until equilibrium conditions are achieved. Since adsorption studies are conducted for known adsorbate concentrations, one must compensate for the constant depletion of adsorbate. This is done by using very high initial concentrations so that a small decrease has little effect, or by using very large solution to soil ratios at low adsorbate concentrations. Either attempt to hold the concentration relatively constant may result in serious deviation from real soil systems. High ionic concentrations are almost never realized in soils, nor are very high solution to soil ratios (Zasoski and Burau, 1978; Sparks, 1985). Additionally, the exchanged species remain in the vicinity of the colloidal surface and continue to compete with the incoming adsorbate, thereby affecting the kinetics of the reaction. For the above reasons, the batch technique is not the preferred technique to study the



kinetics of ionic reactions on clay minerals and soils(Morgan and Stumm, 1964; Barrow and Shaw, 1979; Zasoski and Burau, 1978; Schweich et al., 1983; van Riemsdijk, 1984; Sparks, 1985).

Column flow techniques, as first used by Thompson(1850), were constructed to represent movement of solutions through field soils. However, it is now generally accepted that solution movement in soils is not well represented by columns since the soil in the column is often pretreated, i.e., dried, ground, and sieved(Davidson et al., 1983; Schweich et al., 1983). The soil pretreatment, as well as the packing technique must be rigorously standardized so that meaningful comparisons and conclusions can be made from column studies(Nielsen and Biggar, 1961; Nielsen and Biggar, 1962; Biggar and Nielsen, 1963; Schweich et al., 1983; van Riemsdijk, 1984).

Assuming a proper packing technique is used, the column flow techniques offer several advantages over batch techniques. These include i) use of narrow soil to solution ratios with adsorbate concentrations that approach field conditions, ii) measurements at initial time steps of the reaction are possible, iii) displaced species are removed from the vicinity of the reaction site, and iv) the concentration of the adsorbate does not change as the reaction proceeds.(Zasoski and Burau, 1978; Sparks and Rechcigl, 1982). Sparks et al.(1980) introduced a short column technique which eliminated the packing problems inherent in the previous flow techniques. This miscible displacement technique involves the introduction of an adsorbate solution of

known concentration onto a thin wet layer of soil. The adsorption reaction is then followed by monitoring the increasing concentration of the leachate with time. At an apparent equilibrium, the effluent concentration equals that of the initial adsorbate solution. The desorption reaction is studied in a similar way, the reaction being followed by monitoring the decreasing concentration of the previously adsorbed ion. In either case, the reaction is followed by determining the ionic concentration in solution. This means that any process which affects a change in concentration will be interpreted as adsorption or desorption.

For the miscible displacement technique, the dilution of incoming adsorbate solution by the liquid used to load the adsorbent onto the filter, or the washing out of leftover adsorbate solution during desorption should result in concentration changes not due to adsorption or desorption. These concentration changes are potential sources of error. The effect of dilution may be particularly significant when studying micronutrient and anion exchange systems which are known to adsorb very small quantities of ions. In these cases the dilution effect or washing out effect alone may account for the total amounts *adsorbed* or *desorbed*. Regardless of the adsorbent used, some solution will be held back or entrained on top of the filter. This entrained solution cannot be completely removed by suction, and the total amount will be dependent on the water-holding capacity of the adsorbent. The dependence of the amount of entrained fluid on the nature of adsorbent means that the magnitude of the dilution effect will be different for each



adsorbent. The objectives of this portion of the dissertation were to determine the magnitude of the dilution effect and to develop a method to account for it.

## 1.2 Materials and Methods

Initially, the miscible displacement technique (Sparks et al., 1980) was used to assess the magnitude of error caused by the dilution or washing out of adsorbate solution. Using no adsorbent and acid-washed sand, gravimetric determinations of entrained fluid were conducted. Then determinations of boron (B) adsorption and desorption were carried out.

A new device was constructed which allows quantification of the dilution effect (Fig. 1.1). The basic components for the construction of this device include the barrel and plunger from a 30 mL B-D syringe, and a modified 25 mm Nuclepore Swin Lok Filter Holder. The filter holder is modified and glued to the top of the syringe barrel, and the base of the barrel is threaded to provide plunger height adjustment. The device enables one to add and to maintain a known quantity of fluid to a known amount of adsorbent regardless of the adsorbent used. The new device replaces the miscible displacement filter apparatus; the added fluid represents the entrained fluid on the miscible displacement filter. Operation of this apparatus is simple, a magnetic stirring bar is placed in the chamber above the plunger, a known amount of adsorbent is loaded into the reaction

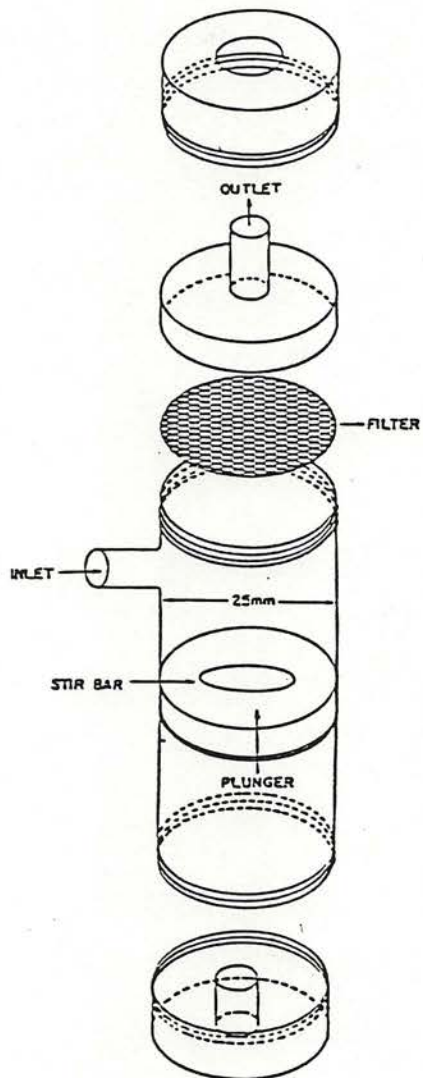


Figure 1-1: Schematic diagram of the stirred-flow reaction chamber.

chamber, a 0.2 $\mu$ m Gelman Metrical Membrane Filter and the top are attached, and a known volume of *entrained* fluid is added using a hypodermic syringe. The plunger is then used to displace the excess air from within the reaction chamber, thus enabling a known volume to be diluted or washed out. This volume is maintained throughout the adsorption and desorption reactions. A peristaltic pump is used to maintain a flow rate of one mL min<sup>-1</sup> and an LKG Ultrorac II 2070 fraction collector is used to monitor the reaction at two min intervals. A magnetic stirrer is used to ensure adequate mixing in the reaction chamber; stirring speed is kept to a minimum, about 100 rpm, to minimize abrasion of the adsorbent (Wu and Gschwend, 1986).

Standard dilution and wash-out curves were determined for the desired volume of entrained solution. These standard curves were identical and were used to quantify the dilution effect. Since this volume is then used for all adsorbents, the effect of dilution can be subtracted from the dilution-plus-adsorption curve or the dilution-plus-desorption curve for all adsorbents. The standard dilution curves were run in triplicate using no adsorbent and acid-washed sand as an inert adsorbent. Adsorption-desorption studies for B using the Ap horizon of a Chester loam soil (fine-loamy, mixed, mesic Typic Hapludult) and K-Ca exchange on a Georgia kaolinite were carried out.

Boron studies were conducted using a 2  $\mu$ g B mL<sup>-1</sup> solution and 1 gram of soil. Boron was determined using a modified azomethine-H method



(Parker and Gardner,1981). Potassium exchange studies were conducted using a  $50 \mu\text{g K ml}^{-1}$  solution and 1 gram of well crystalized Washington County Georgia kaolinite obtained from the University of Missouri Source Clays Depository. Potassium in solution was determined using atomic absorption spectrophotometry.

### 1.3 Results and Discussion

The results of the initial work using the earlier miscible displacement technique(Sparks et al., 1980) with no adsorbent(Fig. 1.2), and with acid-washed(Fig. 1.3) sand were similar. For these systems, where no B adsorption or desorption would be expected, the miscible displacement technique predicts both to occur. However, the total amounts can be predicted quite well using the gravimetrically determined value for entrained fluid multiplied by the concentration of the initial B solution. Although such a calculation allows the total error to be determined, it does not provide a concentration distribution with time. Moreover, since the amounts of entrained fluid differed for the same adsorbent, the possibility of developing a standard curve to describe the error was deemed unlikely.

The standard curves developed for the new technique using no adsorbent(Fig. 1.4) and acid-washed sand were essentially the same. Each was conducted in triplicate; the CV values of the combined triplicate runs, at each time step, were less than 5% indicating excellent reproducibility. This

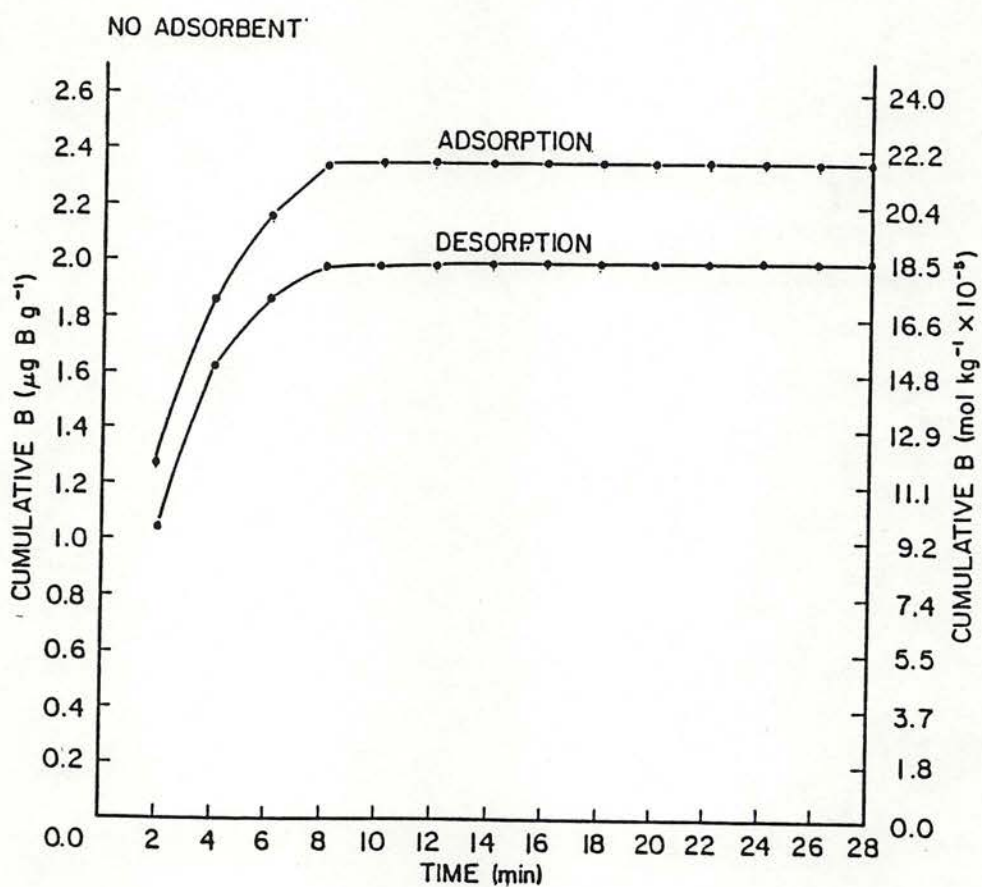


Figure 1-2: Apparent adsorption and desorption of B, determined using the original miscible displacement technique with no adsorbent.

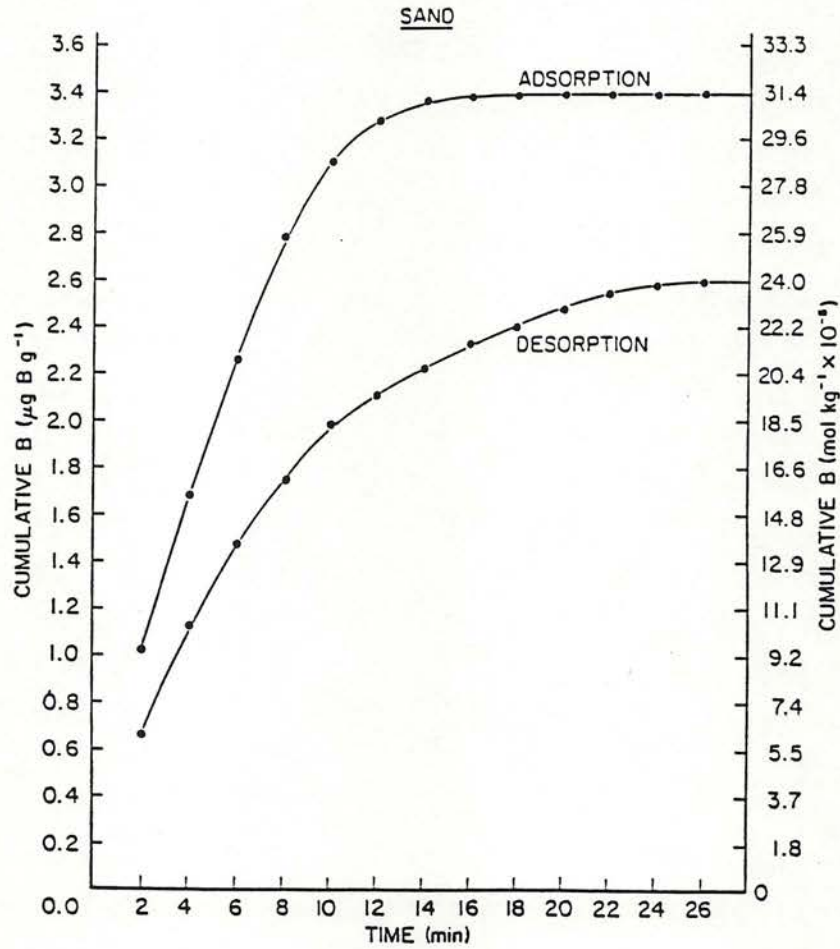


Figure 1-3: Apparent adsorption and desorption of B, determined using the original miscible displacement technique with acid-washed sand as the adsorbent.



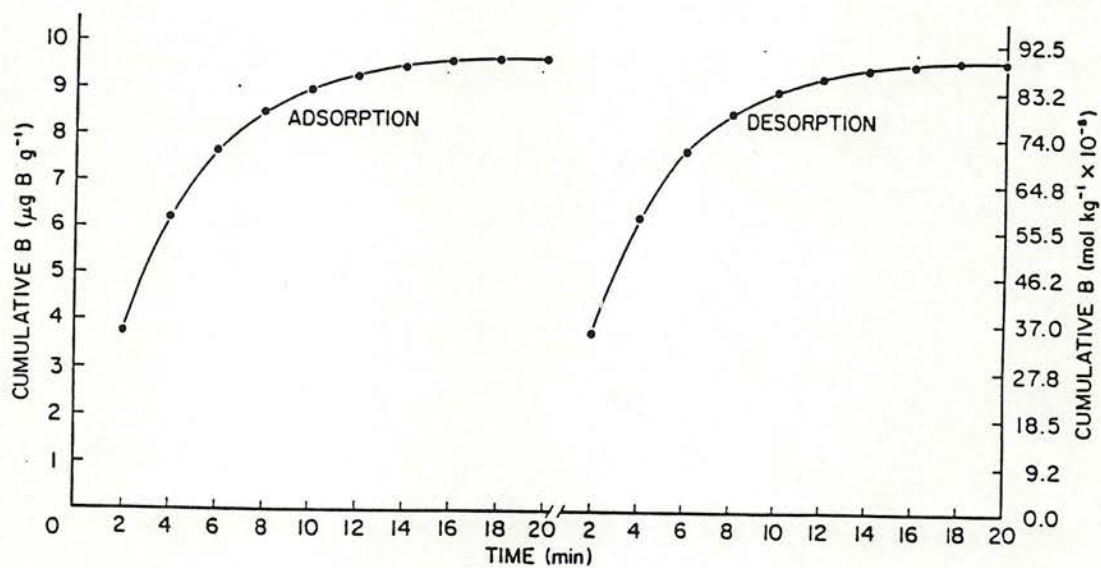


Figure 1-4: Standard B dilution curves for the stirred-flow chamber with no adsorbent.

means that the presence of an inert material (sand) did not affect the dilution process by accelerating or inhibiting the mixing process. Therefore, one can conclude that the mixing process will not be affected by the presence of an adsorbent. Standard curves for K were also run in triplicate with similar CV values (<5%). When the K curves were scaled down to the B curves, no significant difference was seen. These findings indicate the reproducibility of the standard curve is sufficient to attempt to differentiate adsorption and desorption processes from dilution processes.

The adsorption and desorption of B on Chester soil was used to represent a low capacity adsorption system. This system had been studied previously using the miscible displacement technique (Sparks et al., 1980) and B adsorption and desorption had been predicted. However, we found by determining the amount of entrained fluid, that the predicted amount of adsorbed and desorbed B was entirely due to the dilution or wash-out error. This means that no B was adsorbed or desorbed. When this system was studied using the new technique the adsorption-desorption curves were no different from the standard curves, therefore no B adsorption or desorption would be predicted (Fig. 1.5). These results for Chester soil are not surprising since the pH of the soil was equal to 4.8.

