

NITROGEN RETENTION AND MOVEMENT IN A VARIABLE CHARGE  
SOIL

By

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## RESUMEN

Para evaluar el efecto de aplicación de cal y de frecuencia de fertigación con nitrógeno en la concentración de  $\text{NH}_4^+$  y  $\text{NO}_3^-$  en un suelo Coto, se llevaron a cabo dos experimentos de campo en Isabela, PR, uno en marzo, 2002, y otro en febrero, 2003. No se observaron diferencias significativas entre los tratamientos de cal ni de fertigación en el estudio de campo. A pesar de la presencia de óxidos de hierro, que poseen un punto de carga cero alto, la presencia de otros minerales con punto de carga cero bajo, así como materia orgánica, resultaron en un punto de carga cero menor que el pH natural de este suelo. La presencia de fosfato y sulfato pudieron haber influenciado la falta de capacidad de retención de nitrato en Coto. Estos resultados coinciden con el estudio de adsorción en el laboratorio, el cual indica que ocurrió repulsión de nitrato. Se realizaron isotermas de adsorción negativa bajo tres niveles de pH y nueve concentraciones de  $\text{NO}_3^-$ . Estas muestran que la repulsión de aniones causa adsorción negativa y que nitrato puede moverse más rápido que el agua en este suelo.

Como parte del estudio de campo, se utilizaron dos métodos para estimar lixiviación de N. El análisis de percolación mostró pérdidas por lixiviación del 26% del N total aplicado como fertilizante el primer año, y 15% para el segundo año. El método de balance de N resultó en estimados que fueron casi el doble de los resultados obtenidos por percolación. Ya que con el método de percolación no se tomó en consideración el N lixiviado bajo condiciones no saturadas, y con el balance de

nitrógeno no se tomó en consideración el N en las raíces ni en los pimientos cosechados, la cantidad real de nitrógeno lixiviado debe encontrarse entre los dos estimados. Considerando que el suelo Coto es uno de alta permeabilidad, se recomienda que al establecer un plan de manejo para este suelo se tome en consideración la posibilidad de lixiviación de nitratos.

## ABSTRACT

A study was conducted to evaluate the effect of lime application and frequency of N fertigation on  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations on Coto clay. Two field experiments were established at Isabela, PR, one in March, 2002, and another in February, 2003. No significant differences were observed between lime treatments or between fertigation treatments in the field. Despite the presence of high point of zero charge iron oxides, other low point of zero charge minerals, along with organic matter content, resulted in a low point of zero salt effect in the samples. The occurrence of phosphate and sulfate may have influenced the lack of nitrate retention capacity for this soil. Results coincide with the batch studies that indicate nitrate repulsion occurs in this soil. Negative adsorption isotherms were constructed under three pH levels and nine  $\text{NO}_3^-$  solution concentrations. These show that anion repulsion causes negative adsorption and that  $\text{NO}_3^-$  may move faster than water in Coto clay.

As part of the field experiment, two methods were used to estimate nitrogen leaching. A percolation analysis suggested losses by leaching in the order of 26% of the total N applied as fertilizer the first year, and 15% the second year. A nitrogen balance approach doubled the estimated N losses from the percolation method. Since the percolation did not account for nitrogen leached under unsaturated flow conditions, and the N balance method did not account for N uptake by plant roots or fruit, the actual N leached was probably between the two estimates. Considering the high permeability of

Coto clay, potential nitrate leaching must be considered when establishing a management plan for this soil.

## TABLE OF CONTENTS

Chapter 1: Introduction .....	1
Chapter 2: Previous Literature .....	4
2.1 Nitrogen in the soil.....	4
2.2 Nitrate leaching .....	7
2.3 Soil surface charge .....	9
2.4 Anion adsorption.....	11
2.5 Nitrogen modeling .....	18
2.6 Coto clay .....	20
Chapter 3: Materials and Methods .....	22
3.1 Soil sampling and characterization .....	22
3.2 Retention studies .....	25
3.3 Field study .....	26
Chapter 4: Results and Discussion.....	35
4.1 Soil characterization.....	35
4.2 Retention study .....	48
4.3 Field results .....	534
4.4 N leaching .....	65
Chapter 5: Summary and Conclusions.....	75
Cited Literature .....	77

## LIST OF TABLES

<b>Table 1.</b> Particle size distribution of Coto clay from the Experiment Station at Isabela, PR.....	36
<b>Table 2.</b> Selected physical properties of Coto clay from the Experiment Station at Isabela, PR.....	36
<b>Table 3.</b> Selected chemical and mineralogical properties of Coto clay from the Experiment Station at Isabela, PR.....	36
<b>Table 4.</b> Mineral identification for X-ray diffractograms.....	40
<b>Table 5.</b> Measured CEC and AEC at different pH levels for the 0-20 cm and the 20-40 cm depths.....	47
<b>Table 6.</b> Linear partition coefficients, $K_p$ , and correlation coefficients, $R^2$ , for adsorption isotherms.....	53
<b>Table 7.</b> Average soil nitrate-N concentrations (mg/kg) at different soil depths, by lime level and by year.....	56
<b>Table 8.</b> Nitrate-N and ammonium-N leached during the 2002 season.....	69
<b>Table 9.</b> Nitrate-N and ammonium-N leached during the 2003 season.....	69
<b>Table 10.</b> Components of the nitrogen balance for both seasons (kg/ha).....	73

## LIST OF FIGURES

<b>Figure 1.</b> The nitrogen cycle.....	5
<b>Figure 2.</b> Field experiment site: Isabela, Puerto Rico.....	26
<b>Figure 3.</b> Experimental layout of the field, first season.....	28
<b>Figure 4.</b> Experimental layout of the field, second season.....	28
<b>Figure 5.</b> Potentiometric titration curves for the 0-20 cm depth.....	42
<b>Figure 6.</b> Potentiometric titration curves for the 20-40 cm depth.....	43
<b>Figure 7.</b> Ion adsorption curves for the 0-20 cm depth.....	45
<b>Figure 8.</b> Ion adsorption curves for the 20-40 cm depth.....	45
<b>Figure 9.</b> Original vs. equilibrium nitrate solution concentration in retention study; 0-20 cm depth.....	49
<b>Figure 10.</b> Original vs. equilibrium nitrate solution concentration in retention study; 20-40 cm depth.....	50
<b>Figure 11.</b> Adsorption isotherm for the 20-40 cm depth, at native pH.....	52
<b>Figure 12.</b> Nitrate-N concentration by depth, 3-27-02.....	57
<b>Figure 13.</b> Nitrate-N concentration by depth, 4-12-02.....	57
<b>Figure 14.</b> Nitrate-N concentration by depth, 4-26-02.....	58
<b>Figure 15.</b> Nitrate-N concentration by depth, 5-10-02.....	58
<b>Figure 16.</b> Nitrate-N concentration by depth, 5-24-02.....	59
<b>Figure 17.</b> Nitrate-N concentration by depth, 6-07-02.....	59



<b>Figure 18.</b> Nitrate-N concentration by depth, 6-21-02.....	60
<b>Figure 19.</b> Nitrate-N concentration by depth, 7-08-02.....	60
<b>Figure 20.</b> Nitrate-N concentration by depth, 2-18-03.....	61
<b>Figure 21.</b> Nitrate-N concentration by depth, 3-04-03.....	61
<b>Figure 22.</b> Nitrate-N concentration by depth, 3-17-03.....	62
<b>Figure 23.</b> Nitrate-N concentration by depth, 3-31-03.....	62
<b>Figure 24.</b> Nitrate-N concentration by depth, 4-14-03.....	63
<b>Figure 25.</b> Nitrate-N concentration by depth, 4-28-03.....	63
<b>Figure 26.</b> Nitrate-N concentration by depth, 5-14-03.....	64
<b>Figure 27.</b> Nitrate-N concentration by depth, 5-30-03.....	64
<b>Figure 28.</b> Estimated percolation past the root zone during the 2002 season.....	65
<b>Figure 29.</b> Estimated percolation past the root zone during the 2003 season.....	66
<b>Figure 30.</b> NH <sub>4</sub> -N concentrations (mg/kg) at the 60-80 cm depth, 2002.....	67
<b>Figure 31.</b> NO <sub>3</sub> -N concentrations (mg/kg) at the 60-80 cm depth, 2002.....	67
<b>Figure 32.</b> NH <sub>4</sub> -N concentrations (mg/kg) at the 60-80 cm depth, 2003.....	68
<b>Figure 33.</b> NO <sub>3</sub> -N concentrations (mg/kg) at the 60-80 cm depth, 2003.....	68
<b>Figure 34.</b> Comparison of estimated N losses by leaching by season; percolation method vs. N balance method.....	71

