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EFFECT OF LIMING AND FERTIGATION FREQUENCIES ON NITROGEN RETENTION ON COTO CLAY

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ABSTRACT: Nitrate leaching through the soil profile can result in a significant loss of fertilizer N, and may be a source of nitrate concentration in groundwater. Highly weathered soils may exhibit substantial anion exchange capacity (AEC), which retards the movement of anions such as NO_3^- through the profile. However, AEC decreases as soil pH increases with agronomic practices such as liming. A study was conducted to determine the effect of lime application and frequency of N fertigation on NH_4^+ and NO_3^- concentrations on Coto clay. A field experiment was established at the UPR Experiment Station at Isabela, PR, using peppers as the test crop. Two lime treatments (lime or no lime) and two fertigation frequencies (weekly or bi-weekly applications) were evaluated. Soil samples were collected every two weeks at four depths and analyzed for NH_4^+ and NO_3^- by steam distillation. During the first year, probably due to spatial variability and buffering capacity of the Coto clay, the limed plots did not reach the expected pH level. Consequently, no significant differences were observed between lime treatments. No significant differences between fertigation treatments were observed either. During the second year, lime application was doubled, and pH in the limed plots increased from an average of 4.6 to approximately 6.4. Nitrogen analyses of soil and plant material from the second year is currently under way. Results are also presented from laboratory studies conducted to evaluate NO_3^- adsorption characteristics of Coto clay. Adsorption isotherms were conducted under three pH levels and nine NO_3^- solution concentrations.

INTRODUCTION

Increased NO_3^- concentrations in groundwater due to leaching from intensive crop production systems have become an environmental and economic concern (Andraski et al., 2000). High concentrations of NO_3^- in surface and groundwater can cause eutrophication of our water reserves. Also, concentrations of NO_3-N above 45 mg L^{-1} may cause serious health problems like methemoglobinemia, or "blue baby syndrome" (Spalding and Exner, 1993).

Nitrate losses from agricultural fields can be minimized by following agronomic practices to reduce erosion, leaching, and to promote a more efficient crop uptake. The capacity of the soil to adsorb or retain nitrate may contribute to reducing its movement through the soil profile (Bellini et al., 1996; Qafoku et al., 2000). Highly weathered soils may exhibit a net positive charge at low pH (anion exchange capacity), which retards the movement of anions such as NO_3^- through the profile. However, these soils are usually limed to reduce toxic levels of exchangeable Al^{3+} and improve their fertility. Liming will improve crop performance but may decrease the soil capacity to retain nitrate, thus promoting its movement to lower depths, out of the root zone.

Eick et al. (1999) evaluated the surface charge properties and nitrate adsorption capacity of four Louisiana subsoils by determining Point of Zero Net Charge and measuring nitrate adsorption isotherms, and found that net positive charge retarded NO_3^- movement significantly. Another parameter that influences anion retardation is ionic strength (Ishiguro et al., 1992; Bellini et al., 1996), with higher solution concentrations resulting in a lower retardation coefficient (Katou et al., 1996; Qafoku et al., 2000).

Studies have also shown that there are other factors that can reduce or even eliminate nitrate retention, such as the presence of phosphate (Melamed et al., 1994), sulfate or fluoride (Eick et al., 1999). A study is needed to better understand the relationship of soil chemical and physico-chemical characteristics to nitrate movement in the acid soils of Puerto Rico.

The objectives of this investigation were to determine the effect of lime application and frequency of N fertigation on NH_4^+ and NO_3^- concentrations on Coto clay and to study NO_3^- adsorption at different pH levels and nitrate concentrations.

MATERIALS AND METHODS

Field Study

A field experiment was established during March 2002, at the UPR Experiment Station at Isabela, PR, using peppers as the test crop. Two lime treatments (lime or no lime) and two fertigation frequencies [weekly (F1) or bi-weekly (F2) applications] were evaluated. The limed plots received a broadcast lime application of 7.41 tons/ha. The lime was incorporated into the soil prior to planting.

A total nitrogen rate of 225 kg/ha was applied by fertigation, using KNO_3 and urea as the fertilizer sources. The F1 treatment (weekly) received a total of 12 fertigations, and the F2 treatment received 6 fertigations in a 3-month period. Soil samples were collected from each plot every two weeks at 20-cm increments, down to 80 cm. The samples were analyzed for NH_4^+ and NO_3^- concentrations by steam distillation, after extraction with 2 M KCl and two hours' shaking time (Mulvaney, 1996).