When the new device was used to study the adsorption of K on Ca-saturated kaolinite a significant difference existed between adsorption and dilution (Fig. 1.6). The dilution effect greatly increased the prediction of total

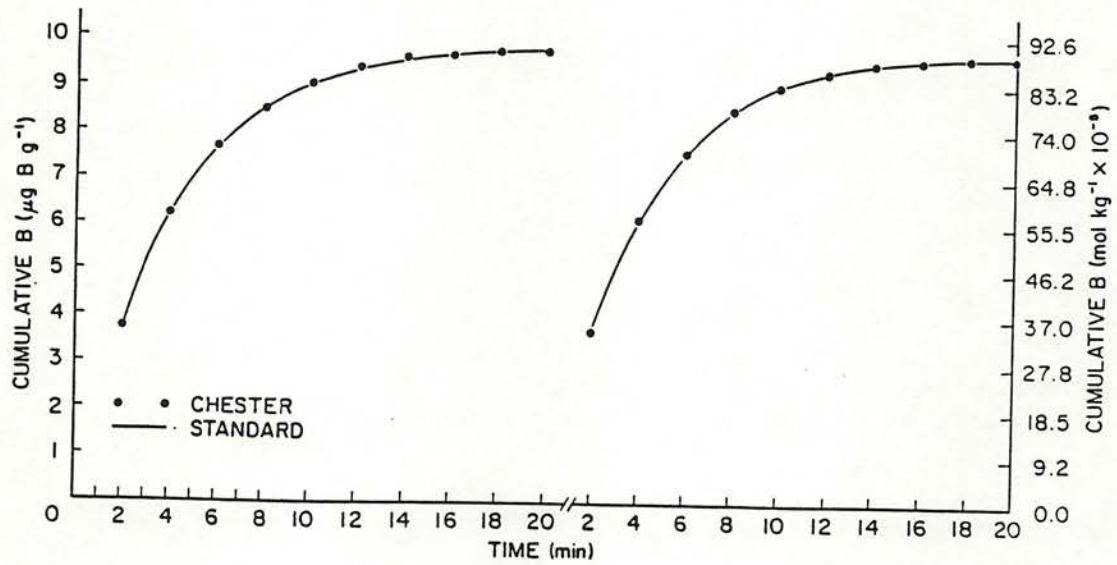


Figure 1-5: Adsorption-desorption of B on Chester soil compared with the standard dilution curve.



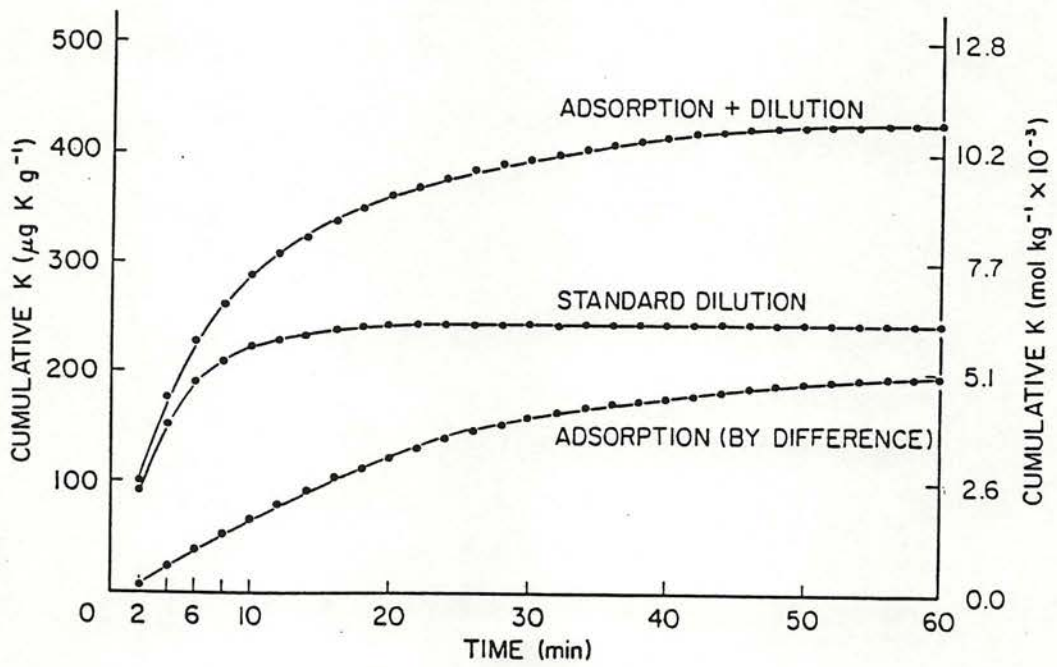


Figure 1-6: Adsorption of K on Ca-saturated kaolinite using the stirred-flow reaction chamber.

K adsorbed. When the standard curve is subtracted from the dilution-plus-adsorption curve the amount of K removed from solution by adsorption is determined. The total K adsorbed was about  $40 \mu\text{g K g}^{-1}$  less than that predicted by the original miscible displacement technique (Sparks and Jardine, 1984). Although gravimetric determinations of entrained fluid were not originally taken, recent work would indicate that between 0.8 and 0.9 mL of entrained fluid would be expected. This would lead to an overestimation of total K adsorbed equal to  $40\text{-}45 \mu\text{g K mL}^{-1}$ . Similarly when desorption of K by Ca was followed (Fig. 1.7), the amounts desorbed were overestimated since the entrained solution at the end of the adsorption run was equal in concentration to the initial adsorbate solution ( $50 \mu\text{g K mL}^{-1}$ ). The washing out of this solution results in the overestimation of adsorbed K. When the standard curve for desorption is subtracted from the combined curve, the amount of desorbed K is determined. If the adsorption and desorption processes are compared several conclusions can be made (Fig. 1.8). The exchange reaction is reversible although the desorption of K by Ca is faster than the reverse. The difference in reaction rates is also seen when these reactions are plotted according to first-order kinetics (Fig. 1.9). The preference for Ca on kaolinite is confirmed by the positive  $\Delta G^\circ$  values (Table 1) calculated using a kinetics approach (Sparks and Jardine, 1981). The presence of entrained fluid increases both  $k_a'$  and  $k_d'$  but does not greatly affect the thermodynamic conclusions i.e.,  $k_a'/k_d'$  does not change markedly. When compared to the original technique, the cumulative amounts of adsorbed and desorbed K are different, however, both methods predict that i) the reactions

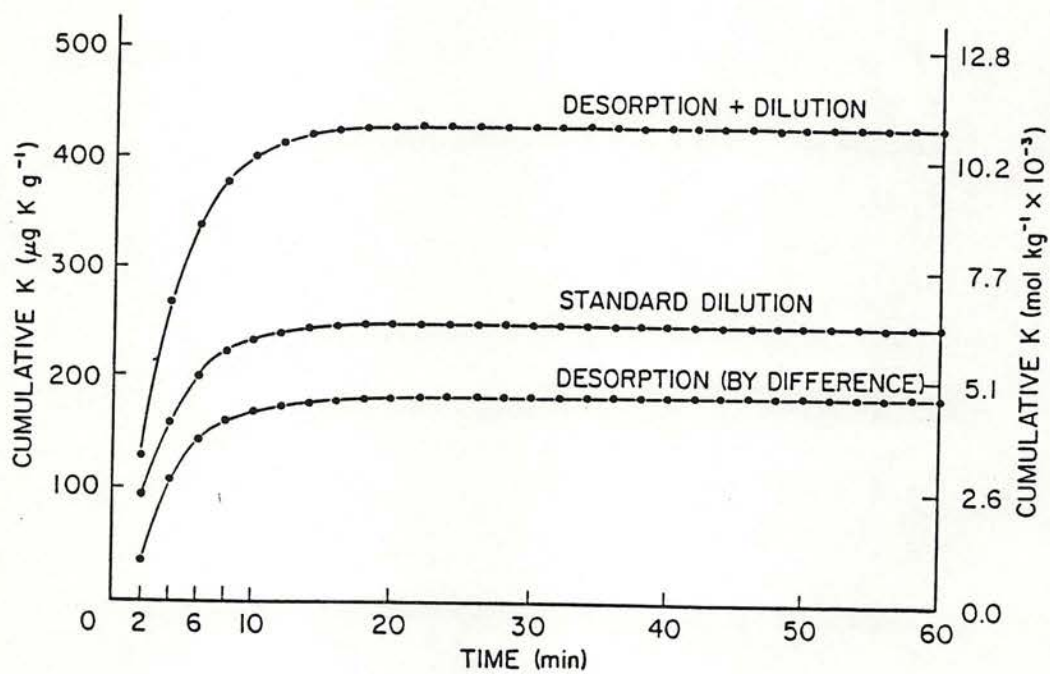


Figure 1-7: Desorption of K from kaolinite using the stirred-flow system.



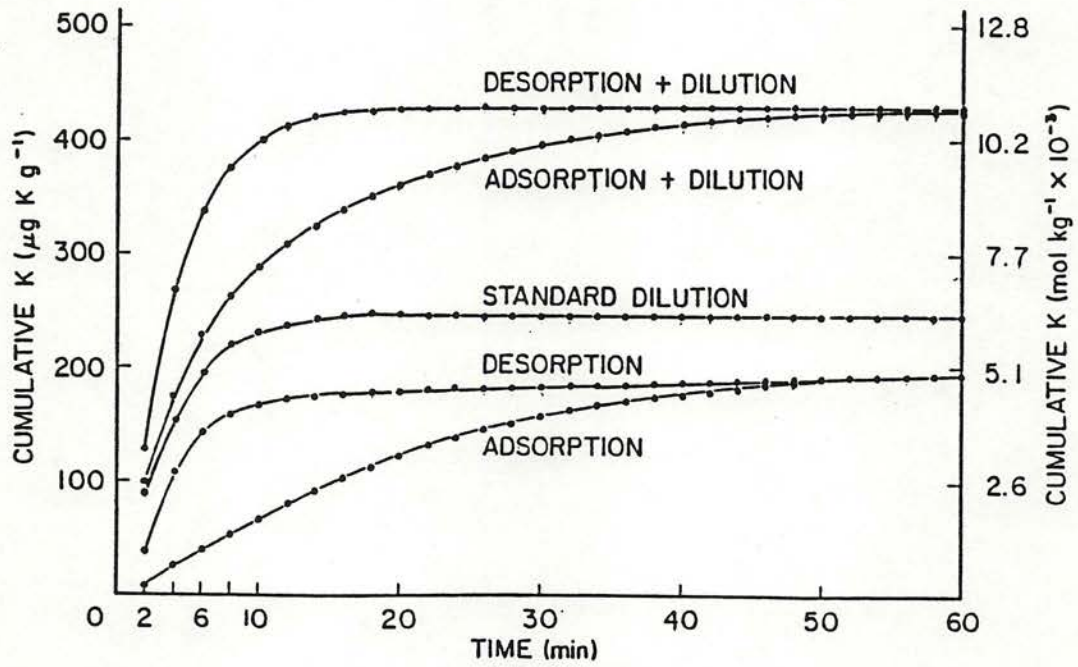


Figure 1-8: Adsorption and desorption of K on kaolinite as a function of time.

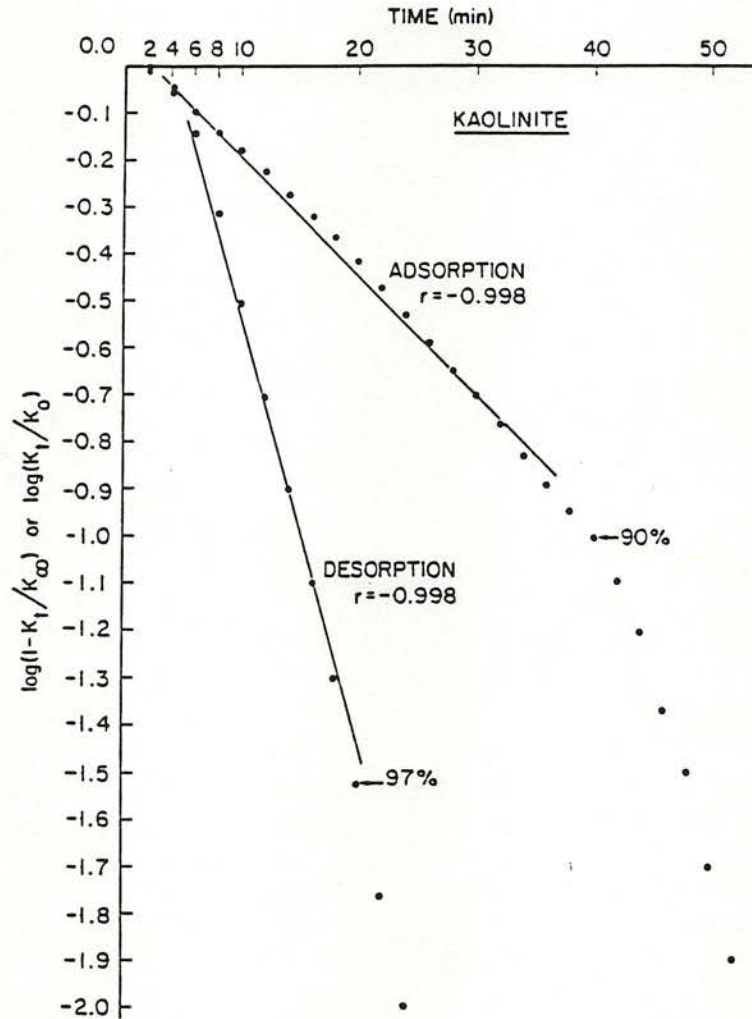


Figure 1-9: Adsorption-desorption of K on kaolinite plotted according to first-order kinetics.

**Table 1-1:** Apparent adsorption and desorption rate coefficients, and resultant  $\Delta G^\circ$  values, for K-Ca exchange on kaolinite.

	$k_a$	$k_d$	$\Delta G^\circ$
	(h <sup>-1</sup> )	(kJ mol <sup>-1</sup> )	
With dilution effect	2.04	8.34	3.4
Minus dilution effect	1.56	5.88	3.3



are reversible, ii) the reactions conform to first-order kinetics, and iii) Ca is preferred over K. This means that for this system, where only one type of reaction site is expected, the presence of entrained fluid affected the adsorption and desorption processes equally. Further work is needed to determine the effect of entrained fluid on systems having more than one type of reaction site. In such a system, dilution may affect only the initial part of the reaction, and therefore, only the kinetics determined for the first reaction site.

A final comment should be made concerning the stirring of the soil solution. Stirring may eliminate or greatly reduce the film diffusion component of the reaction(Boyd et al., 1947). However, a kinetic comparison of the new method to the original method is confounded by the fact that both diffusion and dilution processes are present in the original technique. A recent study designed to compare kinetic methodologies with the classic equilibrium approach of Argersinger(Argersinger et al., 1950) included a traditional batch technique, the miscible displacement technique, and a vigorously-mixed batch technique(Ogwada and Sparks, 1986). Ogwada and Sparks clearly show that as agitation increases, the effect of diffusion is minimized, and the kinetically derived  $\Delta G^{\circ}$  values approach those of the equilibrium approach. Kinetically derived values based on the stirred-flow system compare well to the vigorously-mixed batch technique and the equilibrium approach(Table 1.2). These data agree with the purely theoretical work of Skopp(1986) which concludes that a dilute, dispersed suspension

**Table 1-2:** Comparison of equilibrium and kinetic approaches for determining  $\Delta G^\circ$  of K-Ca exchange on soil.

System	$\Delta G^\circ$ kJ mol <sup>-1</sup>
Kinetic Approach	
Miscible Displacement	-0.80
Traditional batch	-2.39
Vigorously mixed batch	-3.82
Stirred-flow	-4.51
Equilibrium Approach	-4.74

represents an ideal kinetic system. Thus it appears that a kinetic approach can be successfully employed to obtain thermodynamic data if diffusion is minimized.

#### 1.4 Conclusions

It has been demonstrated that the fluid entrained on the filter of the miscible displacement apparatus is a significant source of error, especially for low adsorption capacity systems. The method proposed appears to account for the dilution or washing out effect. Regardless of adsorbent used, the amount of fluid *entrained* is held constant, meaning that its effect on concentration should be the same for every adsorbent. The proposed stirred-flow technique appears to refine the original miscible displacement technique in that a known source of error has been eliminated, yet the advantages of a flow technique are retained, and the kinetically based conclusions remain essentially unchanged. Additionally, the stirred-flow system minimizes the diffusional component of the reaction allowing one to obtain thermodynamic data using a kinetic approach.