**Figure 35.** Nitrogen uptake by plants during the 2002 season.....73

**Figure 36.** Nitrogen uptake by plants during the 2003 season.....74

## LIST OF APPENDICES

<b>Appendix A.</b> X-ray diffractograms obtained with mineralogy analyses.....	85
<b>Appendix B.</b> Pictures of field experiment.....	88
<b>Appendix C.</b> Tabular data from the retention study.....	91
<b>Appendix D.</b> Nitrate adsorption isotherms.....	94
<b>Appendix E.</b> Weather data used to estimate percolation.....	97
<b>Appendix F.</b> Evaluation of percolation and nitrogen leaching from a sweet pepper crop grown on an Oxisol in northwest Puerto Rico (Harmsen et al., 2003).....	104

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## *Chapter 1*

### **INTRODUCTION**

Excessive use of nitrogen fertilizers has been identified as a significant source of groundwater contamination (Spalding and Exner, 1993; Smith et al., 1999; Andraski et al., 2000). Increased nitrogen concentration in surface and groundwater due to intensive crop production has become an environmental and economic concern.

Being an anion, nitrate ( $\text{NO}_3^-$ ) is not adsorbed by most soils and its leaching is difficult to control in soils that have rapid drainage. Nevertheless, studies have shown that movement and transport of some anions is retarded on highly weathered soils, since they exhibit a substantial Anion Exchange Capacity (AEC) (Ishiguro et al., 1992; Bellini et al., 1996; Katou et al., 1996; Qafoku et al., 2000). These studies have also shown that liming naturally acid soils and subsoils is associated with a decrease in AEC. This reduction results in less nitrate retention, which makes it more susceptible to leaching.

Other studies have shown that there are other factors that can reduce or even eliminate nitrate retention. Melamed et al. (1994) demonstrated that application of phosphate reduced anion retention by increasing soil surface negative charge. Therefore, liming and fertilization will affect nitrate

movement and balance in these soils. Further studies are needed to better understand the effect of liming on nitrogen movement and crop uptake in acid soils in the tropics. As a preliminary step, this study focused on the characterization of nitrogen retention in a variable charge soil in Puerto Rico.

Only a limited number of samples can be collected from the field during a study. This could be a source of experimental error, since there will be some gaps between data points, in both time and space. This type of error may be decreased by use of a computer model, which, in conjunction with the field study, may provide continuity between data points. Computer models are also useful in helping us better understand complex systems by integrating all the information obtained in a study. They can also be used to predict results in real-world systems and to optimize selected system variables (like nitrogen application and frequency or lime levels).

The relationship between soil chemical parameters and transport parameters in variable charge soils is not well documented (Bellini et al., 1996). Therefore, the prediction of anion movement through these soils in crop simulation models is still empirical in nature (Bowen et al., 1993). This study will provide specific information on nitrate movement in a variable charge soil for consideration in a solute transport model.

The goal of this project was to evaluate nitrate movement and retention in a highly weathered soil. The specific project objectives were to:

1. Evaluate the Coto clay for soil characteristics that may affect nitrate adsorption.
2. Study nitrate adsorption isotherms at different pH levels and nitrate concentrations.
3. Evaluate the distribution through the soil profile of nitrate and ammonium in a pepper field at different lime and fertigation levels, and estimate ammonium and nitrate leaching.



## *Chapter 2*

### **PREVIOUS LITERATURE**

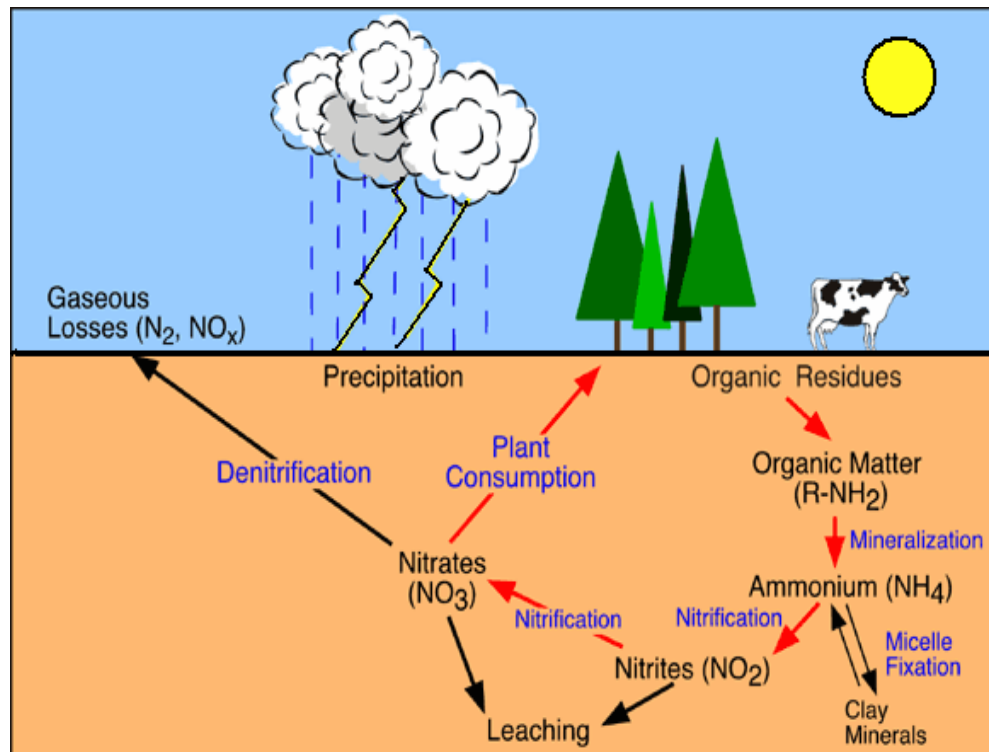
#### **2.1 Nitrogen in the soil**

Understanding the behavior of nitrogen in the soil system helps to maximize crop production while reducing the impacts of N fertilization on the environment. Nitrogen can be found in soil in various forms, with 95% or more present as organic N (Tisdale et al., 1993). In the inorganic nitrogen forms nitrate ( $\text{NO}_3^-$ ) or ammonium ( $\text{NH}_4^+$ ), it can move into a soil profile or be taken up by plants.

The amount of a specific form of nitrogen present at a given time depends on physical, chemical, biological and environmental factors that affect N transformations and losses from the soil. Some of these factors are soil water content, pH, temperature, soil aeration, microbial activity, presence of plants, liming, and applied fertilizers.

A diagram of the nitrogen cycle is illustrated in Figure 1. It shows the ways nitrogen enters the soil, the main processes by which it is transformed, and the ways it is lost. Nitrogen can be added to the soil through plant and animal residues, as inorganic fertilizer, or through rainwater containing  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . It may also be fixed through electrical, combustion, industrial, and

biological processes by which molecular nitrogen ( $N_2$ ) is combined with  $H_2$  or  $O_2$ . Once in the soil, N can undergo different transformations through the processes of mineralization, immobilization, nitrification, denitrification, volatilization, and fixation (Davidson et al., 1978).



**Figure 1.** The nitrogen cycle (taken from Pidwirny, 2003)

Mineralization, the conversion of organic N to  $NH_4^+$ , occurs through the activity of heterotrophic organisms. It is favored by high temperatures,

adequate soil moisture and an adequate  $O_2$  supply. Immobilization is the conversion of inorganic nitrogen to organic N. Microorganisms will immobilize  $NH_4^+$  or  $NO_3^-$  in the soil if there is a high C:N ratio in decomposing organic matter (Davidson et al., 1978).

Nitrification is the conversion of  $NH_4^+$  to  $NO_2^-$  and, finally, to  $NO_3^-$ . It is favored by a large supply of ammonium, pH levels in the range of 4.5 to 10, the presence of oxygen, soil moisture contents equal to or less than  $1/3$  bar matric suction, and temperatures between  $30^\circ$  to  $35^\circ$  C. It occurs rapidly, and is very common, since the environmental factors that encourage plant growth also benefit the nitrifying organisms.