A second field experiment was established during February 2003. Conditions were the same as those of the first year, except the amount of lime applied to the limed plots was doubled (14.82 tons/ha). This addition was to achieve a pH level closer to the recommended 6.5.

Soil Characterization

The soil at the experimental site is a Coto clay, classified as a very-fine, kaolinitic, isohyperthermic Typic Eutrustox. Samples were collected from two depths (0-20 cm and 20-40 cm) for characterization and for the adsorption study.

The samples were air dried, mechanically ground, and passed through a 2-mm sieve. Selected chemical, physical, and mineralogical properties are presented in Table 1. Soil pH readings were taken in a 1:2 soil/water ratio by using an Orion model EA 940 pH meter. Organic matter was determined with the Walkey-Black method (Nelson and Sommers, 1996). Particle size distribution was determined after fractionating the samples for mineralogical analyses. The mineralogy of the clay fraction was determined by x-ray diffraction after pretreatment using standard procedures (Kunze and Dixon, 1986). Free iron oxide content was determined by using the citrate-bicarbonate-dithionite method (Jackson et al., 1986).

Potentiometric titrations

The methodology of Marcano-Martínez and McBride (1989) and van Reij and Peech (1972) was used to determine the PZSE for the samples. For each depth 4 g air-dried soil was added to 40 ml of electrolyte solution (0.1, 0.01, and 0.001 N KCl); pH was adjusted (before reaching the final 40 ml volume) with measured amounts of HCl or KOH to achieve a range from 3 to 7. The tubes were capped and shaken twice daily for one hour over a 3-day period.

After this time the samples were centrifuged and supernatant pH was measured. The amounts of H^+ and OH^- adsorbed by the samples were determined by subtracting the amount of acid or base necessary to bring 40 ml of electrolyte solution (without soil) to the same pH.

Table 1. Selected chemical, physical, and mineralogical properties of Coto clay.

Depth (cm)	pH[a]	OM	Sand	Silt	Clay	Fe_2O_3	Mineralogy[b]
		%					
0-20	4.2	2.76	35.10	19.35	45.55	14.50	k, go, gi, i, chl
20-40	3.9	1.54	28.72	1.85	69.43	14.41	k, q, go, i, chl

[a] 1:2 soil/water ratio.

[b] k=kaolinite, go=goethite, gi=gibbsite, i=illite, q=quartz, and chl=chlorite

Batch study

To study the effect of pH on nitrate retention, three lime treatments (0, 2, and 4 g $CaCO_3$ kg^{-1}) were applied by first mixing with air-dried soil, then wetted to approximately field capacity with deionized water and incubated for 3 weeks. The samples were then re-dried and re-sieved, and final pH was measured. In the 0- to 20-cm depth, pH levels changed from 4.2 to 5.2 and 6.1, in the respective lime treatments. In the 20- to 40-cm depth, pH changed from 3.9 to 4.5 and 5.6, respectively.

For each depth and each lime treatment ten grams of soil were placed in 50 ml centrifuge tubes. Samples were washed twice with 20 ml 0.1 M KCl by shaking for two hours to determine the presence of retained NO_3^-. Immediately after washing, 20 ml of $Ca(NO_3)_2$ solution, at one of nine concentrations (zero, 1, 2, 4, 6, 8, 10, 15, and 20 $mmol_c$ L^{-1} NO_3^- - N), was added to each tube. The tubes were placed on a shaker at room temperature (25° C). After equilibrating for 2 h, the suspension was centrifuged and the equilibrium concentration of NO_3^- was determined by steam distillation.

RESULTS AND DISCUSSION

Field Study

During the first year of the field experiment (2002) great spatial variability resulted in pH levels ranging from approximately 4.1 to 5.4 in the untreated plots, and from 4.4 to 6.1 in the limed plots. No significant variation in NO_3^- nor NH_4^+ concentrations was observed between the lime and no lime treatments at depths over 20 cm. Nor was any significant difference observed between the fertigation treatments. Nitrate and ammonium concentrations did not vary significantly at depths over 20 cm (Table 2). A higher concentration of both parameters was observed at the depth of 0-20 cm.

Average nitrate concentrations at the 60- to 80-cm depth, when multiplied by bulk density (1.33 gm cm^{-3}) and average volumetric moisture content for the season (0.3 cm^3 cm^{-3}) showed solution concentrations of 46.9 mg L^{-1} and 46.1 mg L^{-1} for the lime and no lime treatments, respectively. These values are close to, but higher than, 45 mg L^{-1}, the EPA safe drinking water standard for NO_3-N (Code of Federal Regulations, 1987). Considering this vertical interval to be below the root zone, potential nitrate leaching and, consequently, groundwater contamination, should be a concern under conditions similar to those of this study.