## CHAPTER 2

### CHARGE PROPERTIES AND NITRATE RETENTION

#### 2.1 Literature Review

The retention of  $\text{NO}_3$  in the humid, eastern USA is usually considered to be an insignificant component of nitrogen(N) management(Bremner, 1965; Scarsbrook, 1965; Stanford, 1982). Recently however, a number of researchers, using crops such as barley(*Hordeum sativum L.*), wheat(*Triticum sativum L.*), and corn(*Zea mays L.*) have found residual  $\text{NO}_3$ , i.e., soil  $\text{NO}_3$  levels in early spring, to be highly correlated with yield(Meisinger et al., 1982; Magdoff et al., 1983; Meisinger et al., 1983; Fox and Piekielek, 1984; Magdoff et al., 1984). These data indicate the importance of early spring  $\text{NO}_3$  levels to N management. *Residual*  $\text{NO}_3$  implies that the  $\text{NO}_3$  found has been carried through the winter from previous N fertilizer treatments, however, the contribution from recently mineralized N must also be considered. Meisinger and co-workers(1982 and 1983) report that the amount of residual  $\text{NO}_3$  significantly increased as previous N fertilizer treatments to corn increased, despite the fact that corn yield did not,

indicating the potential for residual  $\text{NO}_3$  is largely dependent upon previous excess N fertilization. The fate of excess applied N is extremely important since it may affect the quality of groundwater as well as the yield of the following crop (Robertson et al., 1977a and b; Liebhardt et al., 1979; Ritter and Chirnside, 1982).

The fate of  $\text{NO}_3$  in the soil is also of great concern to those land spreading organic wastes such as poultry manure, sludge, and compost. The nitrogen contained in these materials is largely organic and undergoes mineralization and nitrification. The  $\text{NO}_3$  thus produced is a potential fertilizer, as well as pollutant, and must be managed. Management factors should include the capacity of the soil to retain  $\text{NO}_3$ . This enables one to estimate the fertilizer potential, and leaching hazards incurred after land spreading. Although  $\text{NO}_3$  retention appears to be a significant N management factor, one needs to ascertain the mechanism of retention, physical or chemical, before attempting to correctly include it in a management scheme. Knowledge of the mechanism of retention would allow one to better estimate the significance of residual  $\text{NO}_3$  based on soil type, rainfall, or management factors.

Physical retention refers to reduced  $\text{NO}_3$  leaching, often caused by reduced amounts of winter rainfall. If the profile is not thoroughly leached, the nitrate ions, especially those present in soil micropores, may not be completely washed out of the profile during the winter (Starr, 1983). These



ions, measured as residual  $\text{NO}_3$  would then be available to the spring crop. Although physical retention most certainly affects the rate of  $\text{NO}_3$  movement through soils, it is beyond the scope of this dissertation and will only be used to explain  $\text{NO}_3$  retention should this study prove chemical retention to be insignificant.

Chemical retention refers to an interaction between solution ions and colloid surfaces. The types of interaction vary with ionic and colloidal species, but can be generally categorized as inner-sphere and outer-sphere surface complexes (Sposito, 1981; Sposito, 1984). An inner-sphere surface complex, often referred to as specific adsorption, has no solvent molecules between the colloid surface and the adsorbed ion. This interaction tends to be covalent or ionic in nature and therefore quite strong. Outer-sphere complexes, usually electrostatic in nature, have at least one solvent molecule between the colloid surface and the ion, and are relatively weaker.

Nitrate retention has not been studied on Mid-Atlantic soils, however on tropical soils from Chile, Mexico, and Hawaii it was found to be predominantly due to electrostatic attraction (Singh and Kanehiro, 1969; Kinjo and Pratt, 1971a and b; Kinjo et al., 1971; Espinoza et al., 1975). The soils used were oxides of Fe and Al, or kaolinitic, and possessed a significant pH dependent charge. For these type surfaces, an increase in  $\text{H}^+$  activity resulted in an increase in positively charged sites, and a corresponding increase in  $\text{NO}_3$  adsorption. Therefore, a useful first step toward determination of  $\text{NO}_3$



adsorption potential is a characterization of the pH dependent charge.

Charge characterization involves the determination of zero point of charge (ZPC), where ZPC refers to the pH value at which the net surface charge is zero (SSSA, 1979). This information, in conjunction with the soil pH, allows one to predict the net surface charge of the soil. If the soil pH is greater than the ZPC, the soil's surface charge will be negative and predominantly cations will be retained. Conversely, should the soil pH be less than the ZPC, positive charges will be predominant, and the  $\text{NO}_3$  adsorption potential will be significant.

The techniques used to determine the ZPC include electrokinetic, potentiometric, and determination of AEC and CEC at various pH values (Huang, 1981; Parker et al., 1979; Sposito, 1981). Often these methods do not agree, resulting in slightly different definitions for what has been determined (Sposito, 1981; Sposito, 1984). Potentiometric titration of soils bathed in differing electrolyte concentrations are said to determine the point of zero salt effect (PZSE) (Parker et al., 1979). The PZSE equals PZC only when neither electrolyte ion can be specifically adsorbed, e.g., a truly inert electrolyte has been used (Parker et al., 1979; Sposito, 1981; Sposito, 1984). Electrokinetic methods determine the isoelectric point (IEP), which again equals the ZPC only when specific adsorption does not occur (Parker et al., 1979). Measurement of the pH at which CEC equals AEC determines the point of zero net charge (PZNC), however the PZNC is not expected to equal

the PZC unless the net surface charge density of outer-sphere complexes is zero(Sposito, 1981). The relationship of the various zero points is dependent upon the electrolyte, the nature of the surface, and the experimental technique, however if proper assumptions are made and the proper technique employed, the prevailing charge can be characterized over a range of pH values(Parker et al., 1979; Sposito, 1981).

Measurement of the AEC at the existing soil pH provides a direct determination of the capacity of the soil to adsorb anions. The methodology is based on the finding that Cl and  $\text{NO}_3$  form only outer sphere, electrostatic, complexes with soil colloids(Gillman, 1979; Rhoades, 1982). When combined, AEC and charge characterization provide a macroscopic determination of the soil's capacity to retain  $\text{NO}_3$  over a range of pH conditions. However, neither method provides kinetic or mechanistic information.

Accordingly, the stirred-flow kinetic methodology described in Chapter I was employed to kinetically study the adsorption of  $\text{NO}_3$ . This methodology will also allow one to discern the competitive effect of other anions. The objectives of this portion of the dissertation are i) to estimate the prevailing surface charge of the soils over a range of pH values, ii) to determine the AEC and estimate the  $\text{NO}_3$  adsorption potential at ambient soil pH and iii) to study the kinetics of  $\text{NO}_3$  adsorption as affected by competing anions.



## 2.2 Materials and Methods

The soils used represent nine major soil series from the Mid-Atlantic region. These include seven Coastal Plain soils and two Piedmont soils. The Coastal Plain soils include an Evesboro(coated, mesic Typic Quarzipsamment), a Kenansville(loamy, siliceous, thermic Arenic Hapludult), a Leon(sandy, siliceous, thermic Aeric Haplaquod), a Matapeake(fine-silty, mixed, mesic Typic Hapludult), and a Sassafras(fine-loamy, siliceous, thermic Typic Hapludult) sampled from Delaware, a Dothan(fine-loamy, siliceous, thermic Plinthic Paleudult) from Virginia, and Matapeake(fine-silty, mixed, mesic Typic Hapludult) and Mattapex(fine-silty, mixed, mesic Aquic Hapludult) soils sampled from Maryland. The Maryland soils were included since these were used by Meisinger et al.(1982; 1983). The Piedmont soils include a Chester(fine-loamy, mixed, mesic Typic Hapludult) from Delaware, and Cecil(clayey(*kaolinitic*), thermic Typic Hapludult) from Virginia. All soils were collected by horizon, rather than by depth, so that characteristics of each horizon can be differentiated. The soils were selected to represent important agricultural soils, as well as, the extremes in kaolinite(Cecil) and Fe-oxide(Dothan) content.

The physicochemical and mineralogical properties of the horizons from each soil series(Table 2.1), except the Maryland Matapeake and Mattapex, were available, or were determined using previously reported procedures(Evans, 1983).



**Table 2-1:** Chemical, physical, and mineralogical properties of selected soils.

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Soil = Cecil\*

Depth	Horizon	pH	CEC	OM	Sand	Silt	Clay	Fe-ox	Mineralogy <sup>+</sup>
cm			cmol/kg		%				
0-3	A	4.37	8.78	2.10	61.7	23.8	14.4	0.42	K, CV, G
3-20	E	4.56	8.07	0.60	61.7	23.8	14.4	0.33	K, CV, G
20-60	Bt1	4.65	5.72	0.38	33.2	17.0	49.8	2.60	K, CV, G
60-163	Bt2	5.07	3.97	0.27	31.2	23.8	45.0	2.70	K, CV, G
163-196	C	4.82	6.46	0.15	39.8	44.3	15.9	1.40	K, CV, G

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\* Sampled from Virginia Polytechnic Inst. and State Univ. Cecil research pit, data are from VPI.

+ K=kaolinite, CV=chloritized vermiculite, G=gibbsite.

## Soil = Dothan\*

Depth	Horizon	pH	CEC	OM	Sand	Silt	Clay	Fe-ox	Mineralogy <sup>+</sup>
cm			cmol/kg		%				
0-23	A	5.74	4.20	1.28	70.0	20.9	9.0	0.23	VC, K, Q, G
23-38	E	6.25	4.00	0.23	59.5	24.2	16.2	0.26	VC, K, Q, G
38-76	Bt1	4.87	4.80	0.34	44.0	21.8	34.2	1.24	K, VC, G, Q
76-96	Bt2	4.66	7.20	0.23	36.4	10.8	52.8	1.80	K, VC, G, Q
96-152	Btv	4.33	7.80	0.16	42.8	10.9	46.3	3.60	K, VC, G, Q

\* Sampled from Greensville Co., VA, Sparks et al., 1980.

+ VC=chloritized vermiculite, K=kaolinite, Q=quartz, G=gibbsite.

## Soil = Kenansville\*

Depth	Horizon	pH	CEC	OM	Sand	Silt	Clay	Fe-ox	Mineralogy <sup>+</sup>
cm			cmol/kg		%				
0-9	Ap	6.8	6.09	1.30	83.9	14.7	1.4	0.11	K, Q, CV, C
9-23	E	7.0	2.78	0.17	77.9	19.5	2.6	0.20	K, Q, CV=C
23-28	EB	7.2	4.22	0.15	84.5	11.2	4.3	0.29	K, Q, CV, M
28-34	Bt1	7.0	5.74	0.13	81.3	7.3	11.4	0.31	K, Q, CV, M
34-47	Bt2	7.0	6.11	0.04	77.3	12.1	10.6	0.42	K, Q, CV, M
47-56	Bt3	7.0	4.64	0	82.0	13.5	4.5	0.23	K, Q, CV, M
56+	C	7.1	3.58	0	89.5	8.2	2.3	0.13	K, Q, CV, M

\* Sparks et al., 1986. Potassium field studies.

+ K=kaolinite, Q=quartz, CV=chloritized vermiculite, C=chlorite, M=mica.



## Soil = Matapeake\*

Depth	Horizon	pH	CEC	OM	Sand	Silt	Clay	Fe-ox	Mineralogy <sup>+</sup>
cm			cmol/kg		-----%				
0-25	Ap	6.1	7.23	1.70	29.8	58.6	11.8	1.05	K=CV, Q, M
25-53	Bt1	6.3	9.37	0.35	26.2	50.2	23.6	0.85	CV, K=Q, M
53-69	2Bt2	6.2	5.45	0.04	63.9	20.6	15.5	0.60	K, CV, Q, M
69-97	2C1	5.3	4.54	0	74.0	14.2	11.8	0.34	K, Q, CV, M
97-152	2C2	5.3	2.19	0.04	75.7	19.5	4.8	0.15	K, Q, CV, C

\* Sparks et al., 1986. Potassium field studies.

+ K=kaolinite, CV=chloritized vermiculite, Q=quartz, M=mica, C=chlorite.

## Soil = Sassafras\*

Depth	Horizon	pH	CEC	OM	Sand	Silt	Clay	Fe-ox	Mineralogy <sup>+</sup>
cm			cmol/kg		%				
0-20	Ap	6.0	5.17	2.00	65.5	25.3	9.2	0.65	K, Q=CV, G
20-36	EB	5.8	4.74	0.50	57.2	27.8	15.0	0.85	K, Q=CV, G
36-66	Bt	5.0	6.66	0.20	58.8	14.7	26.5	1.45	K, Q, CV, M
66-84	BC	5.0	6.89	<0.1	76.3	7.5	16.2	2.60	K, Q, G, M
84-89	C1	5.2	5.80	<0.1	76.6	7.6	15.8	2.50	K, Q, C=M
89-152	C2	5.0	5.83	<0.1	73.6	13.7	12.7	1.15	K, Q, M, G

\* Sparks et al., 1986. Potassium field studies.

+ K=kaolinite, Q=quartz, CV=chloritized vermiculite, G=gibbsite.

Depth	Horizon	pH	CEC	OM	Sand	Silt	Clay	Fe-ox	Mineralogy <sup>+</sup>
cm			cmol/kg		%				
Soil = Chester <sup>*</sup>									
0-15	Ap	5.0	5.57	3.30	28.0	57.0	15.0	1.36	K, CV, Q, M
40-66	B2t	5.4	3.06	0.40	2.2	64.8	33.0	1.76	K, CV, M, Q
Soil = Evesboro <sup>*</sup>									
0-18	A	4.2	0.35	1.05	94.7	3.0	2.3	0.09	CV, K, Q, G
68-165	B	5.0	0.14	0.18	95.4	3.2	1.4	0.04	K, CV, M, Q
Soil = Leon <sup>*</sup>									
0-13	A1	3.8	0.70	3.10	87.3	9.0	3.7	0.03	Q, CV, K, M
33-48	B2h	4.3	1.07	3.20	88.2	8.9	2.9	0.04	Q, K, CV, M

\* Evans, C. E. 1983. M.S. Thesis, University of Delaware.

+ K=kaolinite, CV=chloritized vermiculite, Q=quartz, M=mica, G=gibbsite.



Briefly, the soil pH was determined in a water slurry(1:1 w/v) using an Orion 901 Ionalyzer and an Orion combination electrode. The cation exchange capacity was determined by compulsive exchange using 1 M  $\text{NH}_4\text{OAc}$  buffered at pH 7, or Mg-Ca exchange. The organic matter content was determined using a modified Walkley-Black procedure. The mineralogy of the  $<2 \mu\text{m}$  clay fraction was determined using X-ray diffraction(XRD). The Fe-oxide content was determined using the Na-citrate-bicarbonate-dithionate method. Particle size distribution was determined by the Bouyoucas hydrometer method.

A potentiometric titration method was used to determine PZSE(Parker et al., 1979). Sodium chloride was used as the indifferent electrolyte to minimize specific adsorption, therefore  $\text{PZSE} = \text{PZC} = \text{PZNC}$ . Soil samples of 4 g each were placed in 39 30 mL plastic vials. The vials were arranged in 3 groups of 13 tubes. Each set was used for equilibration at different molar concentrations, e.g., 0.1 M, 0.01 M, and 0.001 M NaCl. For each set 10 mL of NaCl was added, then increasing amounts of HCl or NaOH were added in 0.5 mL increments, and distilled-deionized water added to give a final volume of 20 mL. Titration curves for the solution minus soil were conducted and used as blanks. The pH value for each tube was determined after 1 h and again after 2 days. The amount of  $\text{H}^+$  or  $\text{OH}^-$  adsorbed by the soil at any given pH value is equal to the amount of HCl or NaOH added minus the amount required to bring the blank to an equal pH. The amount of  $\text{H}^+$  or  $\text{OH}^-$  adsorbed was plotted against the pH for each

electrolyte concentration, and the intersection of the 3 curves determines PZSE.

The AEC was determined using the method of Gillman(1979) as described by Rhoades(1982). The soil was saturated with  $\text{BaCl}_2$  by adding 20 mL 0.01 M  $\text{BaCl}_2$  to 2 g of soil in a preweighed centrifuge tube, and shaking for 2 hours. The sample was centrifuged and the supernatant discarded. The soil was then equilibrated with 0.002 M  $\text{BaCl}_2$  by shaking with 20 mL aliquots, centrifuging, and discarding the supernatant. The amount of entrained 0.002 M  $\text{BaCl}_2$  was determined gravimetrically after the final equilibration. The sample was then equilibrated with 0.005 M  $\text{MgSO}_4$  by adding 10 mL and shaking for 1 hour. Using a 0.0015 M  $\text{MgSO}_4$  solution (ionic strength = 0.006) as a reference to approximate the ionic strength of the soil solution, the electrical conductivity(EC) of the sample was adjusted to equal the reference and equilibrated overnight. The sample was again compared to the reference, with adjustment and equilibration repeated until the sample and reference were approximately equal. The final volume of solution was determined gravimetrically, and after centrifugation, the Mg and Cl concentrations were determined using atomic absorption and an ion specific electrode, respectively. The Mg removed from solution is used to determine the CEC, and the final Cl concentration minus the Cl entrained gives the AEC. Determinations were conducted in duplicate; reproducibility was excellent with CV values averaging < 3%.