Nitrogen can be lost from waterlogged or flooded soils by denitrification (Harmsen et al., 1991). This is a process that takes place under anaerobic conditions. The lack of oxygen may cause certain bacteria to shift from aerobic respiration to obtaining their  $O_2$  from  $NO_2^-$  and  $NO_3^-$ , releasing the gaseous forms  $N_2$  and  $N_2O$ .

Losses by volatilization of ammonia ( $NH_3$ ) usually happen from surface application of ammonium-N fertilizers. This process is bolstered by high pH levels; therefore it is negligible in acid or neutral soils (Burt et al., 1998). Another possible way to lose N is ammonium fixation, which may happen in the presence of expandable clay minerals.

Nitrogen becomes a concern to water quality when it is lost in the form of nitrate. When water moves through the soil profile it may carry nitrate with it, allowing it to reach ground water (Burt et al., 1998). This process is called leaching. Conditions that promote percolation also increase  $\text{NO}_3^-$  leaching, since it is very soluble in water and highly mobile. High nitrate concentrations in the soil, along with intense precipitation or excess irrigation in a highly permeable soil will result in leaching losses.

## **2.2 Nitrate leaching**

In 1974, Congress passed the Safe Drinking Water Act, which requires the U.S. Environmental Protection Agency (EPA) to determine safe levels of chemicals in drinking water. These are based on potential health risks. The Maximum Contaminant Level (MCL) for nitrogen as nitrate allowed in drinking water is 10 mg/L (USEPA, 1976). Excessive levels of nitrate in drinking water may cause serious health effects such as methemoglobinemia (also referred to as blue baby syndrome), stomach cancer, and depression of the cardiovascular, central nervous and respiratory systems. In addition, high nitrate levels contribute to the eutrophication of surface waters. Eutrophication is the process by which high nutrient concentrations in aquatic ecosystems stimulate blooms of algae (e.g., phytoplankton), which often leads to low oxygen (hypoxia) or no oxygen

(anoxia) in bottom waters due to the decomposition of these algal blooms (Smith et al., 1999). This results in a high rate of fish death and a decrease in water quality (Forsberg, 1998).

Improper nitrogen fertilizer management has been identified as a major contributor to excess nitrate concentrations in ground water. Potassium nitrate and ammonium nitrate, both widely used as fertilizers, are the primary inorganic nitrates which may contaminate drinking water (US Environmental Protection Agency, 2004).

A study by Andraski et al. (2000) illustrated a direct relationship between  $\text{NO}_3^-$  loss by leaching and N application rates that exceed crop needs. They established two trials of four cropping-manure management systems representative of farming practices used for corn production in Wisconsin. They applied treatments that consisted of seven N rates (0 – 204 kg N/ha) that remained constant throughout the four different management systems, regardless of the initial soil nitrate-N contents. Results showed that nitrate leaching estimates, based on water budget and soil water  $\text{NO}_3^-$  concentrations, ranged from 3 to 88 kg/ha. Average losses at the highest N rate were 47 and 63 kg  $\text{NO}_3\text{-N/ha}$  for the first and second trial respectively. The difference is related to excess precipitation following treatment establishment and fertilizer N applications for the second trial.

A study in north-central Puerto Rico indicated that nitrate concentrations within the Laguna Tortuguero ground-water drainage basin were close to or above 10 mg/L  $\text{NO}_3\text{-N}$  (Conde-Costas and Gómez-Gómez, 1998). Fertilizer used for pineapple cultivation, as well as septic tank effluents from rural communities, were suggested as the main sources of nitrate. The study also indicates that approximately 90% of the nitrogen applied as fertilizer in pineapple fields was in transit in the vadose zone, and would eventually reach the groundwater system.

In 1990 The Health Department of Puerto Rico closed several drinking water wells in the Manati area due to nitrate levels exceeding 10 mg/L of  $\text{NO}_3\text{-N}$  (Cabán, 1990). The US Geological Survey (1999) created a program that had among its objectives to conduct studies to determine the amount of nitrate in storage in the vadose zone and its rate of movement toward the water table in both unsewered communities and agricultural areas with different hydrogeological conditions.

### **2.3 Soil surface charge**

Soils in the humid tropics cover almost 22% of the earth's surface (Appel, 2003). These soils, which include Oxisols, Ultisols, Andisols, and acid Alfisols, are dominated by amphoteric (variable charge) minerals and amorphous colloids. This means that, depending on soil pH, net surface

charge in these systems can be positive, negative, or zero. For these soils in which surface charge is pH dependent, the zero point of charge (ZPC) is defined as the pH value at which net particle charge is zero (Parks and de Bruyn, 1962).

The point of zero salt effect (PZSE) and the point of zero net charge (PZNC) are the most common methods of determining ZPC. The PZSE (Parker et al., 1979) is the pH value at which net proton surface charge density is unaffected by differences in ionic strength. It is often defined as the pH value at which acid-base titration curves for varying ionic strengths crossover. The PZNC is the pH value at which cation exchange capacity (CEC) equals anion exchange capacity (AEC).

Several studies have been conducted to compare potentiometric titration (PZSE) to ion adsorption (PZNC) techniques for determining point of zero charge in soils and pure minerals (van Reij and Peech, 1972; Hendershot and Lavkulich, 1983; Marcano-Martínez and McBride, 1989). In general, these have reported that there is no good correlation between the two measures.

Marcano-Martínez and McBride (1989) attributed this difference to the presence of permanent negative charge colloids in the soil system. Van Reij and Peech (1972) proposed that strongly adsorbed  $\text{Al}^{3+}$  remains on permanent negative charge sites in the system through the potentiometric

titration method, as opposed to its displacement during ion adsorption measurements. Another explanation may be the differences in pH where a balance exists between the adsorption of  $H^+$  and  $OH^-$  (potentiometric titration) and the anion and cation of an electrolyte (ion adsorption) (Hendershot and Lavkulich, 1983).

## **2.4 Anion adsorption**

Adsorption has been defined as the partitioning of a dissolved species onto a solid surface (EPA, 1999). Adsorption processes determine the amount of nutrients and other chemicals retained on the soil, affecting their transport. The forces responsible for these processes include physical forces (such as the relatively weak Van der Waals force), hydrogen bonding, electrostatic bonding, and coordination reactions (Tan, 1982).

Anions that are electrostatically and indifferently attracted to positive charges on soil surfaces are referred to as “non-specifically adsorbed anions”. Their adsorption is considered physical and reversible, since there is no electron transfer or sharing between ion and soil surface. Nitrate falls into this category. Anions that are strongly adsorbed at specific sites on the soil surface, forming a chemical bond with the surfaced group, are referred to as “specifically adsorbed anions” (Greenland and Hayes, 1981). These reactions involve coordinate covalent bonding, and are very stable.



On the other hand, negative adsorption of anions (or anion exclusion) occurs at colloidal surfaces that have a negative charge. Anions are repelled from the surface, producing two regions in the aqueous solution. Near the surface the solution is relatively depleted of the ion. A corresponding region, far from the surface, is relatively enriched in the ion (Sposito, 1984).

To study ion adsorption in soils the two most commonly used methods are batch tests and flow-through column experiments. Batch tests are easy to prepare and consist of mixing the soil with a solution containing a known concentration of the element of interest for a specified period of time (enough for equilibrium to be reached). The solution is then separated from the solid, and the concentration of the element remaining in the solution is measured. The difference in concentration is the amount adsorbed to the soil. Plots of the solute concentration per unit mass in the sorbed phase versus the solute concentration in the aqueous phase, under equilibrium conditions, are called isotherms. These are usually presented using the Langmuir, Freundlich, or linear isotherm equations (Healy, 1990).

The Langmuir equation is characterized by a decreasing slope as concentration increases, assuming there is a fixed number of adsorption sites and that vacant sites decrease as the adsorbent becomes covered. It can be expressed as:

$$q = K_1 C_b / (1 + K_1 C) \quad (1)$$

where

$q$  = amount of adsorption (adsorbate per unit mass of adsorbent)

$K_1$  = constant related to binding strength

$C$  = equilibrium, or, final, adsorptive concentration in solution

$b$  = maximum amount of adsorbate that can be adsorbed

The Freundlich equation, on the other hand, does not predict an adsorption maximum and can be expressed as:

$$q = K_d C^{1/n} \quad (2)$$

where  $q$  and  $C$  were defined previously,

$K_d$  = distribution coefficient

$n$  = correction factor

If  $n = 1$ , then the relationship becomes linear, and can be described by the equation:

$$q = K_p C \quad (3)$$

where  $q$  and  $C$  were previously defined,

$K_p$  = partition coefficient

A partitioning mechanism is usually suggested by a linear adsorption isotherm, and  $K_p$  provides a measure of the ratio of the amount of material adsorbed to the amount in solution.

