

M. A. B. F. - 4116
22

Nitrate sorption in the profile of an acid soil*

M.D. CAHN¹, D.R. BOULDIN¹ and M.S. CRAVO²

¹*Department of Soil, Crop and Atmospheric Sciences, Cornell University, Ithaca, NY 14853, USA*
and ²*EMBRAPA Centro de Pesquisa Agroflorestal da Amazonia, C.P. 455, Manaus, AM 69.000, Brazil*

Received 23 July 1991. Revised January 1992

Key words: acid soils, Cl^- sorption, NO_3^- sorption

Abstract

Sorption of NO_3^- by different horizons of a highly weathered, acid tropical soil was measured in laboratory batch experiments. Sorption was found to increase with depth, ranging from small amounts in the 0–15 cm layer to amounts that would be roughly equivalent to 25 to 50% of the NO_3^- in the 90–120 cm layer at water and NO_3^- contents commonly found under field conditions. Calculations, based on sorption isotherms, demonstrated how sorption may be important for managing N in a tropical acid soil. Sorption of Cl^- was also found in the range of 0.1 and 2.0 mol m⁻³. In this range of concentrations sorption of NO_3^- and chloride were found to be independent, suggesting that anion exchange sites were far from saturated.

Introduction

Nitrate leaching is an important factor for managing soils in the humid tropics. Acid soils of the tropics have been shown to retain NO_3^- despite large fluxes of water through the soil profiles (Black and Waring, 1976; Jones, 1976; Ng kee kwong and Deville, 1984; Wong et al., 1987). This retention of NO_3^- has been attributed to physical and chemical properties characteristic of these soils.

Wetselaar (1962) and Wild Babiker (1976) hypothesized that preferential flow of water through macropores in well aggregated soils leaves behind NO_3^- in micropores. Tritiated water and dye studies of Seyfreid and Rao (1987) support this hypothesis; however, they contend that preferential water flow occurs only

under saturated conditions through 'conducting pore sequences'. Many acid soils in the tropics are so permeable that rainfall intensity infrequently exceeds infiltration rates.

Anion sorption may also cause retention of NO_3^- . Several workers have reported significant sorption of NO_3^- in tropical acid soils (Black and Waring, 1976; Kinjo and Pratt, 1971; Ng kee kwong and Deville, 1984; Parmar et al., 1980; Singh and Kanehiro, 1969). The mechanism of sorption of NO_3^- is theorized to be due to coulombic attraction of NO_3^- and positively charged sites on kaolinitic and allophanic materials, and protonated hydroxyl groups of aluminum and iron oxides (Hingston et al., 1972; Singh and Kanehiro, 1969). Consequently NO_3^- sorption increases with increasing electrolyte concentration and with decreasing pH (Singh and Kanehiro, 1969).

While the properties of NO_3^- sorption such as the role of pH, mineralogy, surface area, and organic matter have been investigated (Black and Waring, 1979), most studies were conducted

* Contribution from the Department of Soil, Crop and Atmospheric Sciences, New York State College of Agriculture and Life Sciences, Cornell University, Ithaca, NY 14853. SCAS paper No. 1726. This research is part of the TropSoils program.

with solutions of concentrations of 0.5 to 50 cmol L^{-1} NO_3^- (Black and Waring, 1979; Kinjo and Pratt, 1971; Singh and Kanehiro, 1969). These concentrations are outside the 0.001 to 0.100 cmol L^{-1} NO_3^- range commonly found under field conditions (Arora and Juo, 1982; Black and Waring, 1976; Wong et al., 1987). For the purpose of modeling the transport of NO_3^- in agronomic soils, sorption isotherms need to be measured at concentrations representative of those likely to be found under field conditions. We conducted batch equilibration experiments to quantify NO_3^- sorption by an oxisol of the central Amazon basin with amounts equivalent to adding 8 to 150 kg ha^{-1} of N to a layer 15 cm thick.

Materials and methods

Soil used in the sorption study was composited from samples of a field, used for maize experiments over the last 5 years (Cahn, 1991), and located at the Centro de Pesquisa Agroflorestal de Amazonia, (CPAA) 30 km northeast of Manaus, Brazil. CPAA is the national research center for agroforestry of the Amazon and is operated by the Empresa Brasileira de Pesquisa Agropecuaria (EMBRAPA). The soil is classified by U.S. soil taxonomy as a very fine kaolinitic, isohyperthermic Typic Acrudox (Melgar, 1989) or by Brazilian soil taxonomy, a yellow latosol. Average clay content of the soil is 80% (Melgar, 1989), average pH is 4.5, and effective cation exchange ranges between 1.0 and 3.0 cmol kg^{-1} (Cahn, 1991).