The kinetics of  $\text{NO}_3$  adsorption was studied using the stirred-flow reaction chamber described in Chapter 1. A magnetic stirring star was placed in the chamber above the plunger, 1 g of air-dry soil was loaded into the reaction chamber, a  $0.8 \mu\text{m}$  Nuclepore Membrane Filter, with a Millipore AP prefilter, and the top were attached, and a known volume of *entrained* fluid was added using a hypodermic syringe. The plunger was then used to displace the excess air from within the reaction chamber, thus enabling a known volume to be diluted or washed out. This volume was maintained throughout the adsorption and desorption reactions. A peristaltic pump was used to maintain a flow rate of  $1 \text{ mL min}^{-1}$  and a LKG Ultrorac II 2070 fraction collector was used to monitor the reaction at 2 min intervals. Adsorbate solutions of  $\text{NO}_3$ ,  $\text{Cl}$ , and  $\text{SO}_4$  were made to be equal in negative charge concentration, and equivalent to the EPA safe drinking water standard for  $\text{NO}_3\text{-N}$  ( $10 \mu\text{g N mL}^{-1}$ ). Potassium was used as the cation for all solutions. Only the Cecil Bt2 (24-64 cm) horizon was used for the kinetic analysis. All  $\text{Cl}$ ,  $\text{NO}_3$ , and  $\text{SO}_4$  determinations were made using a Waters 430/501 ion chromatography system with an acetonitrile-glycerol-borate mobil phase. Kinetic analyses were not duplicated.



### 2.3 Results and Discussion

The PZSE values for the Cecil, Dothan, and Matapeake soils were low, and were exceeded for all horizons by the native soil pH (Table 2.2). These data indicate little development of positive charge would be expected. The PZSE for the Dothan profile does not agree with the ZPC as determined by electrophoresis in that the PZSE is much lower for all horizons (Elliot and Sparks, 1981). Elliot and Sparks noted a decrease in ZPC when Na was used as the swamping electrolyte, rather than Ca, and attributed the downward shift to specific adsorption of Ca. However, the PZSE was still lower than the ZPC determined with Na. This discrepancy may indicate that both permanent and variable charge components are present, resulting in a PZSE shift away from the electrophoretic ZPC. Uehara and Gillman (1980) confirm this, stating that the PZSE will shift below the ZPC if the permanent charge component is negative. Thus, the PSZE is expected to be lower than the ZPC reported by Elliot and Sparks (1981).

The AEC conveys a meaning quite different from the PZSE. In all soils, except the Leon, Evesboro, and Chester soils, the AEC is significant and increases with depth. (Fig. 2.1a).

The negative values for AEC, often seen for surface horizons, results from procedural anomalies. The AEC is determined as the difference between  $Cl_{(\text{entrained} + \text{adsorbed})}$  and  $Cl_{\text{entrained}}$ , however, measurement of  $Cl_{(\text{entrained} + \text{adsorbed})}$  became difficult when large volumes of water or  $MgSO_4$  were needed

Table 2-2: Comparison of PZSE and native soil pH for three soil profiles.

Depth (cm)	Horizon	pH	PZSE
Soil = Dothan			
0-23	A	5.74	3.50
23-38	E	6.25	3.50
38-76	Bt1	4.87	3.50
76-97	Bt2	4.66	3.75
97-152	Btv	4.33	4.25
Soil = Cecil			
0-3	A	4.37	3.00
3-20	E	4.56	4.35
20-60	Bt1	4.65	4.00
60-183	Bt2	5.07	4.25
163-196	C	4.82	3.85
Soil = Matapeake			
0-20	Ap	5.77	3.50
20-53	B1	4.58	3.60
53-66	B21t	4.54	3.40
66-79	B22t	4.65	3.65
79-114	B23t	4.57	3.72

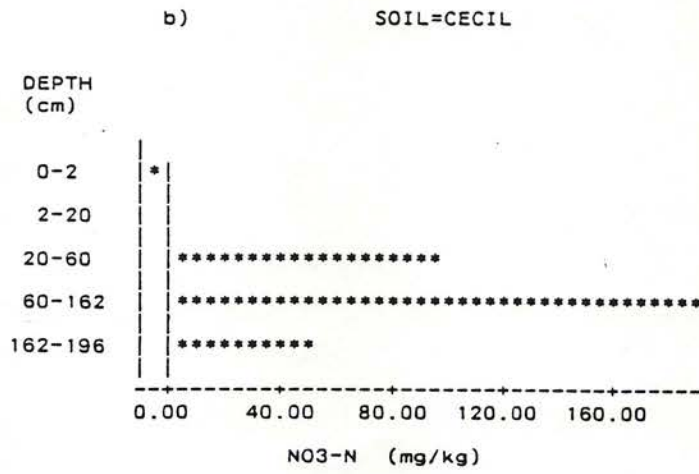
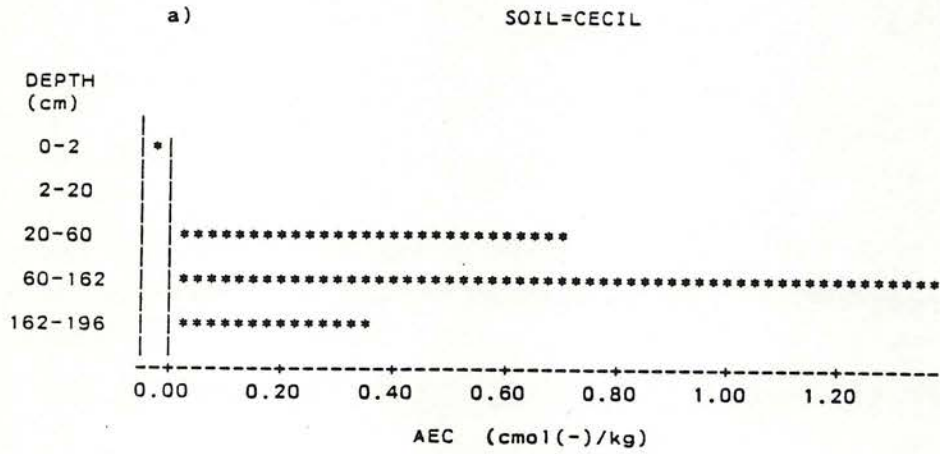
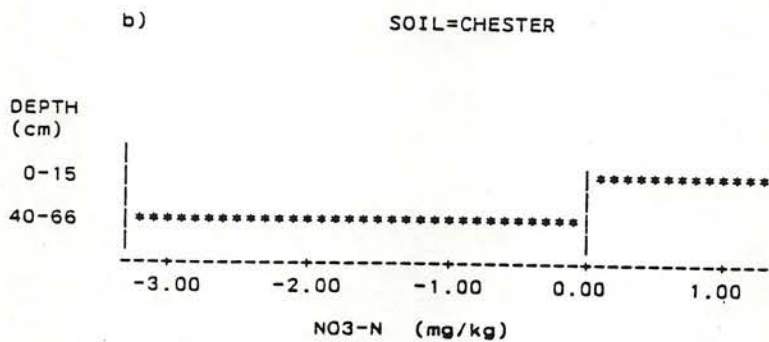
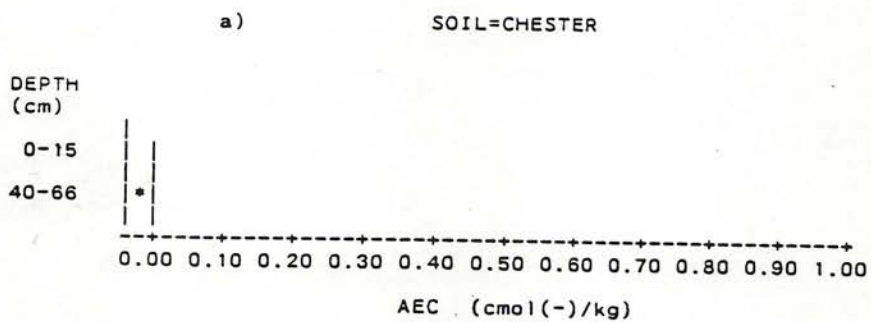
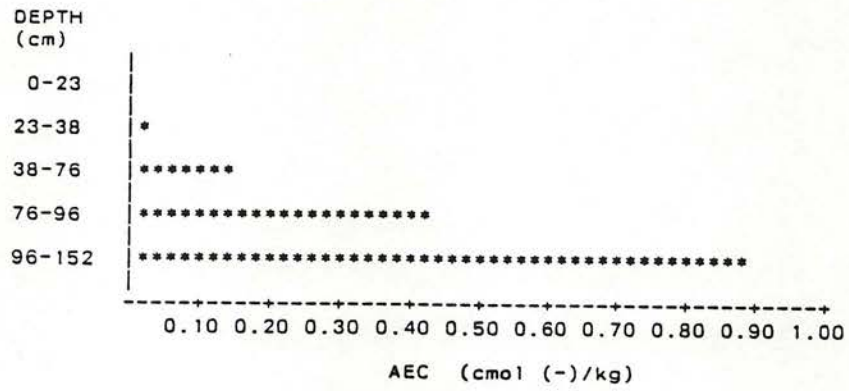


Figure 2-1: Anion exchange capacity(a) and nitrate-N adsorption potential(b) as a function of depth for the ten soil profiles.

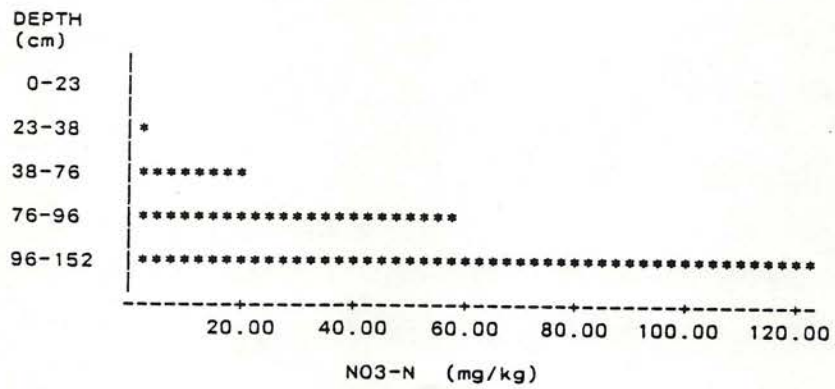


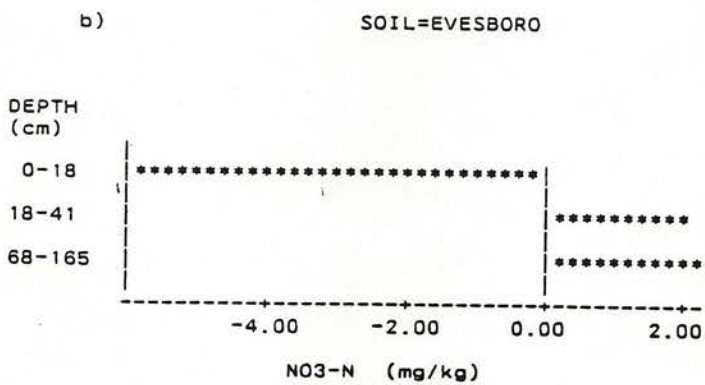
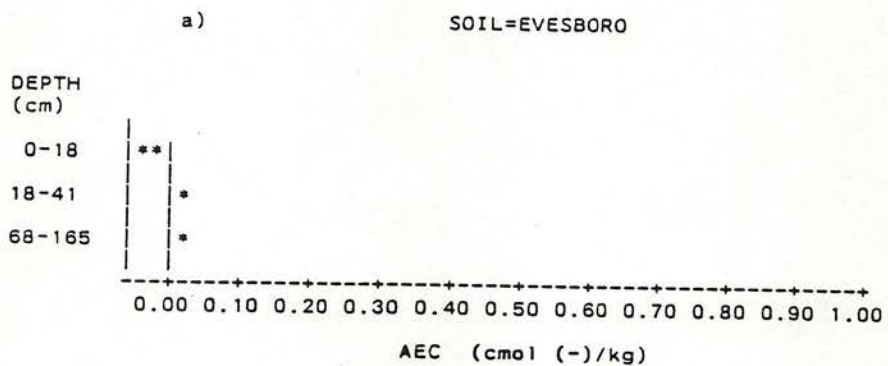


a) SOIL=DOTHAN



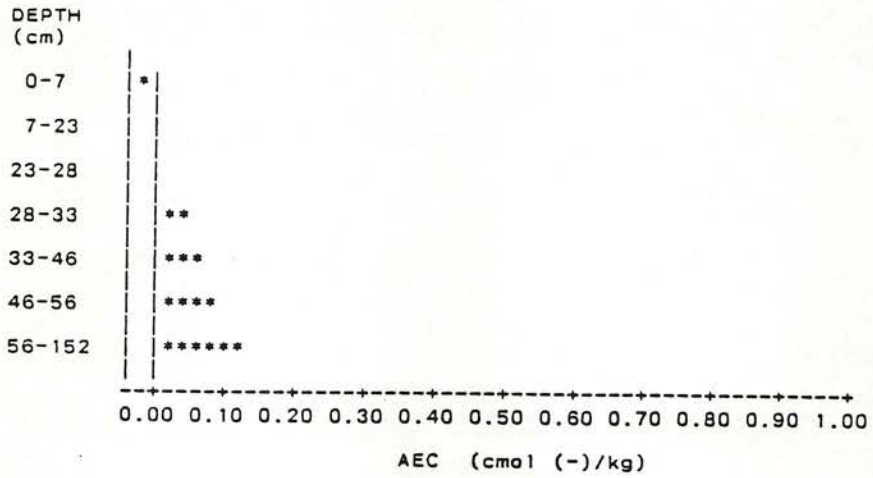
b) SOIL=DOTHAN



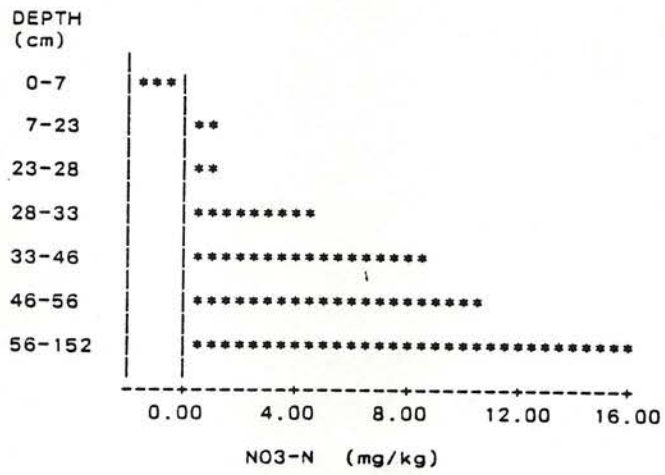


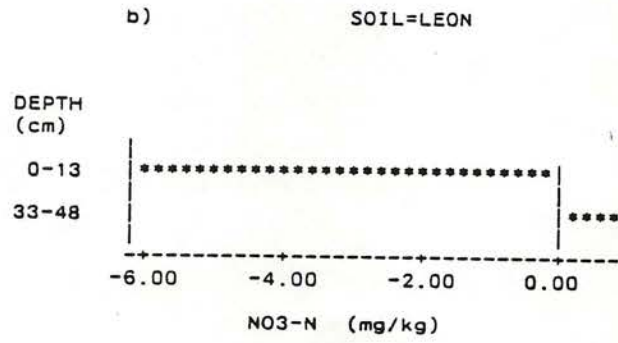
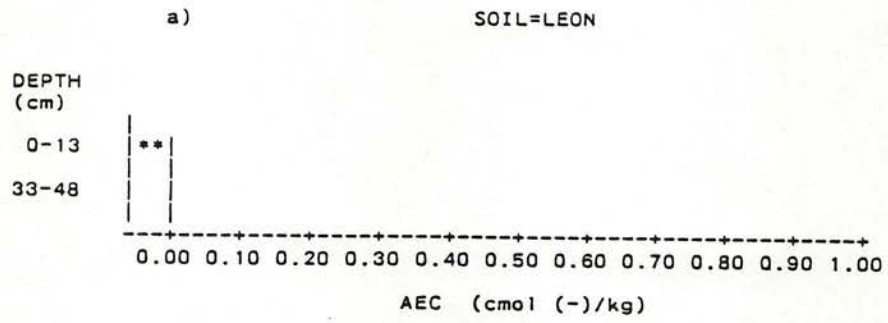