Column experiments provide a more realistic simulation of field conditions and consist of passing a solution with a known concentration of

the element of interest through a soil column. The outflow from the end of the column is collected and analyzed, and plots of the outflowing solution's solute content vs. time are called breakthrough curves (BTC). The effect of adsorption on solute transport can be characterized by a dimensionless parameter known as the retardation factor or the retardation coefficient (R), which can be defined as the ratio of the velocity of the water moving through the soil to the contaminant velocity (Freeze and Cherry, 1979).

In variable charge soils, pH is a very important factor affecting movement of anions through the soil profile. These soils have the potential to adsorb anions and retard their movement to groundwater. A column study done on a very acid Ultisol from Georgia showed that raising the pH by applying lime decreased the soil AEC and the retardation coefficient for nitrate (Bellini et al., 1996). They found that liming with 2.08 g  $\text{Ca}(\text{OH})_2/\text{kg}$  of soil reduced the retardation coefficient (R) from 2.39 (at pH 4.26) to 1.12 (at pH 6.56). Increasing the lime level also affected the Breakthrough Curve (BTC) while leaching with a  $\text{CaCl}_2$  solution, shifted the curve to the left toward that for a non-anion-adsorbing soil.

Bellini et al (1996) also tested the effect of electrolyte concentration on R. The soils were leached with solutions of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{CaCl}_2$  at four concentrations and found that higher concentrations resulted in lower R.

Nevertheless, this second experiment was conducted only on untreated soil and was not replicated.

Similar results were obtained by Ishiguro et al. (1992) in a column study on an Andisol from Japan. They applied different concentrations of a  $\text{SrBr}_2$  solution to the soils after having them leached with a  $\text{CaCl}_2$  solution. The experiment was conducted at different pH levels (4.2 – 7.65), and under saturated and unsaturated conditions. At lower pH, and also at lower solution concentrations, movement of bromine through the soil was significantly slower. They found that soil AEC decreased and CEC increased as pH increased, and both of them increased as the total concentration increased.

In order to prove that the relationship between AEC and R holds for a variety of soils, Qafoku et al. (2000) conducted a column study with sixteen variable charge subsoils from Georgia, South Africa, Australia, Sumatra, Japan, and Hawaii. They applied four lime treatments and four different concentrations of  $\text{Ca}(\text{NO}_3)_2$  leaching solution in order to create different AEC's in the subsoils. Their results coincided with previous findings: increasing either pH levels or leaching solution concentrations reduced  $\text{NO}_3^-$  retardation.

Qafoku et al. (2000) calculated  $\text{NO}_3^-$  adsorption in units of mmol/kg in an air-dried soil and the change in molarity of input solution attributed to adsorption in units of mmol/L. The isotherms obtained appear linear in the

range of concentrations used in this experiment (5 to 30 mmol/L). However, if they are forced to pass through the origin (based on the assumption that when  $\text{NO}_3^-$  concentration in the solution is zero, the amount of  $\text{NO}_3^-$  adsorbed is also zero) the two isotherms at pH 4.26 and 4.45 appear to be curvilinear near the origin. Thus, they concluded that increasing subsoil pH would affect both the amount of nitrate adsorbed and the slope of the isotherm curves.

The experiment was conducted with  $\text{NO}_3^-$  concentrations starting at 5 mmol/L and with only three other different concentrations. Using a greater number of different concentrations between 0 and 5 mmol/L may provide a more accurate shape of the curves of the adsorption isotherms.

Another factor that affects the mobility of anions through the soil is the addition of other anions. Melamed et al. (1994) investigated how adsorbed phosphate affected the transport of bromine through Oxisol soil columns. Phosphate is specifically adsorbed by Fe and Al oxides, increasing the net negative charge of oxide surfaces. This study showed that phosphate applications reduced anion retention by increasing the negative surface charge of the soil by 0.7 – 1.1 mmol<sub>c</sub> per mmol of P added.

Eick et al. (1999) evaluated the surface charge properties and nitrate adsorption capacity of four acid subsoils in Louisiana. They evaluated Point of Zero Net Charge and conducted nitrate adsorption isotherms on untreated

and chloride-saturated soils. Nitrate adsorption was shown to relate to net positive charge in the soil. This study demonstrated that acid subsoils high in variable charge minerals retarded  $\text{NO}_3^-$  movement significantly.

Eick et al. (1999) also found that untreated soils had reduced nitrate adsorption at low concentrations due to the presence of sorbed sulfate or sorbed fluoride. At low concentrations nitrate does not effectively compete for exchange sites with sulfate and fluoride, which are retained more strongly.

Other studies have observed the effect of relative adsorption on anion transport. Gvirtzman and Gorelick (1991) evaluated transport velocities of tritium, chloride and sulfate on Israeli soils. They found that the anions traveled at approximately twice the velocity of tritium, which was used as a tracer. This result was attributed to anion exclusion restricting the number of active pore networks available for anion transport. Since anions were excluded from small pores, anion transport is restricted to the larger pores.

Bradford et al. (2003) carried out column experiments to evaluate transport behavior of negatively charged colloids through soils. They developed numerical models indicating that only a portion of pore space is accessible to mobile colloid particles. These colloids will move through larger pores and, therefore, participate in the more conductive ranges of pore water velocity, traveling faster than a conservative solute tracer.

## 2.5 Nitrogen modeling

Given the increasing emphasis placed on nitrogen movement in the soil and the many factors involved in its mobility and transformations, computer simulation models can be useful management tools. Several of these models have been developed to calculate nitrogen budgets, transformations and movement under varying environmental conditions. However, they have typically considered only the major N reactions.

Bowen et al. (1993) conducted a study on an Oxisol in central Brazil using the N submodel of CERES-Maize. They tested the submodel for its ability to simulate N mineralization, nitrate leaching, and N uptake by maize. In order to obtain more realistic results, the researchers modified the model to account for delayed leaching due to nitrate retention in the subsoil. They defined the fraction of total nitrate in a layer ( $NS_i$ ) that is in solution and can move from one layer to the next with the downward flow of water:

$$NS_i = 1/R = 1 / [1 + (k_i \rho_i / \theta_i)] \quad (4)$$

where

$R$  = retardation factor

$k_i$  = estimated adsorption coefficient (nitrate adsorbed/nitrate in solution;  $\text{cm}^3/\text{g}$ ) for layer  $i$

$\rho_i$  = bulk density ( $\text{g}/\text{cm}^3$ ) for layer  $i$

$\theta_i$  = volumetric water content ( $\text{m}^3/\text{m}^3$ ) for layer  $i$  at the drain upper limit.

The modified model provided a more accurate simulation of inorganic N in the soil profile, better predictions of N uptake and improved the overall fit of simulated to observed data. Nevertheless, the researchers stated that further work is needed to determine the importance of nitrate retention in other soils and how best it might be described in a crop simulation model.

Harmsen et al. (1991) modified the VS2DT model to simulate reactive nitrogen transport. The new model was referred to as VS2DNT. It is two-dimensional and assumes nitrate and ammonium to be mobile, organic nitrogen immobile. Comparison of the initial run of the model and observed nitrate concentration in the soil resulted in overestimation in lower layers and underestimation in the top layer. When a value of  $K_d = 0.55 \text{ cm}^3/\text{g}$  for nitrate was used in the 0-10 cm layer, a more realistic result was obtained.

Simunek et al. (1999) developed HYDRUS-2D, a model for simulating water, heat and multiple solute movements in two-dimensional variably saturated media. Although this model has the ability to solve sophisticated problems, it still handles nitrogen transport as a sequential first-order decay chain reaction, whereas the complete nitrogen cycle is a multidirectional chain.



A study is needed so that models like these can be modified to solve multidirectional chain reactions. Modifications should also take into account pH-dependent reactions such as anion adsorption. This would provide a better understanding of the relationship of liming to N movement and crop uptake in the acid, variable charge soils of Puerto Rico and other subtropical and tropical regions.

## **2.6 Coto clay**

The Coto series consists of very deep, well drained, moderately permeable soils (Soil Survey, 2004). The soil is classified as a very-fine, kaolinitic, isohyperthermic Typic Eutruxox. It is distributed through the North-central and Northwestern coastal plains of Puerto Rico. The series is of moderate extent, with about 13,000 acres. In this area of Puerto Rico, the mean annual precipitation is about 69 inches and the mean annual temperature is about 25°C.