Samples were collected at 15-cm intervals of depth to 120 cm from 32 plots of 5 by 8 m dimensions during November 1988, May 1989, November 1989, and March 1990. Half of the plots received calcitic limestone (4,000 kg ha^{-1} of CaCO_3), incorporated to 15-cm depth, during October, 1988. Soil was air-dried and ground to pass through a sieve of 2-mm openings. Composite samples, representative of 0–15, 15–30, 30–60, 60–90, and 90–120 cm horizons, were made by combining 20 g of soil from 12 to 13 randomly chosen plots of each sampling date. Each composite sample was blended 2 hrs in a twin shell dry mixer. The gravimetric water content was de-

termined for each composite sample so that exchangeable NO_3^- could be calculated on an oven-dry basis.

Soil from each horizon was equilibrated with $\text{Ca}(\text{NO}_3)_2$ solutions of concentrations of 0, 0.36, 1.07, 2.14, 2.86, 4.29, 7.14 mole m^{-3} of NO_3^- . In order to study the effect of cations on NO_3^- sorption, solutions of KNO_3 with concentrations of 1.07 or 2.86 mole m^{-3} were also equilibrated with soil from each layer. Soil of the 60–90 cm horizon was equilibrated with 0.0, 0.5, 1.0, 2.0 mole m^{-3} KCl solutions to determine whether Cl^- sorption was significant. Treatments were duplicated. Twenty-gram samples of air-dry soil and 20 mL of solution were added to 50-mL plastic centrifuge tubes. Tubes were agitated and centrifuged 15 minutes at 3000 rpm to obtain a clear supernatant. A kinetic study of NO_3^- sorption showed that after 1 h the concentration of NO_3^- in solution did not change appreciably. Supernatants were decanted and filtered through 0.1 μm polycarbonate filters. The chemical composition of the supernatant and solution remaining in soil were assumed to be equivalent. Supernatant solutions were analyzed for Cl^- , NO_3^- , and SO_4^{2-} with a Dionex 2000i ion chromatograph, equipped with a HPIC-AG3 separator column.

Inorganic nitrogen ($\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$) was extracted from bulk samples with 2 M KCl at a solution-soil ratio of 5 to determine initial levels of NO_3^- (N_0). Ammonium and NO_3^- were analyzed by MgO-Devarda's alloy steam distillation as described by Keeney and Nelson (1982). Water extracts of bulk soil, analyzed by ion chromatography, did not contain significant levels of nitrite.

Sorbed NO_3^- was calculated by the equation:

$$N_x = \frac{[V \times N_x + N_0 \times W - N_1(V + V_0)]}{W} \quad (1)$$

where N_x is the amount of sorbed NO_3^- per weight W of oven-dry soil, N_1 is the concentration of NO_3^- in solution after equilibration, N_1 is the concentration of NO_3^- in volume V added to the soil, N_0 is the initial amount of NO_3^- per weight of oven-dry soil, and V_0 is the volume of water initially in the air-dry soil.

To empirically describe the relationship be-

tween the concentration of NO_3^- in the soil solution and the amount sorbed on the soil. Freundlich equations of the type

$$X = aS^b \quad (2)$$

where X = amount of sorbed NO_3^- per unit weight of soil, mol kg^{-1} , S = NO_3^- concentration in solution, mol m^{-3} , and a and b are parameters, were fit to the data with one equation for each layer. The Freundlich equation best describes data of dilute adsorbate concentrations, where a maximum sorption was not determined (Bohn et al., 1979).

Results and discussion

The possible differences in sorption of NO_3^- from Ca and K solutions were tested by regressing the concentrations of NO_3^- remaining in solution with the 2 salts after reaction with the soil. The resulting regression had a slope of 0.99 an intercept of 0.002 and an R^2 of 0.95. On this basis the sorption was judged to be the same for both salts and the data were combined.

Data presented in Figure 1 showed that NO_3^- sorption increased with depth and NO_3^- concentration. Parameters of isotherms (Eq. 2) for each depth are presented in Table 1 together with pH and initial NO_3^- content.

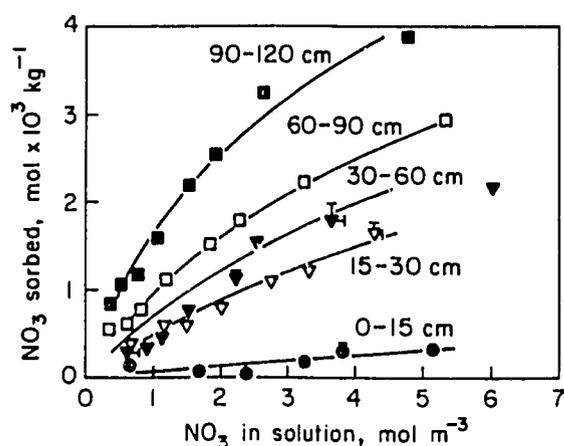


Fig. 1. Nitrate concentrations sorbed on soil plotted against NO_3^- concentrations in solution for five depths of soil. Symbols are experimental points, lines are of the type equation (2) with parameters presented in Table 2.