a) SOIL=KENANSVILLE

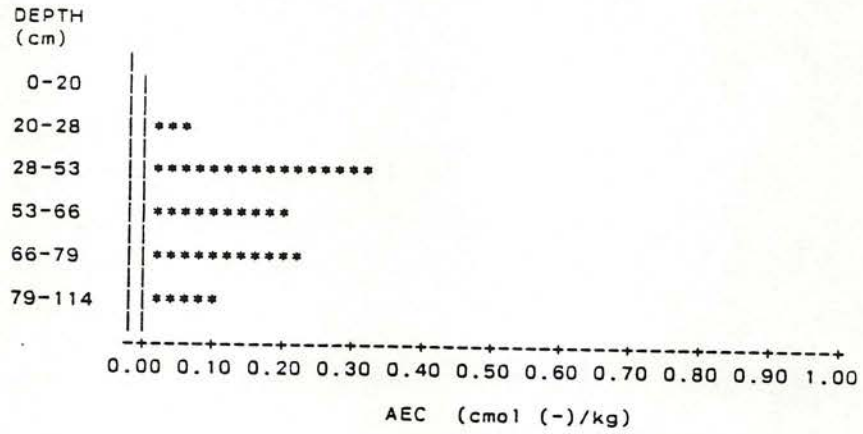


b) SOIL=KENANSVILLE

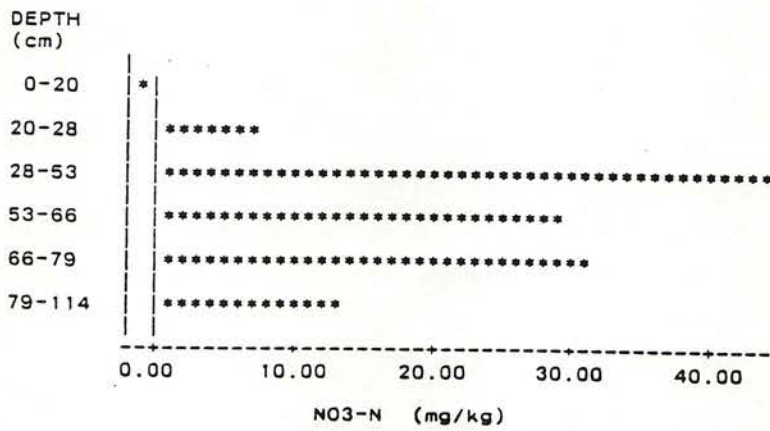




a) SOIL=MATAPEAKE, MD

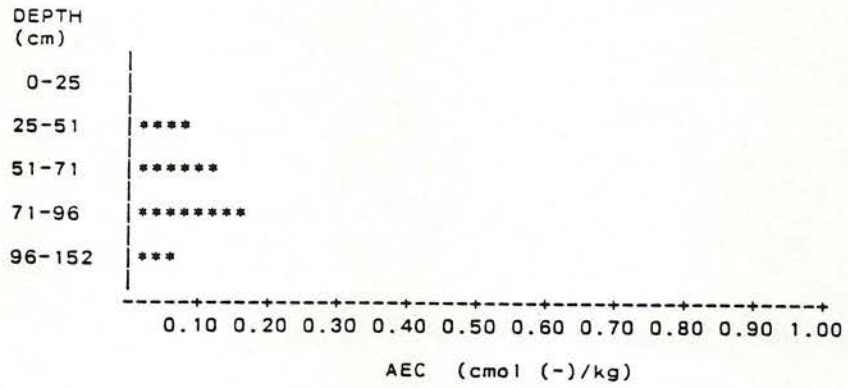


b) SOIL=MATAPEAKE, MD

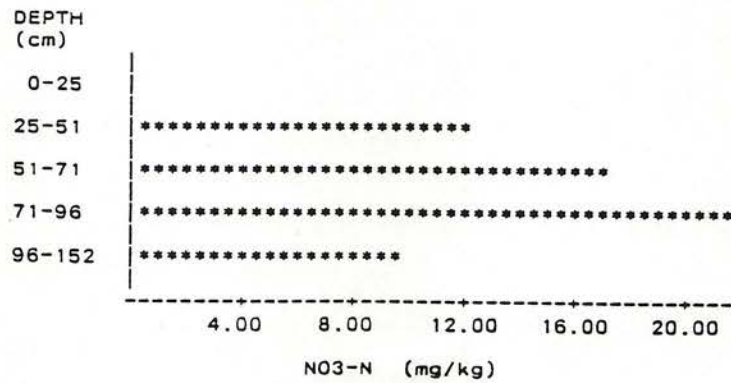


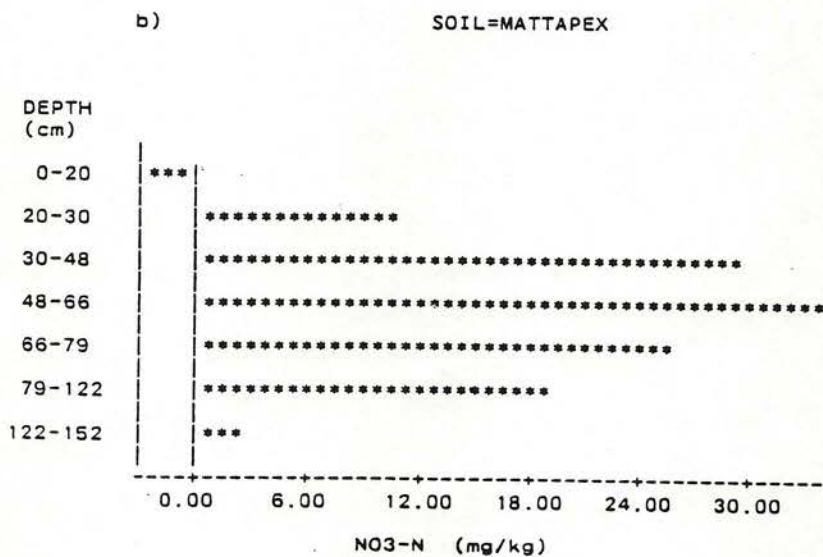
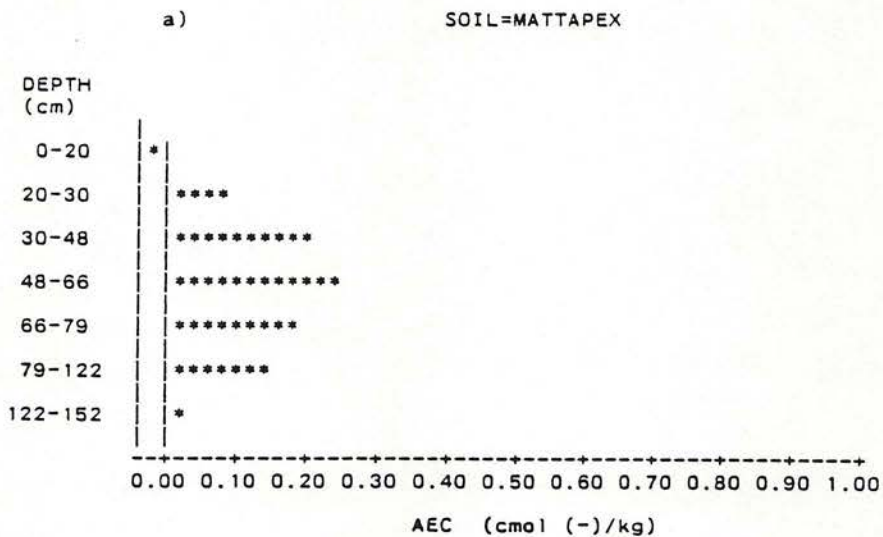


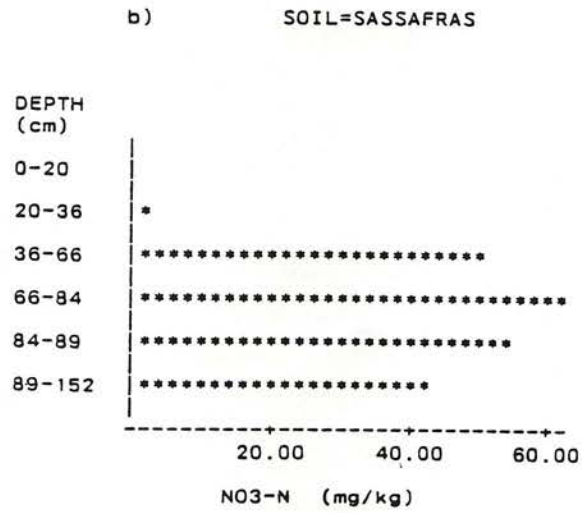
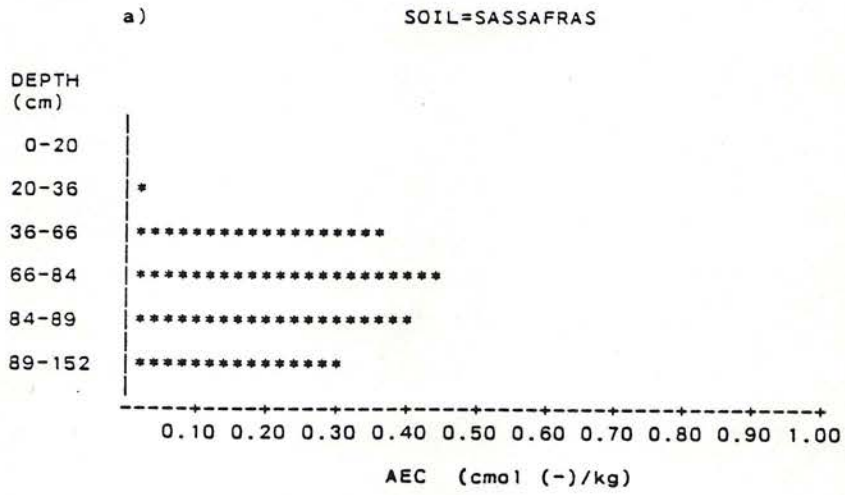
a) SOIL=MATAPEAKE, DE



b) SOIL=MATAPEAKE, DE









for equilibration with 0.0015 M  $\text{MgSO}_4$ . When large volumes were needed Cl concentration became very low, and detection with the electrode was difficult, often resulting in negative differences. Thus, negative values for AEC should be considered as zero AEC.

The  $< 2 \mu\text{m}$  clay fraction of the soils possessing significant AEC is predominated by kaolinite (Table 2.1), thus the increase in AEC with depth can be qualitatively explained by the increase in clay content. However, using simple correlation coefficients, one finds that the clay content ( $r=0.79$ ) and the Fe-oxide content ( $r=0.82$ ) are implicated in the development of AEC. For the Delaware and Maryland soils, clay content or Fe-oxide content can be used to explain the differences among soils, e.g., the Sassafras soil has the highest clay content as well as the highest Fe-oxide content, and possesses the highest AEC. This relationship between kaolinite content or Fe-oxide content and AEC is expected in view of the  $\text{NO}_3$  adsorption work previously cited. The Chester soil does not conform in that it is predominated by kaolinite with a high Fe-oxide content, but develops no AEC. There are no obvious data to explain the performance of the Chester soil. A broader system of differentiation, based on soil type, can also be used to predict AEC, however, caution is indicated since the AEC of the Matapeake soils differed in magnitude and depth.

AEC and PZSE were not correlated ( $r < 0.10$ ) for the Cecil, Dothan, and Matapeake soils. Thus PZSE was of no use in predicting the

AEC, i.e., AEC was significant at  $\text{pH} > \text{PZSE}$ , therefore determination of PZSE was discontinued. It is likely that PZSE was of no use for these soils since both permanent and variable sources of charge are present. The induced positive charge must be equal in magnitude to the variable plus permanent charge components and PZSE is therefore exaggeratedly low.

The significance of AEC can be more readily appreciated by converting AEC to nitrate-N adsorption potential(NAP), where NAP is the amount of  $\text{NO}_3\text{-N}$  potentially retained given the AEC(Fig. 2.1b). Since such a direct conversion does not make use of bulk density, total profile nitrate can only be estimated, however, the NAP easily explains the amount of residual nitrate seen by Meisinger and co-workers(1982, 1983). Additionally, the increase in AEC with depth for the Maryland Matapeake and Mattapex soils occurs at a depth similar to the increased residual  $\text{NO}_3$  concentrations reported by Meisinger et al.(1982; 1983). These findings indicate that chemical retention of  $\text{NO}_3$  can be a significant factor toward the amount of residual  $\text{NO}_3$  found in soils of the Mid-Atlantic region.

The  $\text{NO}_3$  - Cl exchange system is seen to be rapid and reversible, exhibiting no hysteresis, indicating simple electrostatic exchange, i.e., only outer sphere complexes are formed(Fig. 2.2). This agrees with the conclusions drawn using tropical soils high in kaolinite and Fe-oxides(Singh and Kanehiro, 1969; Kinjo and Pratt, 1971a and b; Kinjo et al., 1971; Espinoza et al., 1975). The adsorption and desorption reactions conformed to first-order kinetics,

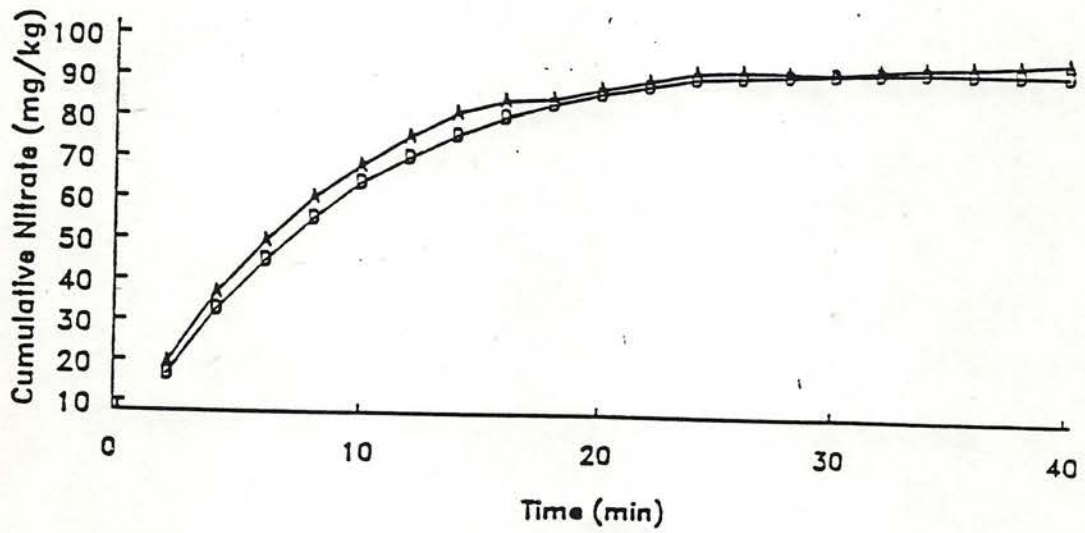


Figure 2-2: Adsorption(A) and desorption(D) of  $\text{NO}_3$  as a function of time on Cecil soil.



further indicating a simple retention mechanism, e.g., electrostatic attraction(Fig. 2.3). In addition to the adsorption-desorption of  $\text{NO}_3$  on a Cl-saturated soil, the adsorption-desorption of Cl on a  $\text{NO}_3$ -saturated soil was also monitored. These reactions were stoichiometric and conformed to first-order kinetics, confirming only electrostatic retention was operating, and allowing calculation of  $\Delta G^\circ$ . In either case the reaction was nearly 100% reversible, and Cl was preferred, as evidenced by  $+\Delta G^\circ$  value for  $\text{NO}_3$  adsorption and the  $-\Delta G^\circ$  value for Cl adsorption(Table 2.3).

The total amount of  $\text{NO}_3$  or Cl adsorbed was nearly equal(Table 2.3), but only accounted for approximately 11% of the NAP, indicating the presence of more competitive anions during the kinetic studies. This can be explained by the different presaturating conditions used for the AEC and adsorption-desorption procedures. The AEC procedure initially saturates the soil with 0.02 M Cl, whereas the adsorption-desorption procedure initially saturates with 0.0007 M Cl or  $\text{NO}_3$ . Thus at the very high initial Cl saturation the more competitive anions, e.g., electrostatically bound  $\text{SO}_4$  and phosphates are exchanged and removed allowing Cl adsorption and increasing AEC. This explanation was confirmed by presaturating a sample at 0.02 M Cl, then adsorbing  $\text{NO}_3$ . Under these conditions  $\text{NO}_3$  adsorption accounted for 92% of the NAP(Fig. 2.4). The effect of more competitive anions was further evaluated by including  $\text{SO}_4$ . Nitrate adsorption on soil presaturated with  $\text{SO}_4$  accounted for only 5% of the NAP, indicating  $\text{SO}_4$  is much more competitive than  $\text{NO}_3$ (Fig. 2.5). These findings imply that a distinction must

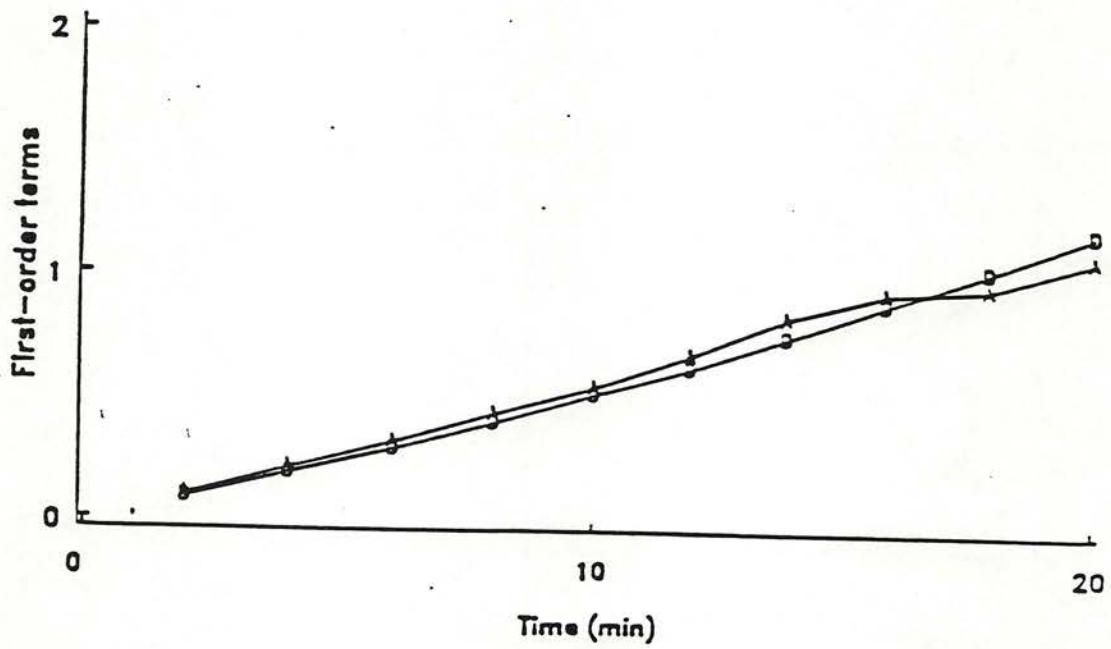


Figure 2-3: First-order plots of  $\text{NO}_3$  adsorption(A) and desorption(D) on a Cl saturated Cecil soil.