This soil was formed from volcanic and plutonic rocks in the mountainous interior of Puerto Rico (Beinroth, 1982). The volcanic and plutonic core of central Puerto Rico experienced an uplift during the Early Miocene. Major streams quickly incised valleys, carrying large amounts of sediment northward from the interior to the newly emerged coastal limestone and karst formation. These were then gradually deposited into developing

karst depressions and intrakarst plains. The clay and quartz residuum resulted from weathering of these materials during this long time span.

According to the Soil Survey (2004), there are no other known series in the same family. The Bayamon, Catalina, Cotito, Delicias, Hanamaulu, Kapaa, Kunuweia, Lawai, Makopili, Matanzas, Nipe, Pooku, Puhi, and Rosario series are similar soils in related families. The Bayamon and Delicias soils are more strongly weathered than Coto. The Catalina soils are redder, and have clay mineralogy dominated by iron oxides. The Cotito, Matanzas, and Puhi soils have base saturation values higher than 35 percent in all parts of the oxic horizon. The Hanamaulu, Lawai and Makopili soils have an umbric surface horizon. The Kapaa and Pooku soils have sheets that contain 30 percent or more gibbsite. The Kunuweia and Nipe soils are extremely weathered and have much lower cation retention values. The Rosario soils have serpentine rock within 40 inches of the surface.

Of the mentioned series, only Bayamon, Catalina, Cotito, Delicias, Matanzas, Nipe, and Rosario are present in Puerto Rico. Together with Coto, which covers 1.3% of the island's surface, they account for 15% of the area of Puerto Rico. The others are present in Hawaii.

### *Chapter 3*

## **MATERIALS AND METHODS**

### **3.1 Soil sampling and characterization**

Composite samples of Coto clay were collected at the Isabela Experiment Station on January, 2002, 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. Soil pH readings were taken in a 1:2 soil/water ratio using an Orion model EA 940 pH meter. Soil organic matter content was determined by the Walkey-Black carbon oxidation method (Nelson and Sommers, 1996). Free iron oxides content was determined using the citrate-bicarbonate-dithionite method (Jackson et al., 1986).

Exchangeable nitrate and ammonium were determined by steam distillation after extraction with 2M KCl (Mulvaney, 1996). Total nitrogen was determined by the Kjeldahl method (Bremner, J. M., 1996). Organic nitrogen was calculated by subtracting inorganic nitrogen from the total N.

Available phosphorus was measured colorimetrically after extraction with Bray No 1 extracting solution (Olsen and Sommers, 1982). Sulfate content was determined indirectly by adding an accurately measured excess

of barium chloride solution to the sulfate solution after extraction with water from the soil (Dunk, R. et al 1969). The unreacted excess barium was determined by atomic adsorption, and used to calculate sulfate concentration.

Point of Zero Net Charge, Anion Exchange Capacity, and Cation Exchange Capacity were determined following Zelazny et al., 1996. Soils were saturated with KCl. Either KOH or HCl was used to adjust the pH to achieve a range from 3 to 6. Subsequently, the adsorbed  $K^+$  and  $Cl^-$  were replaced by  $Na^+$  and  $NO_3^-$  in 0.5 M  $NaNO_3$  solution. Potassium was determined by atomic absorption. Chlorine was measured indirectly (Ezell, 1967) after precipitating it with a known excess of silver. The concentration of unreacted silver was determined by atomic absorption.

The methodology of Marcano-Martinez and McBride (1989) and van Reij and Peech (1972) was used to determine the PZSE for the samples. Forty (40) ml of electrolyte solution (0.1, 0.01 and 0.001 N KCl) were added to 4g air-dried soil. Measured amounts of HCl or KOH were added to adjust pH (before reaching the final 40 ml volume) 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. Acid-base titration curves were developed

Particle size distribution was determined by the centrifuge method (Jackson, 1956) after fractionating the samples for mineralogical analyses. Specific surface was determined using the Ethylene Glycol Monoethyl Ether (EGME) method (Carter et al., 1986). In this procedure, a soil sample is saturated with EGME. Excess EGME is then removed in a vacuum desiccator. The assumptions here are that a monomolecular layer of EGME is left covering the soil surface, and that the area of sample surface covered by a molecule of EGME is known. The results of the test are expressed as Specific Surface Area (SSA), which describes the surface area/unit mass of dry soil with units of  $\text{m}^2/\text{g}$ . The mineralogy of the clay fraction was determined by x-ray diffraction using a Siemens D5000 X-ray diffractometer.

Aggregate stability was determined using a wet sieving method following Kemper and Rosenau (1986). Bulk density ( $\rho_b$ ) was determined from undisturbed core samples (Blake and Hartge, 1986). Particle density was determined using the picnometer method (Blake and Hartge, 1986). Porosity was calculated using the bulk density and particle density results (Danielson and Sutherland, 1986), using the equation:

$$\text{Porosity (\%)} = (1 - \text{bulk density/particle density}) 100. \quad (5)$$

### 3.2 Retention studies

To study the effect of pH and solution ionic concentration on nitrate retention, three lime treatments (0, 2, and 4 g  $\text{CaCO}_3/\text{kg}$ ) were established. The liming treatments were mixed 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 0-20 cm depth pH levels changed from 4.2 to 5.2 and 6.1, in the respective lime treatments. In the 20-40 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  $\text{NO}_3^-$ . Immediately after washing, 20 ml of  $\text{Ca}(\text{NO}_3)_2$  solution, at one of nine concentrations (0, 1, 2, 4, 6, 8, 10, 15, and 20 mmol/L  $\text{NO}_3^- - \text{N}$ ), was added to each tube. The tubes were placed on a shaker at room temperature (25°C). After equilibrating for 2 h, following Eick et al. (1999), the suspension was centrifuged and the equilibrium concentration of  $\text{NO}_3^-$  was determined by steam distillation.

### 3.3 Field study

Two field experiments were established at the UPR Experiment Station at Isabela, located at the northwest of Puerto Rico (Figure 2). The first one was established during March, 2002, and the second during January, 2003.

Before establishing the first year study, soil samples were taken from three sites within the Experiment Station that had not been limed in the previous two years. Three repetitions of each sample were used to measure pH levels. The site with the lowest average pH (4.2 at the 0-20 cm depth) was chosen to ensure naturally acid conditions.



**Figure 2.** Field experiment site: Isabela, Puerto Rico

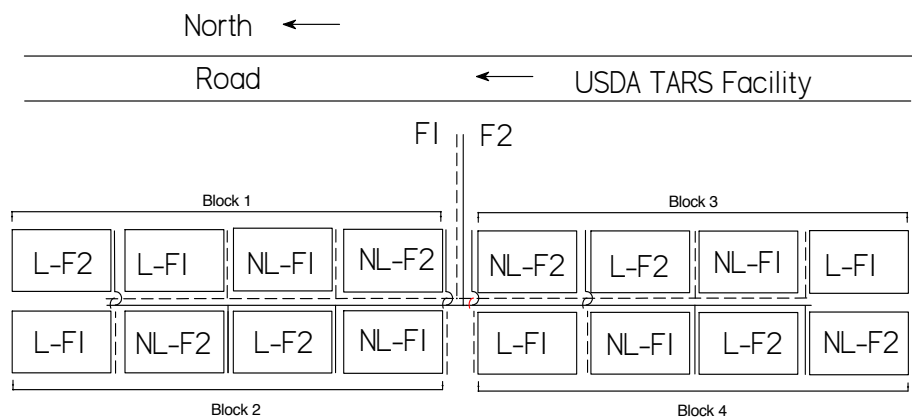
### ***Treatments***

Two lime levels (L = lime, and NL = no lime) and two fertigation frequencies (F1 = weekly fertigation, and F2 = biweekly fertigation) were evaluated. To determine the amount of lime needed to raise the pH of the limed plots to an approximate value of 6.5 a soil-lime incubation study (Sims 1996) was performed.