Table 1. The pH (1:1 soil-water ratio), initial NO_3^- contents (N_n) and parameters in equation (2) fitted to the NO_3^- data for soil samples from different depths

Depth (cm)	pH	N_n ($\text{mol} \times 10^{-1} \text{kg}^{-1}$)	Parameters	
			a	b
0-15	4.98	1.6	8.2×10^{-4}	0.59
15-30	4.44	1.9	4.6×10^{-4}	0.81
30-60	4.47	1.3	4.6×10^{-4}	1.03
60-90	4.54	1.3	9.8×10^{-4}	0.68
90-120	4.58	1.6	1.6×10^{-3}	0.65

Both pH and organic matter have been negatively correlated with anion sorption (Black and Waring, 1979). These relations may explain differences in sorption between the topsoil (0-15 cm) and the subsoil horizons, but would not explain differences among subsoil horizons since pH differences are small and we presume that the differences in organic matter content are also small. Likewise, soil texture, similar throughout the subsoil profile (Melgar, 1987), does not correlate with the pattern of NO_3^- sorption. We speculate that the pattern of NO_3^- sorption in the profile may relate to the compositions of Al and Fe minerals at different depths.

Chloride sorption was found to increase as a function of concentration of Cl^- in solution in the 60-90 cm layer (Table 2). Increasing sorbed Cl^- did not change levels of NO_3^- in solution (Fig. 2b). Likewise, increasing amounts of sorbed NO_3^- did not affect the concentrations of Cl^- in solution (Fig. 2a). The noninterference between sorption of NO_3^- and Cl^- suggests that the anion exchange sites were far from saturated even at the highest solute concentrations chosen for this study.

The effect of NO_3^- sorption on leaching is illustrated by the following. Suppose that 50 kg ha^{-1} of NO_3^- -N is contained in a layer of

Table 2. Concentration of Cl^- in solutions added and after equilibrations (final) with soil from 60-90 cm depth

Concentration ($\text{mol} \times 10^{-3}$)	
Added	Final
0.0	0.1
0.1	0.1
0.5	0.3
1.0	0.6
2.0	1.2

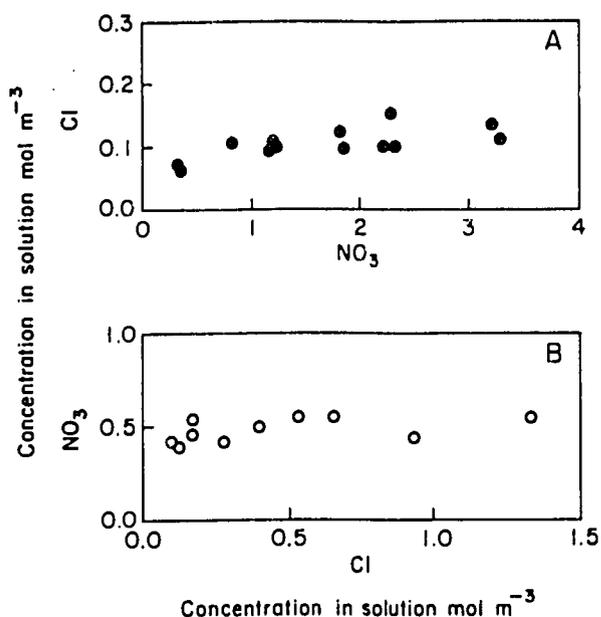


Fig. 2. Effect of adding NO₃⁻ on Cl⁻ in solution (A) and effect of adding Cl⁻ on NO₃⁻ in solution (B).

soil 10 cm thick, the volumetric water content is 50%, and the bulk density is 1 g cm⁻³. Based on the isotherms of Figure 1, (Eq. 2), 89% of the total NO₃⁻ in the surface horizon will be in solution while 29% in the 90–120 cm layer will be in solution. Corresponding calculations for 150 kg of NO₃⁻-N ha⁻¹ are 90% for topsoil and 46% for subsoil layers. Consequently, NO₃⁻ should leach from the topsoil faster than from the subsoil, and the proportion of NO₃⁻ that is in the subsoil should increase with cumulative rainfall.

These effects of sorption were reported in the leaching study of Cahn (1991), who found that NO₃⁻ concentrated in the lower horizon of the Manaus oxisol between 60 and 120 days after fertilizer application. Similarly, Wong et al. (1987) and Jones (1976) found that NO₃⁻ accumulated in the lower horizons of acid Nigerian soils.