Table 2-3: Comparison of  $\text{NO}_3^-$  - Cl exchange on presaturation with the opposing anion.

System	Amount Adsorbed $\text{cmol kg}^{-1}$	Reversibility %	$\Delta G^\circ$ $\text{kJ mol}^{-1}$
$\text{NO}_3^-$ Ads-des	0.24	94	+1.55
Cl Ads-des	0.20	97	-0.25



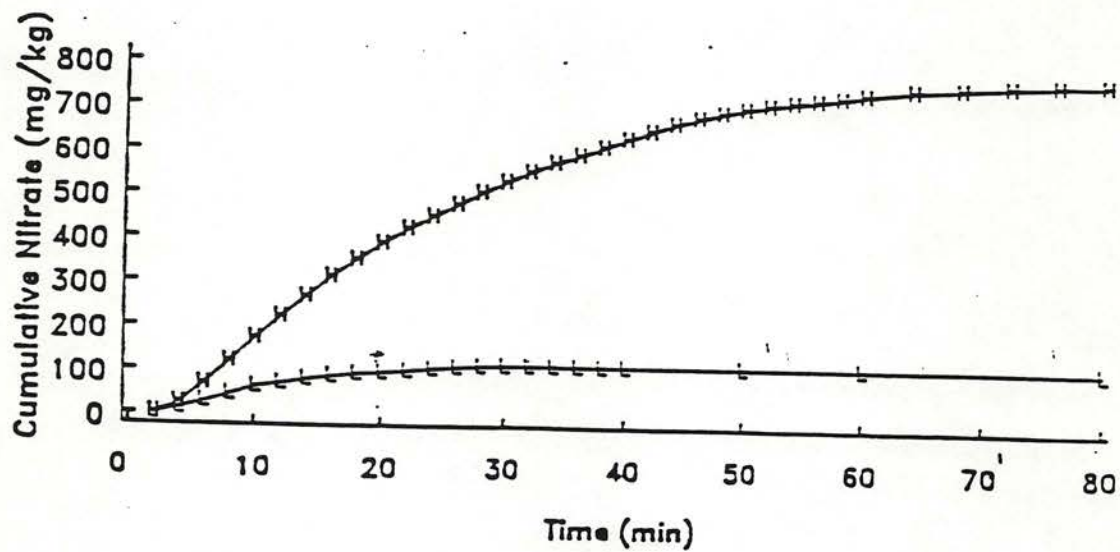


Figure 2-4: Adsorption of  $\text{NO}_3$  as a function of time after presaturation at high ( $H=0.02 M$ ) and low ( $L=0.0007 M$ ) Cl concentration.

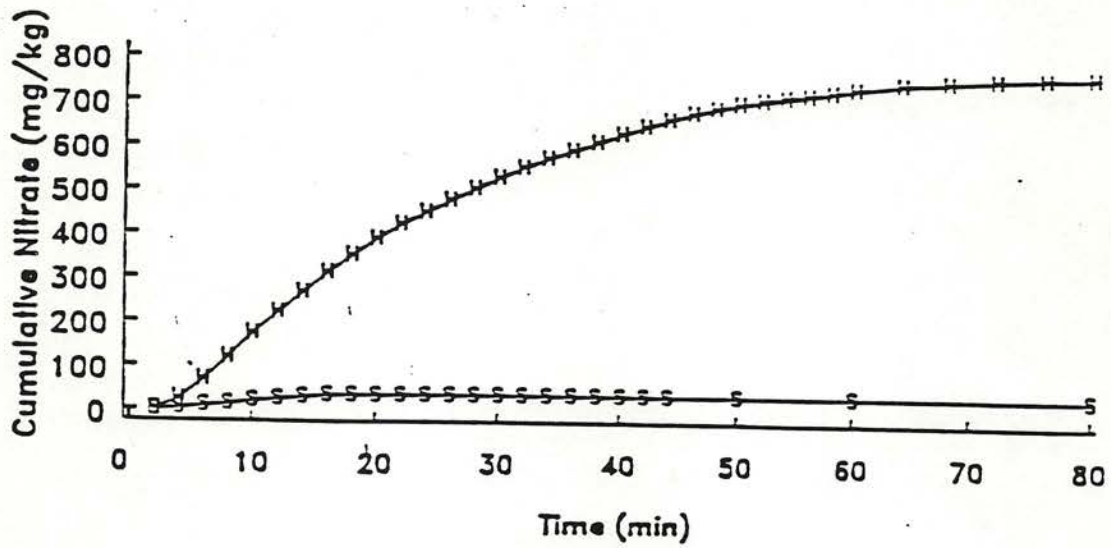


Figure 2-5: Adsorption of  $\text{NO}_3^-$  on a  $\text{SO}_4(\text{S})$  and a  $\text{Cl}(\text{H})$  saturated Cecil soil as a function of time.

be made between AEC, as determined by the recommended procedure (Rhoades, 1982), and *effective* AEC, which should be determined at much lower concentrations that more closely resemble the soil solution.

#### 2.4 Conclusions

Although soils of the humid Mid-Atlantic region are known to be predominantly negatively charged, significant AEC can develop, especially in soils predominated by kaolinite in the clay sized fraction or high in Fe-oxide content. The AEC was negligible at the surface, but increased with depth and kaolinite or Fe-oxide content. Kinetic exchange studies using Cl, NO<sub>3</sub>, and SO<sub>4</sub> indicate that retention is electrostatic in nature. Anion preference shows SO<sub>4</sub> to be strongly preferred, followed by Cl, and then NO<sub>3</sub>. These findings indicate that chemical retention of NO<sub>3</sub>, due to electrostatic attraction by positively charged soil colloids, can be a significant factor in determining the amount of residual NO<sub>3</sub> found in many soils of the Mid-Atlantic region.



CHAPTER 3  
DIFFERENTIATION OF SOIL N FRACTIONS  
USING A KINETIC APPROACH

**3.1 Literature Review**

Many methods, both biological and chemical, have been proposed to estimate the potential N contribution to a crop from the general groups of soil N. These techniques have been reviewed by Bremner(1965) and again by Keeney(1982). When combined, these reviews present over 60 biological methodologies and over 40 chemical extractants that have been employed in an attempt to estimate soil N availability. Obviously, considerable attention has been given to N availability indices, yet no method has been routinely adopted by soil testing labs. The ultimate value of any method is determined by how well it is associated with some parameter of plant growth, e.g., yield or total N uptake of the field grown target crop. The major objection to the biological techniques has been the time required to conduct them(Bremner, 1965; Keeney, 1982; Stanford, 1982). These techniques require from 1 to 72 weeks and therefore would not fit into a routine soil testing

scheme. The chemical extractants have been studied because they are rapid, reproducible, and relatively inexpensive, and therefore fit well into a soil testing scheme. However, being completely empirical, they have not been sufficiently reliable when field tested over a number of years and locations and therefore have not been included in soil testing programs(Keeney, 1982; Stanford, 1982).

Generally the biological indices have been better correlated to plant parameters(Bremner, 1965; Keeney, 1982; Stanford, 1982). Intuitively this might be expected since the release of N is a microbial and not a chemical process. The biological techniques follow the aerobic or anaerobic mineralization of N. These studies are usually performed under strictly controlled conditions, i.e., water content and temperature. Stanford and coworkers(1972, 1974) proposed an incubation technique that, if strictly followed, extracts a potentially mineralizable fraction( $N_0$ ). Stanford defines  $N_0$  as the amount of N mineralized by aerobic incubation at 308 K and field capacity water content according to first-order kinetics(Stanford and Smith, 1972; Stanford et al., 1974). Stanford(1982) proposed that correlation with  $N_0$  be used as a means of initial soil test evaluation since it can be readily compared with soil test values over a wide range of soils.

The easily mineralized pool is usually thought to be most important in providing N to a crop(Jenkinson, 1968; Stanford and Smith, 1972), therefore its quantification has been the focus of much of the N availability

research. To this end, numerous chemical extraction techniques have been proposed (Bremner, 1965; Keeney, 1982; Stanford, 1982). These extractions have been conducted using batch techniques, whereby a known amount of soil is kept in contact with an extractant for a specified period of time. This extraction technique, although simple and rapid, does not provide any information about the reaction itself; it is purely an equilibrium or macroscopic approach.

The research reported in this paper takes a different approach in that we apply a kinetic technique in an attempt to gain information about the chemically induced release of  $\text{NH}_4$  from soils. A kinetic approach has been successfully employed to differentiate ionic adsorption-desorption reactions on clay minerals and soils (Jardine and Sparks, 1984). Their work is based on the use of site blocking reagents, in conjunction with apparent reaction rate differences, which allow differentiation of reaction sites and mechanisms. The reader is referred to recent reviews for a detailed discussion of kinetics as applied to reactions in soils and clay minerals (Sparks, 1985; Sparks, 1986). Kinetics has also been applied to study the microbial conversion of soil organic N to  $\text{NH}_4$ . This application of kinetics, first proposed by Stanford and Smith (1972), provides estimates of potentially available N and apparent rate coefficients for the release of N from soils. Although this approach has been modified and refined in terms of incubation techniques and modeling procedures (Stanford et al., 1973; Stanford and Epstein, 1974; Molina et al., 1980; Smith et al., 1980; Talpaz et al., 1981;



Broadbent, 1986; Deans et al., 1986), microbial studies must still be monitored for several months before kinetically based estimates of N availability can be made. Thus, it should be useful to kinetically study the chemically induced, and therefore more rapid, release of N from soils. The objectives of this research were i) to develop a methodology which allows a time-monitored, rapid, chemical extraction of soil N and ii) to determine if N release reactions can be differentiated through a kinetic analysis of such an extraction. This approach, if successful in differentiating a chemically active pool of soil N, will not only provide chemical evidence for the existence of such a pool, but may provide a valuable basis to which traditional rapid chemical indices of N availability can be compared.

### **3.2 Materials and Methods**

Samples from the Ap horizon of several Delaware soils were used in this study. These included: a Chester loam (fine-loamy, mixed, mesic Typic Hapludult), a Leon loamy sand (sandy, siliceous, thermic Aeric Haplaquod), an Elkton loamy sand (clayey, mixed, mesic Typic Ochraqult), and an Evesboro loamy sand (mesic, coated Typic Quartzipsamment). Soils were air-dried and passed through a 2 mm sieve. The mineralogy of the  $<2 \mu\text{m}$  clay fraction of all these soils is dominated by kaolinite, quartz, and chloritized vermiculite.

#### *Batch Extractions*



Batch extraction techniques were used to characterize the N status of the soils. Exchangeable  $\text{NH}_4$  was determined using a 1 h, 2 M KCl extraction (Keeney and Nelson, 1982). The easily mineralized pool was estimated using a 16 h autoclave method (Keeney, 1982) and extraction with 0.02 M  $\text{KMnO}_4$ - 0.5 M  $\text{H}_2\text{SO}_4$  (Stanford and Smith, 1978). The  $\text{NH}_4$  extracted by these methods was determined using an Orion 95-12 ammonia electrode and an Orion 901 microprocessor ionalyzer (Bremner and Hauck, 1982). Baseline recovery problems were minimized by allowing 5 min intervals between samples (Guilbault et al., 1985). Total N was indexed using a standard macro-Kjeldahl procedure, without salicylic acid (Bremner, 1965). Organic matter was determined using a modified Walkley-Black procedure.

#### *Kinetic Extractions*

Kinetic analyses were conducted with a flow technique utilizing a stirred-flow reaction chamber (Carski and Sparks, 1985), however, a Millipore AP prefilter was used in place of the Nuclepore membrane filter. Operation of this system is simple, a magnetic stir star is placed in the chamber above the plunger, 1 g of air-dry soil is loaded into the chamber, the prefilter and top are attached, and a known volume of starting fluid is added using a hypodermic syringe. The plunger is then used to displace the excess air from within the chamber, thus enabling precise control of the reaction volume. This volume is maintained throughout the extraction. A peristaltic pump is used to maintain a flow rate of  $1 \text{ mL min}^{-1}$  and an LKB UltraRac II 2070

fraction collector is used to monitor the reaction at 2 min intervals. A magnetic stirrer is used to ensure adequate mixing within the chamber in order to minimize the effect of diffusion on the apparent rate coefficients.

Separate kinetic extractions using 0.02 M  $\text{KMnO}_4$ - 0.5 M  $\text{H}_2\text{SO}_4$  and 0.01 M  $\text{CaCl}_2$  were conducted. The 0.02 M  $\text{KMnO}_4$ - 0.5 M  $\text{H}_2\text{SO}_4$  extraction was carried out at 297 K, while the 0.01 M  $\text{CaCl}_2$  extraction was carried out at 368 K. To achieve this elevated temperature, the  $\text{CaCl}_2$  extractant was kept at 372 K, and the chamber was immersed in a 368 K water bath. A heated stir plate was used to stir the bath and the contents of the reaction chamber.

The starting fluid differed for the two extractants. Addition of the acid-permanganate initiated immediate  $\text{CO}_2$  production and thus the reaction volume could not be consistently controlled. This necessitated the use of  $\text{H}_2\text{O}$  as the initial loading solution. Although the acid-permanganate does not reach full strength for approximately 10 min (in the absence of soil), this was not considered to be a problem since each soil was treated precisely the same way. The addition of hot  $\text{CaCl}_2$  did not initiate an evolution of gas, allowing its direct injection into the reaction chamber.

Kinetic extractions were conducted in duplicate and  $\text{NH}_4$  was determined using the Orion 95-12 ammonia electrode. The CV values of the duplicate runs, at each time interval, averaged below 5%.

### 3.3 Results and Discussion

The batch characterization analyses show that the soils have large differences in total N and organic matter contents, but smaller differences exist for the easily mineralized pools (Table 3-1). None of the soils have crop histories which include legumes or manure amendments, thus large differences for the easily mineralized pools were not expected.

Typical  $\text{NH}_4$  release versus time curves, presented for acid-permanganate extraction of the Chester and Elkton soils, indicate an initial rapid release followed by a slower sustained release (Fig. 3-1). Curves for all other extractions, using acid- $\text{KMnO}_4$  and  $\text{CaCl}_2$ , were similar and are not presented.

In order to determine conformity to first-order kinetics, an estimate of the total amount of N to be released ( $N_T$ ) must be made. Plotting the inverse of N released vs. the inverse of time (Stanford and Smith, 1972) was not useful since these were not linear. All reactions were monitored for 160 min with little or no additional release of N occurring after 80 min. Thus,  $N_T$  was taken to be the amount of N released after 80 min, i.e., well after the initial rapid release phase and after an apparent equilibrium had been reached.