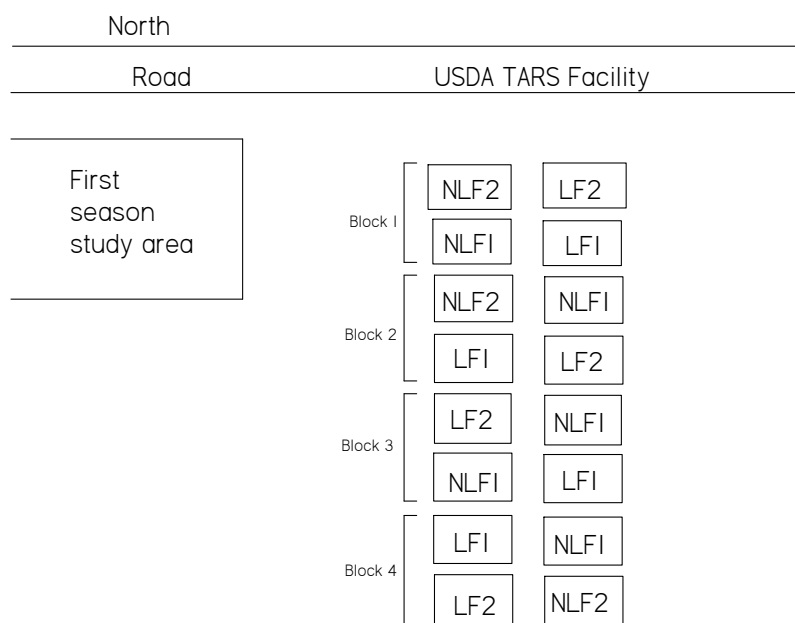
The first year, based on the incubation study, limed plots received a broadcast lime application of 7.41 tons/ha, which was incorporated to the soil prior to planting. However, this did not raise pH levels enough under field conditions. For the second year experiment the amount of lime applied to the limed plots was doubled (14.82 tons/ha). This was done to achieve a pH level closer to the recommended 6.5.

Figure 3 shows the experimental layout of the field study for the first season (2002). Figure 4 shows the layout for the second season (2003). Each site, which measured 0.1 ha, was divided into four blocks. This was done to account for possible differences due to natural slopes in the field. Each block was divided into four plots, one for each treatment, for a total of sixteen plots. The plot size was 67 m<sup>2</sup>. Each plot consisted of four beds, 1.83 m apart, covered with plastic (silver side exposed).





**Figure 3.** Experimental layout of the field study, first season.



**Figure 4.** Experimental layout of the field, second season.

Two rows of sweet peppers (*Capsicum annuum*) were planted per bed. The peppers were transplanted from March 11 through the 13<sup>th</sup> in 2002 and from January 27 through the 28<sup>th</sup> in 2003. Planting distance between rows was 91 cm, and 30 cm within rows. Plant density was approximately 37,000 plants per hectare. Periodic pesticide applications were made to control weeds and insects affecting crop growth.

For each year there was an initial granular application of triple super-phosphate of 224 kg/ha and 80 kg/ha of 10-10-10 fertilizer. Two fertilizer sources were used to provide potassium and nitrogen requirements for pepper:  $\text{KNO}_3$  (13% N, 44%  $\text{K}_2\text{O}$ ) and urea (46% N). These were injected through the drip irrigation system. The total amount of nitrogen applied during the season was 225 kg/ha.

The F1 treatment (weekly applications) received 12 fertigations with 1.47 kg of urea per plot and the F2 treatment (biweekly applications) received 6 fertigations with 2.94 kg per plot in a 3 month period. Total weekly  $\text{KNO}_3$  applications were the same for both treatments (4.48 kg per plot). This was done to prevent the introduction of a K variable in the experiment.

### ***Soil data***

After transplanting, soil samples were collected bi-weekly at 20 cm increments, down to an 80 cm depth from each plot to be analyzed for gravimetric moisture content. After moisture content by weight was determined it was multiplied by bulk density and divided by the density of water ( $1 \text{ g/cm}^3$ ) to convert moisture content to a volume basis. Exchangeable ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) concentrations were analyzed by steam distillation, after extraction with 2 M KCl and two hours shaking time (Mulvaney, 1996). This was done to evaluate N distribution through the soil profile for each treatment.

### ***Plant data***

Each date in which soil samples were collected one plant from each plot was harvested for growth data and nitrogen uptake analysis. Root depth was measured before collecting the plant. Plant samples, without the roots, were oven dried at  $70^\circ\text{C}$ , weighed and mechanically ground. Nitrogen concentration was determined (Horwitz, 1977), and N uptake ( $N_{\text{up}}$ ) (in kg of N per hectare) was calculated by the following relationship:

$$N_{\text{up}} = N_c P_{\text{dw}} \quad (6)$$

where

$N_c$  = measured nitrogen concentration (kg/kg)

$P_{\text{dw}}$  = plant dry weight (kg/ha)

This information was later used to perform a nitrogen balance.

### ***Nitrogen leaching***

Two approaches were used to estimate nitrogen leaching (nitrate plus ammonium). The first estimate was obtained by multiplying the daily percolation flux through the soil profile by the measured concentration of nitrogen within the 60-80 cm depth of soil (Harmsen et al., 2003). This depth was considered to be below the root zone based on bi-weekly measurements of root depth, since no root growth was found at this vertical interval. Nitrate and ammonium leaching was estimated by using the following equations:

$$L_{NO_3} = 0.01 \rho_b NO_3 PERC/\theta_v \quad (7)$$

$$L_{NH_4} = 0.01 \rho_b NH_4 PERC/\theta_v \quad (8)$$

where

$L_{NO_3}$  = nitrate leached below the root zone (kg/ha)

$L_{NH_4}$  = ammonium leached below the root zone (kg/ha)

$\rho_b$  = bulk density (g/cm<sup>3</sup>)

$NO_3$  = nitrate concentration in the 60-80 cm depth interval (mg/kg)

$NH_4$  = ammonium concentration in the 60-80 cm depth interval  
(mg/kg)

PERC = percolation rate (mm)

$\theta_v$  = volumetric moisture content in the 60-80 cm depth interval  
(cm<sup>3</sup>/cm<sup>3</sup>)

The percolation term (PERC) used in these equations was estimated by the use of a water balance, shown in the equation:

$$\text{PERC} = R - \text{RO} + \text{IRR} - \text{ET}_c + \Delta S \quad (9)$$

where

R = rainfall

RO = surface runoff

IRR = irrigation

ET<sub>c</sub> = Crop evapotranspiration

ΔS = change in water stored in the soil profile, given by change in  $\theta_v$

All the units are in mm of water.

In this water balance method, if the water added to the profile on any one day, either by rainfall or irrigation, exceeded the soil moisture holding capacity, the excess water equaled PERC, and  $\theta_v$  equaled field capacity. The field capacity of the soil was determined in-situ by saturating the soil and, after 48 hours, measuring the moisture content.

Once percolation events were identified and their magnitude was determined, values for NO<sub>3</sub> and NH<sub>4</sub> were obtained by linear interpolation of the bi-weekly measurements.

The second approach used to estimate nitrogen leaching was a nitrogen (N) balance, given by the following equation:

$$N_l = N_i + N_a - N_{up} - N_f \quad (10)$$

where

$N_l$  = nitrogen leached (ammonium + nitrate) (kg/ha)

$N_i$  = initial total nitrogen (organic + inorganic)

$N_a$  = nitrogen applied as fertilizer

$N_{up}$  = nitrogen uptake by plants

$N_f$  = final total nitrogen (organic+inorganic)

The units in this equation are all in kg/ha.

Results obtained by Harmsen et al. (2003) with the first approach for estimating nitrate leaching were compared to those obtained by use of the nitrogen balance.

### ***Data analysis***

To compare the effect of the treatments (lime level, fertigation frequency, and their interaction) on ammonium and nitrate concentrations through time in the soil, an analysis of variance (ANOVA) was performed for each depth considered. Analysis of variance was also used to determine the effect of the treatments on plant N uptake through time and on total yield.

All the statistical analyses were performed using the statistical software package InfoStat/E Version 2.0 (Grupo InfoStat, 2002).

## *Chapter 4*

### **RESULTS AND DISCUSSION**

The characteristics of Coto clay that are presented in the first section of this chapter were used to evaluate the potential this soil has to adsorb nitrate. Results from the retention study, which was done to assess the soil's actual retention capacity, are presented after the characterization section. Finally, data from the field studies are presented to support the data obtained in the laboratory study.

#### **4.1 Soil characterization**

The ability of a soil to adsorb nitrate is a function not only of pH, but also of its physical and chemical properties. Clay content, surface area, mineralogy, organic matter and iron oxide content, as well as the presence of competing anions, all interact to influence a soil's potential nitrate adsorption capacity. All these characteristics are presented in Tables 1, 2 and 3.