Although the subsoil retains NO₃⁻, offering a temporary reservoir of N for the crop in the late season, excessive soil acidity inhibits deep root penetration (Cahn, 1991); consequently, NO₃⁻ in the subsoil is destined to leach to lower depths, along with associated cations. Deep-rooting crops, which could tolerate subsoil acidity, might extract NO₃⁻ retained in the subsoil.

Conclusions

The results demonstrated that NO₃⁻ sorption is an important phenomenon at concentrations representative of crop conditions in the soil we studied, particularly in the lower horizons. Nitrate sorption may strongly influence the distribution of NO₃⁻ in an oxisol and should be considered when studying the management of N in these soils.

Further studies will be needed to establish the soil properties for the phenomenon and its spatial distribution both within profiles and among profiles because of its importance to N management. On the one hand sorption tends to retard leaching in the soil in the region deeper than 40 cm; this could serve as a temporary storage for NO₃⁻. Thus NO₃⁻ leached out of the surface layers of the soil early in the season and temporarily stored in the sub-surface layers might be used later in the season. On the other hand, sorption may reduce N uptake and hence the benefits of retarded leaching may not always be as large as expected.

Acknowledgements

Joint publication of research done as part of a title XII Collaborative Research Support Program between EMBRAPA/CPAA, Manaus, Brazil and Cornell University, Ithaca, New York carried out at CPAA. The financial support of USAID through the Title XIII CRSP Subgrant SM-CRSP-01 from North Carolina State University, is gratefully acknowledged.

References

- Arora Y and Juo A S R 1982 Leaching of fertilizer ions in a kaolinitic ultisol in the high rainfall tropics: Leaching of nitrate in field plots under cropping and bare fallow. *Soil Sci. Soc. Am. J.* 46, 1212–1218.
- Black A S and Waring S A 1976 Nitrate leaching and absorption in a Krasnozem from Redland Bacy, Qld. I. Leaching of banded ammonium nitrate in a horticultural rotation. *Aust. J. Soil Res.* 14, 171–180.
- Black A S and Waring S A 1979 Adsorption of nitrate, chloride and sulfate by some highly weathered soils from south-east Queensland. *Aust. J. Soil Res.* 17, 271–282.

- Bohn H L, McNeal B L and O'Conner G A 1979 *Soil Chemistry*. Wiley-Interscience, New York. 329 p.
- Cahn M D 1991 Cation and nitrate leaching in an oxisol of the Brazilian Amazon. Ph. D. Thesis, Cornell University Library, Cornell Univ., Ithaca, NY.
- Hingston F J, Posner A M and Quirk J P 1942 Influence of potassium chloride on nitrification in Bedford silt loam. *J. Soil Sci.* 23, 117-192.
- Jones M J 1976 Water movement and nitrate leaching in a Nigerian savanna soil. *Expl. Agric.* 12, 69-79.
- Keeney D R and Nelson D W 1982 N-inorganic forms. *In* *Methods of Soil Analysis, Part 2*. Eds. A L Page, R H Miller and D R Keeney. *Agronomy* 9, pp 643-698. Madison, WI.
- Kinjo T and Pratt P F 1971 Nitrate adsorption. I. In some acid soils of Mexico and South America. *Soil Sci. Soc. Am. Proc.* 35, 1-36.
- Melgar R J 1989 Nitrogen utilization by annual crops in the central Amazon. Ph. D. Thesis, North Carolina State Univ., Raleigh, NC.
- Ng kee kwong K F and Deville J 1984 Nitrogen leaching from soils cropped with sugarcane under the humid tropical climate of Mauritius. *Indian Ocean. J. Environ. Qual.* 13, 471-474.
- Parmer K A, Uriyo A P and Singh B R 1980 Adsorption of nitrate and chloride in some Tanzanian andecept soils. *Agrochimica* 24, 492-499.
- Seyfried M A and Rao P S C 1987 Solute transport in undistributed columns of an aggregated tropical soil: Preferential flow effects. *Soil Sci. Soc. Am. J.* 51, 1434-1444.
- Singh B R and Kanehiro Y 1969 Adsorption of nitrate in amorphous and kaolinitic Hawaiian soils. *Soil Sci. Soc. Am. Proc.* 33, 681-683.
- Wetselaar R 1962 Nitrate distribution in tropical soils. III. downward movement and accumulation nitrate in the sub-soil. *Plant and Soil* 16, 19-31.
- Wild A and Babiker I A 1976 The asymmetric leaching pattern of nitrate and chloride in a loamy sand under field conditions. *J. Soil Sci.* 27, 460-466.
- Wong M T F, Wild A and Juo A S R 1987 Retarded leaching of nitrate measured in monolith lysimeters in south-east Nigeria. *J. Soil Sci.* 27, 460-466.