Using these values for  $N_T$ , conformity to first-order kinetics was



**Table 3-1:** Batch extractions used to characterize the N status of four soils from Delaware

Soil Type	KCl	Autoclave	Acid-KMnO <sub>4</sub>	Kjeldahl	Organic Matter
			mg N kg <sup>-1</sup>		g kg <sup>-1</sup>
Chester loam	16.2	32.4	23.7	1811	33.0
Leon loamy sand	17.5	18.7	15.4	851	31.0
Elkton loamy sand	2.7	13.7	12.3	576	14.2
Evesboro loamy sand	1.2	6.8	6.4	233	10.5

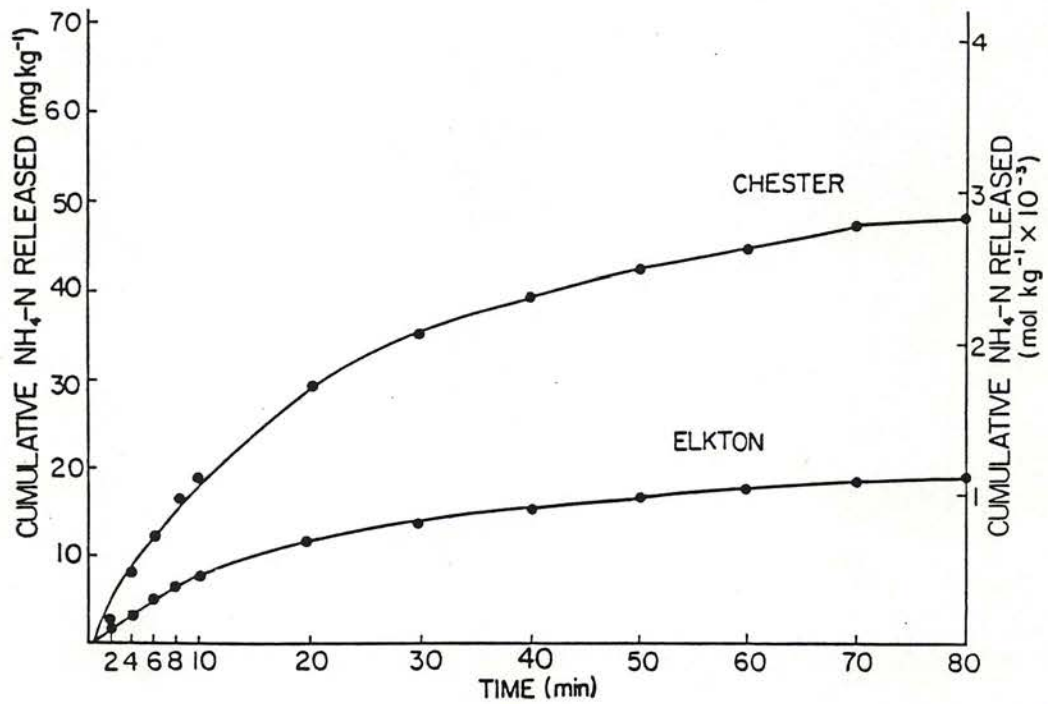
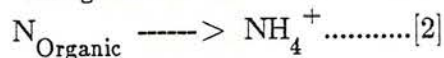
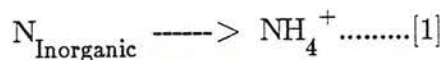


Figure 3-1: Cumulative  $\text{NH}_4\text{-N}$  released on extraction with acid permanganate as a function of time.

checked by plotting  $\log (N_T - N_t)$  versus time, where  $N_t$  is the amount of N released at time t (Fig. 3-2). Although not shown, only the Evesboro soil, which had very low values for total N and the easily mineralized pool, displayed conformity to first-order kinetics over the entire reaction period, the other soils showed an initial nonconformity. The data for the latter soils can be further analyzed by assuming that two simultaneous  $\text{NH}_4$  releasing reactions are occurring (Moore and Pearson, 1981). Previous K -  $\text{NH}_4$  exchange studies indicate that a single first-order equation describes  $\text{NH}_4$  exchange on these soils, thus the contribution from a non-exchangeable pool would be insignificant (Jardine, 1983; Carski, unpublished data). One could then hypothesize that  $\text{NH}_4$  is being released from an inorganic and an organic source as shown below:



Given such a situation, the rate equations would be,

$$-dN_{\text{Inorganic}}/dt = k'_{\text{in}} N_{\text{Inorganic}} \text{ ..... [3]}$$

and

$$-dN_{\text{Organic}}/dt = k'_{\text{or}} N_{\text{Organic}} \text{ ..... [4]}$$

which integrate to,

$$N_{\text{Inorganic}} = N_{\text{in}} \exp -k'_{\text{in}} t \text{ ..... [5]}$$

and

$$N_{\text{Organic}} = N_{\text{or}} \exp -k'_{\text{or}} t \text{ ..... [6]}$$

where  $N_{\text{in}}$  and  $N_{\text{or}}$  represent initial amounts of N in each pool and  $k'_{\text{in}}$  and  $k'_{\text{or}}$  represent apparent rate coefficients for the release of N from



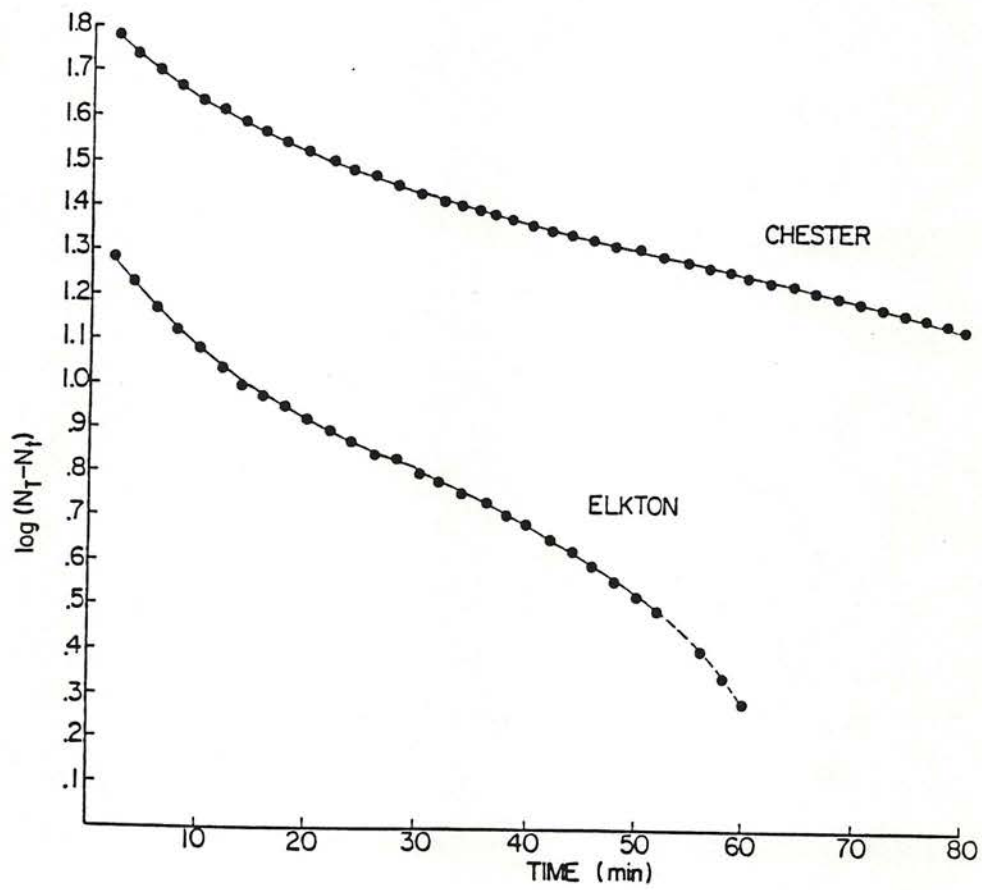


Figure 3-2: First-order kinetic curves for  $\text{NH}_4\text{-N}$  released from Chester and Elkton soils.

each pool. Since the total amount of N that could be released ( $N_T$ ) equals  $N_{in}$  plus  $N_{or}$ , the amount released at any time ( $N_t$ ) equals,

$$N_t = N_T - N_{Inorganic} - N_{Organic} \dots [7]$$

Upon substitution and integration the rate equation becomes,

$$\log (N_T - N_t) = \log (N_{in} \exp -k'_{in} t + N_{or} \exp -k'_{or} t) \dots [8]$$

Further, since the inorganic pool would likely be depleted first, i.e., simple cation exchange is more rapid than acid-permanganate oxidation or heat-induced hydrolysis, the linear portion of the curve represents conformity to first-order kinetics by the organic source as the rate equation reduces to,

$$\log (N_T - N_t) = \log N_{or} - k'_{or} t / 2.303 \dots [9]$$

Equation 9 gives an estimate of the initial organic pool and an apparent rate coefficient for the release of  $NH_4$  from the organic source. This equation is also used to find the contribution, towards total  $NH_4$  released, derived from the organic source at early reaction times. Knowing the total amount and the organic contribution allows calculation of the inorganic contribution. The inorganic values can then be plotted according to a single first-order equation (Fig. 3.3). Using the inorganic release equation, an estimate of the initial inorganic N and an apparent rate of release can be obtained.

Employing the above kinetic equations, estimates of the inorganic

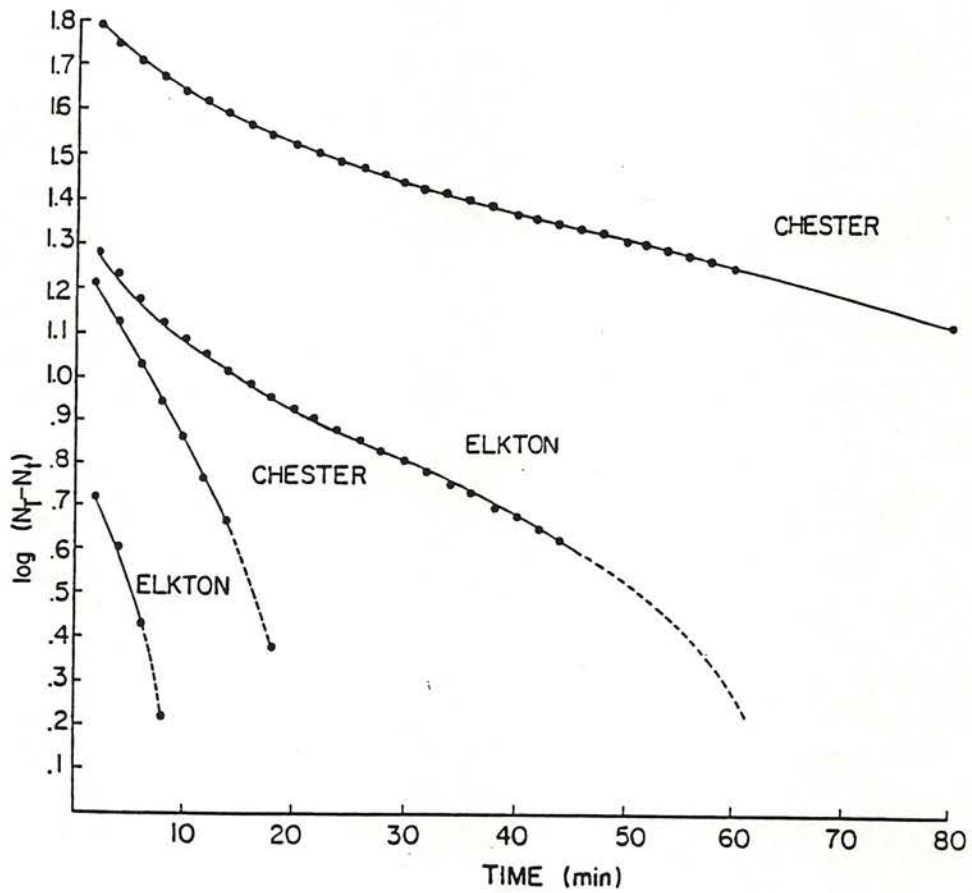


Figure 3-3: First-order kinetic curves for  $\text{NH}_4\text{-N}$  released from an apparent inorganic source, superimposed on Fig. 3.2.



and organic N pools were calculated for the acid-KMnO<sub>4</sub> extraction (Table 3.2).

The kinetically based values for the inorganic and organic N pools exceed the corresponding batch technique estimates. These findings might be expected for the organic predictions since KMnO<sub>4</sub> is continually being replenished, however, one would expect the inorganic pools to be similar. Possibly, since the strength of the KMnO<sub>4</sub> as an oxidant is great and therefore the apparent rate of oxidation high, an easily oxidized organic pool may be included within the inorganic estimate (Moore and Pearson, 1981).

The results for the CaCl<sub>2</sub> kinetic extractions are quite different (Table 3.3). The value for N<sub>T</sub> was again chosen as the amount of NH<sub>4</sub>-N released after 80 min. However, unlike the acid-KMnO<sub>4</sub> extraction, the estimates of the initial inorganic pool are quite close to the 2 M KCl batch estimates. The estimates of the initial organic N pool are much lower for the kinetic technique. Interestingly, the CaCl<sub>2</sub> organic N estimates are very similar to the difference between acid-KMnO<sub>4</sub> kinetic and KCl batch estimates of the inorganic pool. This implies that the acid-KMnO<sub>4</sub> extraction, being more intensive, does not differentiate between the inorganic and an active organic source, thus elevating the acid-KMnO<sub>4</sub> inorganic estimate.

Inspection of the apparent rate coefficients for the inorganic reactions supports this conclusion. These coefficients are higher for CaCl<sub>2</sub> indicating

**Table 3-2:** Apparent rate coefficients( $k'$ ) and size estimates of the initial inorganic( $N_{in}$ ) and organic( $N_{or}$ ) pools derived from extraction with acid-permanganate.

Soil	$k'_{in}$	$N_{in}$	$k'_{or}$	$N_{or}$
	$h^{-1}$	mg N $kg^{-1}$	$h^{-1}$	mg N $kg^{-1}$
Chester	6.24	24.6	0.84	40.7
Leon	7.32	28.2	2.04	23.4
Elkton	11.08	8.1	1.62	14.4
Evesboro	8.50	9.0		

**Table 3-3:** Apparent rate coefficients( $k'$ ) and size estimates of the initial inorganic( $N_{in}$ ) and organic( $N_{or}$ ) pools derived from extraction with heated  $CaCl_2$ .

Soil	$k'_{in}$	$N_{in}$	$k'_{or}$	$N_{or}$
	$h^{-1}$	mg N $kg^{-1}$	$h^{-1}$	mg N $kg^{-1}$
Chester	11.94	16.3	1.80	6.3
Leon	18.72	15.8	3.45	13.5
Elkton	14.16	6.1	2.28	3.5
Evesboro	12.78	5.2		

that a second, slower reaction is acting to decrease the observed rate of the inorganic acid-KMnO<sub>4</sub> reaction. Additionally, the apparent rates of the CaCl<sub>2</sub> organic reactions are higher than the acid-KMnO<sub>4</sub> organic releases indicating the CaCl<sub>2</sub> differentiated organic fraction is more easily degraded than the acid-KMnO<sub>4</sub> differentiated organic fraction.

### 3.4 Conclusions

The kinetic approach presented does allow differentiation of two reactions. These reactions appear to be associated with the release of NH<sub>4</sub> from an inorganic and an organic source. The acid-KMnO<sub>4</sub> extraction differentiates an inorganic plus an active organic fraction from the more resistant organic pool. The CaCl<sub>2</sub> extraction differentiates the inorganic pool from an active organic pool. Thus, although neither extractant gives direct evidence for the existence of a chemically active pool, i.e., three pools were not differentiated by a single extraction, indirect evidence does indicate the existence of a chemically active organic pool.

If it is accepted that an active organic pool has been differentiated, several implications concerning N availability can be drawn; i) the active pool of soil organic N is very small at any given time, ii) this active pool must be replenished as it is consumed in order to provide a significant amount of N to a crop through the growing season, iii) traditional mild extraction techniques which target the active organic pool extract significantly greater



quantities than the actual active pool, and iv) the ranking of these soils in terms of N availability, based on the traditional indices is different than the ranking based on the kinetically differentiated active pool. These implications may help to explain the consistent failure of traditional, single-extraction chemical tests to index the active soil N pool. Further work must be initiated to determine the relationship between the kinetically derived active fraction and plant growth parameters such as yield and total N uptake.

## FUTURE RESEARCH NEEDS

The application of kinetic theory and technique to study chemical reactions of the soil is an exciting, but often frustrating, endeavor. The kinetic approach, still in its infancy, does not yet boast a generally acceptable procedure. All procedures, including the stirred-flow technique described here, are subject to accolades and to criticisms, thus work should continue on development or refinement of kinetic methodologies. This does not imply that kinetically based research should cease until the *ideal* methodology is developed, in fact, often, only when an existing methodology fails to describe a system are advances in methodology made.

Nitrate retention on Mid-Atlantic soils is now known to be the result of AEC. Certainly AEC can be a significant factor in N management and water quality maintenance, but the mediating conditions must be clarified. The occurrence and effect of subsoil exchangeable  $\text{SO}_4$  must be evaluated. Soil type appears to be a useful indicator of potential AEC, but differences between soils of the same series were not addressed. Additionally, the relationships between AEC, pH, anion concentration, kaolinite content, and Fe-oxide content need to be elucidated.

The use of a kinetically analyzed, chemical extraction of soil N appears to be promising. The chemical evidence for the existence of a chemically active pool is significant. At the very least, the N in this active pool is immediately available to a crop and can be accounted for, i.e., subtracted from the amount of recommended N fertilizer. More optimistically, the chemically active fraction may prove to be an excellent index of soil N availability, however, this must be evaluated in the field with crop data. This field evaluation could be conducted using existing field data and corresponding soil samples.