**Table 1.** Particle size distribution of Coto clay from the Experiment Station at Isabela, PR

Depth (cm)	Sand -----%-----	Silt	Clay
0-20	35.10	19.35	45.55
20-40	28.72	1.85	69.43

**Table 2.** Selected physical properties of Coto clay from the Experiment Station at Isabela, PR

Depth (cm)	Bulk density g/cm <sup>3</sup>	Particle density g/cm <sup>3</sup>	Porosity	Aggregate stability %	Surface area m <sup>2</sup> /g
0-20	1.36	2.65	0.49	65.55	129.50
20-40	1.36	2.62	0.49	60.22	137.90

**Table 3.** Selected chemical and mineralogical properties of Coto clay from the Experiment Station at Isabela, PR

Depth (cm)	pH <sup>a</sup>	OM -----%-----	Fe <sub>2</sub> O <sub>3</sub> mg/kg	P mg/kg	SO <sub>4</sub> mg/kg	Mineralogy <sup>b</sup>
0-20	4.2	2.76	14.50	22.13	48.16	k, go, gi, i, chl
20-40	3.9	1.74	14.41	14.71	32.37	k, q, go, i, chl

<sup>a</sup> 1:2 soil/water ratio

<sup>b</sup> k = kaolinite, go = goethite, gi = gibbsite, i = illite, chl = chlorite

### ***Physical, chemical and mineralogical properties***

Particle size distribution analyses indicated that Coto has a clayey texture (Table 1). These results agree with those published by the Natural Resource Conservation Service (Soil Survey, 2004). They reported, for a pedon of Coto clay in Aguadilla, PR, 61.1% clay, 7.9% silt and 31.0% sand for the Ap horizon (0-23 cm depth). For the B1 horizon (23-36 cm depth) they reported 66.6% clay, 6.0% silt and 27.4% sand.

The soil has an average bulk density of 1.36, an average particle density of  $2.63 \text{ g/cm}^3$ , and a calculated porosity of 0.49 at both studied depths (Table 2). High percentages of aggregate stability (65.55% and 60.22% for 0-20 cm and 20-40 cm depths, respectively) demonstrate this is a well structured soil. This may contribute to Coto clay's high permeability, which allows water to move quickly through the profile, potentially carrying nitrate with it. Harmsen et al (2003) reported saturated hydraulic conductivity values of 1,210 cm/day for this soil at the 0-20 cm interval, which is a value similar to sand (900 cm/day).

Water retention and movement, as well as ion exchange capacity, are closely related to specific surface, or surface area, of a soil. Also, the source of variable charge, whether from ion adsorption or dissociation of surface ionizable groups, is due to surface reactions. For that reason surface area of the component minerals becomes more important than the absolute quantity

of the minerals. Nonexpanding layer silicates, such as kaolinite, which have only external surfaces, exhibit surface areas in the range of 10 – 70 m<sup>2</sup>/g. Expanding layer silicates, which also have extensive internal surfaces, give surface areas up to 810 m<sup>2</sup>/g. Results obtained in this study show Coto clay at the experimental site has a large surface area (130 m<sup>2</sup>/g at the 0-20 cm depth). This is more apparent when compared to a study by Appel et al. (2003), where an Oxisol from western Puerto Rico exhibited a surface area of 42 m<sup>2</sup>/g.

As shown in Table 3, pH values, although slightly higher at the 0-20 cm depth (4.2, vs. 3.9 at the 20-40 cm depth), are low at both studied depths. Soil acidity was one of the main reasons this site was chosen for the field study. Organic matter, clay minerals, Fe and Al oxides are all sources of soil acidity. Soil organic matter, for example, has carboxylic and phenolic groups that behave as weak acids.

Organic matter (OM) content of surface soils may range from <0.1% in desert soils to almost 100% in organic soils. For agriculture, an OM content of at least 3% is desirable. OM% results were slightly higher in the top portion of this soil. Van Reij and Peech (1972) have shown the effect of organic matter content in raising a soil's cation exchange capacity (CEC) and, therefore, its negative charge. The main implication of these

observations is that a net positive charge, accompanied by the potential to adsorb nitrate, is more likely to happen in the lower depth studied.

Phosphate results from the Bray I test show P levels of 22 mg/kg in the 0-20 cm depth and close to 15 mg/kg at the 20-40 cm depth. These values are considered favorable for crop growth, with 25 mg/kg being the critical level above which no response to P fertilization is expected (Tisdale et al., 1993). Sulfate concentration results seemed somewhat high, particularly on the surface soil (Table 3). Concentrations of 5-20 mg/kg of soluble  $\text{SO}_4^{2-}$  are common in North American soils.

The presence of phosphate and sulfate may affect this soil's nitrate adsorption potential in a negative direction. Mekar and Uehara (1972) illustrated how adsorbed phosphate increased the CEC of some weathered soils of Hawaii. This study also showed decreased  $\text{NO}_3^-$  and  $\text{Cl}^-$  adsorption in the presence of sulfate.

High iron oxides ( $\text{Fe}_2\text{O}_3$ ) content in the Coto clay at the Isabela Experiment Station implicates a potential increase in nitrate adsorption capacity. The mineralogy results (Table 3) agree with those reported by Jones et al. (1982). They reported the presence of kaolinite, chlorite, gibbsite, quartz, and goethite in their Coto clay samples. Hematite was not identified in their samples. The strong goethite peak displayed by their samples hampered a clear identification of hematite. In our sample, a

doublet, or double peak, is observed at  $33.2^\circ 2\theta$ , in both the 0-20 cm and the 20-40 cm depth samples (See Appendix A). These numbers correspond to the angle of X-ray diffraction particular to goethite and hematite (Table 4). Also, a peak at  $35.0^\circ 2\theta$  was observed in both our samples, suggesting the presence of illite (Table 4).

**Table 4.** Mineral identification for X-ray diffractograms

Mineral	Peaks
Chlorite	$6.2^\circ 2\theta$ (14.24 Å), $25.0^\circ 2\theta$ (3.56 Å)
Gibbsite	$18.2^\circ 2\theta$ (4.87 Å), $20.3^\circ 2\theta$ (4.37 Å)
Goethite	$21.2^\circ 2\theta$ (4.18 Å), $33.2^\circ 2\theta$ (2.69 Å), $36.8^\circ 2\theta$ (2.44 Å), $53.2^\circ 2\theta$ (1.72 Å)
Hematite	$33.2^\circ 2\theta$ (2.69 Å), $54.2^\circ 2\theta$ (1.69 Å)
Illite	$26.6^\circ 2\theta$ (3.35 Å), $26.7^\circ 2\theta$ (3.35 Å), $35.0^\circ 2\theta$ (2.56 Å)
Kaolinite	$12.2^\circ 2\theta$ (7.24 Å), $24.7^\circ 2\theta$ (3.60 Å), $38.4^\circ 2\theta$ (2.34 Å), $62.5^\circ 2\theta$ (1.48 Å)
Quartz	$20.8^\circ 2\theta$ (4.27 Å), $26.6^\circ 2\theta$ (3.35 Å), $64.2^\circ 2\theta$ (1.45 Å)

### *Charge properties*

Acid-base titration curves for the two depths of Coto clay studied are shown in Figures 5 and 6. Since the potentiometric titration method does not take into account any permanent charge the soil might have, some negative charge may exist at the point where the curves intersect (the Point of Zero Salt Effect, PZSE). Permanent charge, also referred to as constant charge, occurs in minerals such as phyllosilicates. It results from the substitution of

ions with differing valence within the crystal units or from crystal imperfections, which creates negatively charged surfaces.

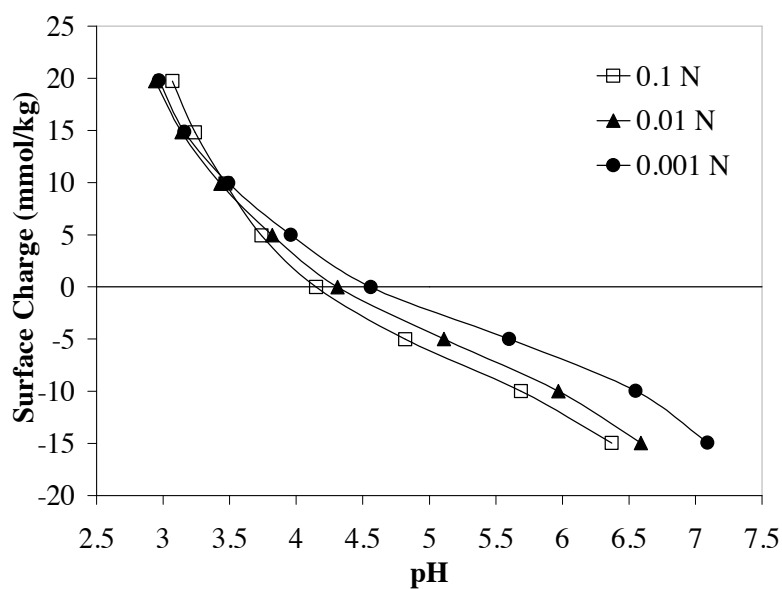
Figure 5 shows that after performing the titrations for measuring PZSE, there was not one exact point of intersection for the three curves in the 0-20 cm depth. The 0.1 N curve intersects the 0.01 N curve at a pH of approximately 3.55, and the 0.001 N curve at approximately 3.46. Both of these values are below the native pH (4.2) at this depth. The main implication of this data is that the soil will have a net negative charge, even at its low native pH.