In the second-year pH level analyses, no significant spatial variation was observed. Plots with no lime showed pH levels averaging 4.6, whereas limed plots reached an average pH of 6.5, as expected. NO_3^- and NH_4^+ analyses for this season, as well as those for nitrogen uptake by plants, are currently under way.

Table 2. Average soil NO_3^- and NH_4^+ concentrations (mg kg^{-1}) for the field study.

	Lime		No Lime	
Soil depth (cm)	NO_3^-	NH_4^+	NO_3^-	NH_4^+
0 - 20	27.2	8.5	21.2	11.9
20 - 40	14.3	5.8	12.3	7.2
40 - 60	14.2	5.4	11.3	6.1
60 - 80	10.6	5.1	10.4	7.9

Potentiometric titrations

The PZSE is the pH at which the net charge is independent of electrolyte concentration. Titration curves for different ionic strengths intersect at this common point. Figure 1 shows that there was not one exact point of intersection for the three curves in the 0- to 20-cm depth. The 0.1 N curve intersects the 0.01 N curve at a pH of approximately 3.55, and the 0.001 N curve at approximately 3.46. Both of these values are below the native pH (4.2) at this depth.

For the 20- to 40-cm depth, Figure 2 shows that the 0.1 N and the 0.01 N curves intersect at a pH of approximately 3.88. The 0.1 N curve intersects the 0.001 N curve at a value close to 3.52. The 0.01 N and the 0.001 N curves intersect at approximately 3.45. These values are also below the native pH (3.9) at this depth.

The mineralogy results (Table 1) for our soil agree with those reported by Jones et al. (1982) for the same soil. Although large quantities of high point of zero charge Fe oxides were found, the presence of organic matter, kaolinite and other low point of zero charge minerals reduced the PZSE in the samples. The greater difference between these values in the 0- to 20-cm depth may reflect the effect of higher organic matter content (Marcano-Martínez and McBride, 1989). These results are consistent with Appel et al. (2003), who reported PZSE values of 3.4-3.5 on an Oxisol from Puerto Rico.

Batch study

Observed values show that there was no NO_3^- adsorption by the Coto clay at the studied depths. Generally, greater amounts of nitrate concentrations were found in the equilibrium solution than in the original solution (Table 3). These results are opposite to those reported by other studies performed on similar soils (Ishiguro et al., 1992; Bellini et al., 1996; Katou et al., 1996; Eick et al., 1999), and suggest either (i) desorption of residual nitrate despite washing with 0.1 N KCl or (ii) microbial or enzyme activity (Kowalenko and Yu, 1996).

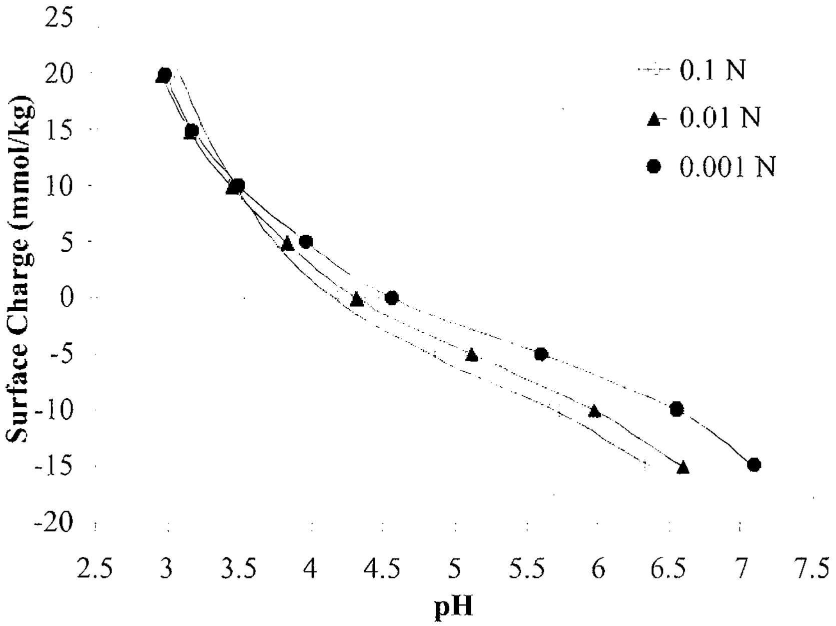

Figure 1. Potentiometric titration curves for the 0- to 20-cm depth.