## LITERATURE CITED

1. Argersinger, W.J., Jr., A.W. Davidson, and O.D. Bonner. 1950. Thermodynamics and ion exchange phenomena. *Trans. Kans. Acad. Sci.* 53:404-410.
2. Axley, J.H. and J.O. Legg. 1960. Ammonium fixation in soils and the influence of potassium on nitrogen availability from nitrate and ammonium sources. *Soil Sci.* 90:151-156.
3. Barrow, N.J. and T.C. Shaw. 1979. Effects of solution: soil ratio and vigor of shaking on the rate of phosphate adsorption by soil. *Soil Sci.* 30:67-70.
4. Biggar, J.W. and D.R. Nielsen. 1963. Miscible displacement: Exchange processes. *Soil Sci. Soc. Am. Proc.* 26:623-627.
5. Boyd, G. E., A. W. Adamson, and L. S. Myers, Jr. 1947. The exchange adsorption of ions from aqueous solution by organic zeolites: 2. Kinetics. *J. Am. Chem. Soc.* 69:2836-2848.
6. Bremner, J.M. 1965. Nitrogen availability indexes. p. 1324- 1345. (In) C.A. Black (ed.) *Methods of soil analysis, part 2.* Agronomy 9. Am. Soc. of Agron., Madison, Wis.
7. Bremner, J.M. and R.D. Hauck. 1982. Advances in methodology for research on nitrogen transformations in soils. p 467-502. (In) F.J. Stevenson (ed.) *Nitrogen in agricultural soils.* Agronomy 22. Am. Soc. of Agron., Madison, Wis.
8. Broadbent, F.E. 1986. Empirical modeling of soil nitrogen mineralization. *Soil Sci.* 141:208-213.
9. Campbell, C.A. and W. Souster. 1982. Loss of organic matter and potentially mineralizable nitrogen from Saskatchewan soils due to cropping. *Can. J. Soil Sci.* 62:651-656.
10. Carski, T.H. and D.L. Sparks. 1985. A modified miscible



- displacement technique for investigating adsorption-desorption kinetics in soils. *Soil Sci. Soc. Am. J.* 49:1114-1116.
11. Chichester, F.W. 1969. Nitrogen in soil organo-mineral sedimentation fractions. *Soil Sci.* 107:356-363.
  12. Davidson, J.M., P.S.C. Rao, and P. Nkedi-Kizza. 1983. Physical processes influencing water and solute transport in soils. p35-48. (In) D.W. Nelson (ed.) *Chemical mobility and reactivity in soil systems.* Soil Sci. Soc. Am. Special Pub. II. Madison, Wis.
  13. Deans, J.R., J.A.E. Molina, and C.E. Clapp. 1986. Models for predicting potentially mineralizable nitrogen and decomposition rate constants. *Soil Sci. Soc. Am. J.* 50:323-326.
  14. Elliot, H.A., and D.L. Sparks. 1981. Electrokinetic behavior of a paleudult profile in relation to mineral composition. *Soil Sci.* 132:402-409.
  15. Espinoza, W., R.G. Gast, and R.S. Adams, Jr. 1975. Charge characteristics and nitrate retention by two Andepts from South-central Chile. *Soil Sci. Soc. Am. Proc.* 39:842-846.
  16. Evans, C.M., 1983. The kinetics and mechanisms of boron adsorption and desorption in Mid-Atlantic Coastal Plain soils. M.S. thesis University of Delaware, Newark DE.
  17. Fox, R.H. and W.P. Piekielek. 1984. Relationships among anaerobically mineralized nitrogen, chemical indexes, and nitrogen availability to corn. *Soil Sci. Soc. Am. J.* 48:1087-1090.
  18. Gillman, G.P. 1979. A proposed method for the measurement of exchange properties of highly weathered soils. *Aust. J. Soil Res.* 17:129-139.
  19. Guilbault, G.C., J.P. Czarnecki, and M.A. Nabi Rahni. 1985. Performance improvements of gas-diffusion ion selective and enzyme electrodes. *Anal. Chem.* 57:2110-2116.
  20. Harris, R.F. 1982. Energetics of nitrogen transformations. p 833-890. (In) F.J. Stevenson (ed.) *Nitrogen in agricultural soils.* Agronomy 22. Am. Soc. of Agron. Madison, Wis.
  21. Huang, C.P. 1981. The surface acidity of hydrous solids. p 183-218

- (In) M.A. Anderson and A.J. Rubin (ed.) Adsorption of inorganics at solid-liquid interfaces. Ann Arbor Science Publishers, Inc. Ann Arbor, Michigan.
22. Ihde, A.J. 1984. The development of modern chemistry. Dover Publications, New York.
  23. Jardine, P.M. 1983. Kinetics and thermodynamics of potassium-calcium exchange in a multireactive soil system. M.S. thesis. University of Delaware, Newark DE.
  24. Jardine, P.M., and D.L. Sparks. 1984. Potassium-calcium exchange in a multireactive soil system: I. kinetics. Soil Sci. Soc. Am. J. 48:39-45.
  25. Jenkinson, D.S. 1968. Chemical tests for potentially available nitrogen in soil. J. Sci. Food Agric. 19:160-167.
  26. Keeney, D.R. and J.M. Bremner. 1964. Effect of cultivation on the nitrogen distribution in soils. Soil Sci. Soc. Am. Proc. 28:653-656.
  27. Keeney, D.R. and J.M. Bremner. 1966. Comparison and evaluation of laboratory methods of obtaining an index of soil nitrogen availability. Agron. J. 58:498-503.
  28. Keeney, D.R. 1982. Nitrogen management for maximum efficiency and minimum pollution. p. 605-649. (In) F.J. Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22. Am. Soc. of Agron., Madison, Wis.
  29. Keeney, D.R. 1982. Nitrogen - Availability indices. p 711-730. In A.L. Page (ed.) Methods of soil analysis, Part 2. Agronomy 9. Am. Soc. of Agron., Madison, WI.
  30. Keeney, D.R. and D.W. Nelson. 1982. Nitrogen-Inorganic forms. p 643-698. (In) A.L. Page (ed.) Methods of soil analysis part 2. Agronomy 9. Am. Soc. of Agron., Madison, Wis.
  31. Kelley, W.P. 1948. Cation exchange in soils. Am. Chem. Soc. Monograph 109. Reinhold Publ. Corp., New York.
  32. Kinjo, T. and P.F. Pratt. 1971a. Nitrate adsorption: I. In some acid soils of Mexico and South America. Soil Sci. Soc. Am. Proc. 35 : 722-725.



33. Kinjo, T. and P.F. Pratt. 1971b. Nitrate adsorption: II. In competition with chloride, sulfate, and phosphate. Soil Sci. Soc. Am. Proc. 35 : 725-728.
34. Kinjo, T., P.F. Pratt, and A.L. Page. 1971. Nitrate adsorption: III. Desorption movement and distribution in Andepts. Soil Sci. Soc. Am. Proc. 35:728-732.
35. Legg, J.O. and J.J. Meisinger. 1982. Soil nitrogen budgets. p 503-566. (In) F.J. Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22. Am. Soc. of Agron., Madison, Wis.
36. Liebhardt, W.C., C. Golt and J. Tupin. 1979. Nitrate and ammonium concentrations of ground water resulting from poultry manure applications. J. Environ. Qual. 8 :211-215.
37. Magdoff, F.R., J.F. Amadon, and J. Aleong. 1983. Evaluation of a nitrogen availability test. Comm. Soil Sci. Plant Anal. 14:427-433.
38. Magdoff, F.R., D. Ross, and J. Amadon. 1984. A soil test for nitrogen availability to corn. Soil Sci. Soc. Am. J. 48:1301-1304.
39. Meisinger, J.J., T.H. Carski, M.A. Nys, and V.A. Bandel. 1982. Residual nitrate nitrogen in Maryland. Agronomy Abstract. p 215. Am. Soc. of Agron., Madison, WI.
40. Meisinger, J.J., T.H. Carski, and V.A. Bandel. 1983. Residual nitrogen in Maryland. Northeast Branch Agronomy Abstract. p 11. Am. Soc. of Agron., Madison, WI.
41. Molina, J.A.E., C.E. Clapp, and W.E. Larson. 1980. Potentially mineralizable N in soil: The simple exponential model does not apply for the first 12 weeks of incubation. Soil Sci. Soc. Am. J. 44:442-443.
42. Moore, J.W., and R.G. Pearson. 1981. Kinetics and mechanisms. 3<sup>rd</sup> ed. John Wiley and Sons, New York, NY.
43. Morgan, J.J. and W. Stumm. 1964. Colloid chemical properties of manganese dioxide. J. Colloid Sci. 19:347-359.
44. Nielsen, D.R. and J.W. Biggar. 1961. Miscible displacement in soils: I. Experimental information. Soil Sci. Soc. Am. Proc. 25:1-4.

45. Nielsen, D.R. and J.W. Biggar. 1962. Miscible displacement: III. Theoretical considerations. *Soil Sci. Soc. Am. Proc.* 26:216-221.
46. Nommik, H. 1965. Ammonia fixation and other reactions involving a nonenzymatic immobilization of mineral nitrogen in soils. p 198-248. (In) W.V. Bartholomew and F.E. Clark (ed.) *Soil nitrogen. Agronomy 10. Am. Soc. of Agron., Madison, WI.*
47. Nommik, H. and K. Vahtras. 1982. Retention and fixation of ammonium and ammonia in soils. p 123-172. (In) F.J. Stevenson (ed.) *Nitrogen in agricultural soils. Agronomy 22. Am. Soc. of Agron., Madison, WI.*
48. Ogwada, R.A., and D.L. Sparks. 1986. A critical evaluation on the use of kinetics for determining thermodynamics of ion exchange in soils. *Soil Sci. Soc. Am. J.* 50:300-305.
49. Olsen, R.A. and L.T. Kurtz. 1982. Crop nitrogen requirements, utilization, and fertilization. p. 567-604. (In) F.J. Stevenson (ed.) *Nitrogen in agricultural soils. Agronomy 22. Am. Soc. of Agron., Madison, WI.*
50. Parker, D.R. and E.H. Gardner. 1984. The determination of hot-water-soluble boron in some acid Oregon soils using a modified azomethine-H procedure. *Commun. in Soil Sci. Plant Anal.* 12:1311-1322.
51. Parker, J.C., L.W. Zelazny, S. Sampath, and W.G. Harris. 1979. A critical evaluation of the extension of zero point of charge (ZPC) theory to soil systems. *Soil Sci. Soc. Am. J.* 43:668-673.
52. Ritter, W.F. and A.E.M. Chirnside. 1982. Ground-water quality in selected areas of Kent and Sussex Counties, Delaware. Agricultural Engineering Department Univ. of Delaware. Newark, DE.
53. Robertson, F.N. 1977a. The quality and potential problems of ground water in Sussex Co., Del. Water Resource Center, Univ. of Delaware, Newark DE.
54. Robertson, F.N. 1977b. The effect of agricultural activity on ground water quality near Millsboro, DE. Water Resource Center, Univ. of Delaware. Newark, DE.



55. Rhoades, J.D. 1982. Cation exchange capacity. p 149-157. (In) A.L. Page (ed.) Methods of soil analysis, part 2. Agronomy 9. Am. Soc. of Agron., Madison, WI.
56. Scarsbrook, C.E. 1965. Nitrogen availability. p. 481-502. (In) W.V. Bartholomew and F.E. Clark (ed.) Soil nitrogen. Agronomy 10. Am. Soc. of Agron., Madison, WI.
57. Schweich, D., M. Sardin, and J-P. Gaudet. 1983. Measurement of a cation exchange isotherm from elution curves obtained in a soil column: preliminary results. Soil Sci. Soc. Am. J. 47:32-37.
58. Singh, B.R. and Y. Kanehiro. 1969. Adsorption of nitrate in amorphous and kaolinite Hawaiian soils. Soil Sci. Soc. Am. Proc. 33:681-683.
59. Skopp, J. 1986. Analysis of time-dependent chemical processes in soils. J. Environ. Qual. 15:205-213.
60. Smith, J.L., R.R. Schnabel, B.L. McNeal, and G.S. Campbell. 1980. Potential errors in the first-order model for estimating soil nitrogen mineralization potentials in soils. Soil Sci. Soc. Am. Proc. 44:996-1000.
61. Sparks, D. L., and P. M. Jardine. 1981. Thermodynamics of potassium exchange in soil using a kinetics approach. Soil Sci. Soc. Am. J. 45:1094-1099.
62. Sparks, D. L., and P. M. Jardine. 1984. Comparison of kinetic equations to describe potassium-calcium exchange in pure and in mixed systems. Soil Science 138:115-122.
63. Sparks, D.L. 1985. Kinetics of ionic reactions in clay minerals and soils. p. 231-266. (In) N.C. Brady (ed.) Advances in Agronomy, Academic Press, New York.
64. Sparks, D.L. 1986. Kinetics of reactions in pure and mixed systems. p. 83-145. (In) D.L. Sparks (ed.) Soil physical chemistry. CRC Press. Boca Raton, FL.
65. Sparks, D.L., L.W. Zelazny, and D.C. Martens. 1980. Kinetics of potassium desorption in soil using miscible displacement. Soil Sci. Soc. Am. J. 44:37-40.

66. Sparks, D.L. and J.E. Rechcigl. 1982. Comparison of batch and miscible displacement techniques to describe potassium adsorption kinetics in Delaware soils. *Soil Sci. Soc. Am. J.* 46:875-877.
67. Sposito, G. 1981. Cation exchange in soils: An historical and theoretical perspective. p 13-30. (In) R.H. Dowdy (ed.) *Chemistry in the soil environment*. Soil Sci. Soc. of Am., Madison, WI.
68. Sposito, G. 1984. *The surface chemistry of soils*. Oxford University Press, New York.
69. Soil Science Society of America. 1979. *Glossary of soil science terms*. Soil Sci. Soc. of Am., Madison, WI.
70. Stanford, G. 1982. Assessment of soil nitrogen availability. p. 651-688. (In) F.J. Stevenson (ed.) *Nitrogen in agricultural soils*. Agronomy 22. Am. Soc. of Agron., Madison, WI.
71. Stanford, G., and S.J. Smith. 1972. Nitrogen mineralization potentials of soils. *Soil Sci. Soc. Am. Proc.* 36:465-472.
72. Stanford, G., M.H. Frere, and D.H. Schwaninger. 1973. Temperature coefficient of soil nitrogen mineralization. *Soil Sci.* 115:321-323.
73. Stanford, G., and E. Epstein. 1974. Nitrogen mineralization - water relationships in soils. *Soil Sci. Soc. Am. Proc.* 38:103-106.
74. Stanford, G., J.N. Carter, and S.J. Smith. 1974. Estimates of potentially mineralizable soil nitrogen based on short term incubations. *Soil Sci. Soc. Am. Proc.* 38:99-102.
75. Stanford, G., and S.J. Smith. 1978. Oxidative release of potentially mineralizable soil nitrogen by acid-permanganate extraction. *Soil Sci.* 126:210-218.
76. Starr, J.L. 1983. Assessing nitrogen movement in the field. (In) D.W. Nelson (ed.) *Chemical mobility and reactivity in soil systems*. Soil Sci. Soc. Am. Special Publication No. 11:79-92.
77. Stevenson, F.J. 1982. Origin and distribution of nitrogen in soil. p. 1-42. (In) F.J. Stevenson (ed.) *Nitrogen in agricultural soils*. Agronomy 22. Am. Soc. of Agron., Madison, WI.



78. Talpaz, H., P. Fine, and B. Bar-Yosef. 1981. On the estimation of N-mineralization parameters from incubation experiments. *Soil Sci. Soc. Am. J.* 45:993-996.
79. Thomas, G.W. 1982. Exchangeable cations. p 159-164. (In) A.L. Page (ed.) *Methods of soil analysis, part 2.* Agronomy 9. Am. Soc. of Agron., Madison, WI.
80. Thompson, H.S. 1850. On the absorbent power of soils. *J. Royal Agric. Soc. Engl.* 11:68-74.
81. Uehara, G., and G.P. Gillman. 1980. Charge characteristics of soils with variable and permanent charge minerals: I. Theory. *Soil Sci. Soc. Am. J.* 44:250-252.
82. United States Department of Agriculture. 1977. The 1978 fertilizer situation. Publication FS-8. Econ. Res. Serv., Wash., D.C.
83. van Riemsdijk, W.H. and A.M.A. van der Kinden. 1984. Phosphate sorption by soils: II. Sorption measurement technique. *Soil Sci. Soc. Am. J.* 48:541-544.
84. Way, J.T. 1850. On the power of soils to absorb manure. *J. Royal Agric. Soc. Engl.* 11:313-379.
85. Way, J.T. 1852. On the power of soils to absorb manure. *J. Royal Agric. Soc. Engl.* 13:123-143.
86. Wu, S. and P.M. Gschwend. 1986. Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. *Environ. Sci. Technol.* 20:717-725.
87. Young, J.L. and R.W. Aldag. 1982. Inorganic forms of nitrogen in soil. p 43-66. (In) F.J. Stevenson (ed.) *Nitrogen in agricultural soils.* Agronomy 22. Am. Soc. of Agron., Madison, WI.
88. Zasoski, R.J. and R.G. Burau. 1978. A technique for studying the kinetics of adsorption in suspensions. *Soil Sci. Soc. Am. J.* 42:372-374.