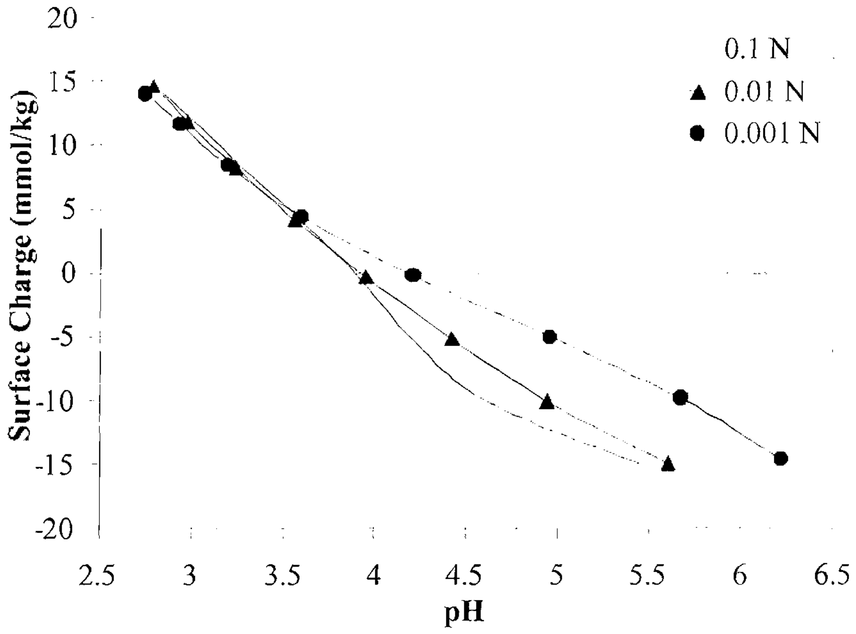

Figure 2. Potentiometric titration curves for the 20- to 40-cm depth.

Table 3. Comparison of original vs. equilibrium solution concentration of NO_3-N (mg/L).

NO_3^- sol. (mg/L N)	Depth (cm)	Lime (g/kg)	pH	eq. NO_3^- (mg/L N)	NO_3^- sol. (mg/L N)	Depth (cm)	Lime (g/kg)	pH	eq. NO_3^- (mg/L N)
0	0 - 20	0	4.2	0.00	8	0 - 20	0	4.2	10.65
		2	5.2	0.69			2	5.2	12.21
		4	6.1	0.11			4	6.1	11.67
	20 - 40	0	3.9	0.00		20 - 40	0	3.9	10.65
		2	4.5	0.22			2	4.5	11.20
		4	5.6	0.22			4	5.6	10.80
1	0 - 20	0	4.2	1.23	10	0 - 20	0	4.2	14.78
		2	5.2	0.91			2	5.2	16.16
		4	6.1	2.43			4	6.1	15.47
	20 - 40	0	3.9	1.30		20 - 40	0	3.9	12.97
		2	4.5	2.03			2	4.5	13.37
		4	5.6	1.92			4	5.6	13.41
2	0 - 20	0	4.2	2.46	15	0 - 20	0	4.2	21.74
		2	5.2	3.55			2	5.2	21.41
		4	6.1	3.30			4	6.1	21.59
	20 - 40	0	3.9	2.43		20 - 40	0	3.9	18.77
		2	4.5	2.86			2	4.5	18.88
		4	5.6	2.75			4	5.6	19.89
4	0 - 20	0	4.2	4.71	20	0 - 20	0	4.2	29.45
		2	5.2	5.94			2	5.2	30.29
		4	6.1	6.12			4	6.1	30.51
	20 - 40	0	3.9	4.35		20 - 40	0	3.9	26.70
		2	4.5	5.18			2	4.5	26.45
		4	5.6	5.14			4	5.6	27.61
6	0 - 20	0	4.2	8.41					
		2	5.2	9.78					
		4	6.1	9.42					
	20 - 40	0	3.9	7.61					
		2	4.5	8.26					
		4	5.6	8.22					

CONCLUSIONS

Low PZSEs suggest negative charge development and, therefore, repulsion of anions. A study to determine anion exchange capacity for the Coto clay at the studied depths is necessary to corroborate this conclusion. Results obtained from the field and nitrate retention studies coincide, however, and indicate little or no nitrate retention capacity for this soil, even at low pH levels. Potential nitrate leaching should be considered when establishing a management plan for the Coto clay.

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