For the 20-40 cm depth, Figure 6 shows 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.

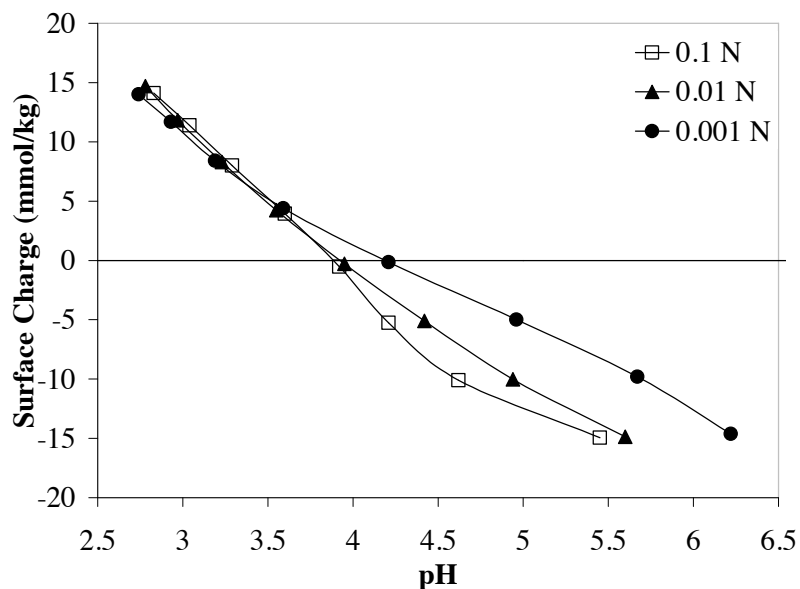
Fox et al. (1981) found that the general pattern for titration curves in Puerto Rico soils is of converging curves, rather than having one clear point of intersection. This was attributed to the presence of soil minerals with a significant component of permanent negative charge. This means that at native pH values a net negative charge is expected.

PZSE values obtained in our study are similar to those reported by Snyder et al. (1993) on clay soils from Puerto Rico (series Fraternidad,

Corozal, Daguey and Nipe). Nevertheless, shifting of the values for different concentrations is in the opposite direction. In their study potentiometric titration curves for different ionic strengths did not meet at one exact pH value either. PZSE was taken at the intercepts with the lower ionic strengths (0.001 and 0.01N NaCl) rather than those for the 0.1 and 0.01N salt solutions. The latter ones shifted toward lower pH values, and this was attributed to possible displacement and hydrolysis of exchangeable aluminum in the presence of the more concentrated solution.



**Figure 5.** Potentiometric titration curves for the 0-20 cm depth.



**Figure 6.** Potentiometric titration curves for the 20-40 cm depth.

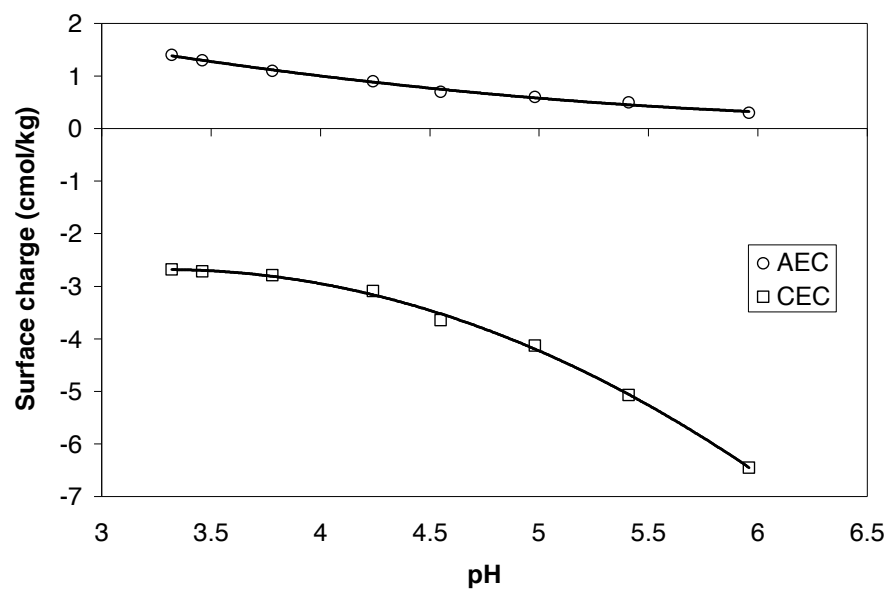
As previously stated, the mineralogy of the clay fraction of Coto is predominantly kaolinitic, although gibbsite, goethite and hematite are present. Measured Point of Zero Net Charge (PZNC) for Fe-oxides range from 6.7 to 8.5 (Sparks, 1995), and from 3.9 to 5.0 for kaolinites (Brady et al., 1996). Nevertheless, the XRD analyses revealed the presence of illite and chlorite, which will contribute to a lower PZSE. The presence of quartz may also influence this result, since its PZNC is approximately 2 (Parks, 1965). It is not surprising, therefore, that for both soil depths the PZSE occurred on the acid side of the native pH.



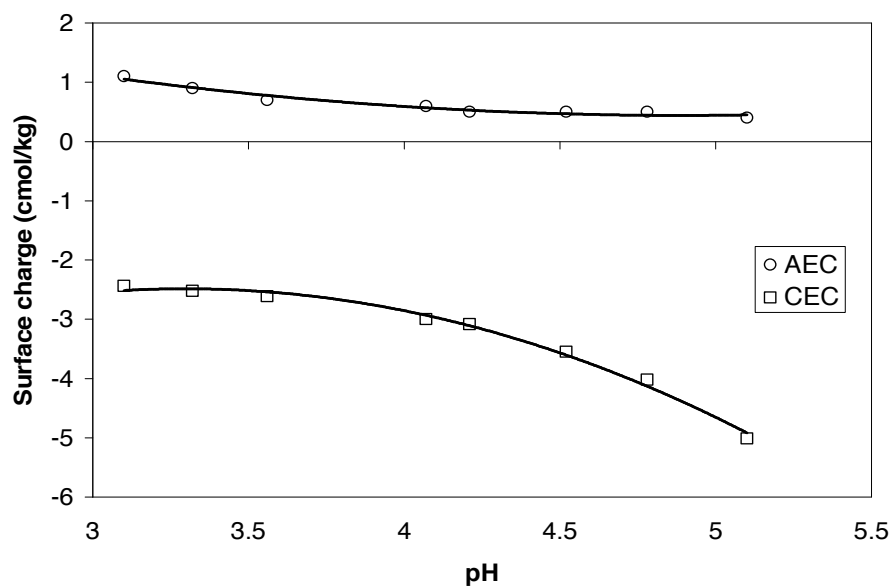
Although a clear point of intersection for the pH vs. charge curves was not observed, the PZSE seems to be lower for the 0-20 cm depth. This difference is probably the result of higher organic matter content in the 0-20 cm depth, since, as previously mentioned, organic matter increases CEC (Marcano-Martinez 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 western Puerto Rico (clayey, oxidic, isohyperthermic Typic Acrorthox), and with Fox (1981) who also reported similar results.

An ion adsorption approach was used to compliment charge properties results obtained by the potentiometric titration method. Surface charge as a function of pH, determined by the adsorption of  $K^+$  and  $Cl^-$ , is displayed in Figures 7 and 8 for the 0-20 cm depth and the 20-40 cm depth, respectively. These graphs show cation exchange capacity (CEC) and anion exchange capacity (AEC) for the soil using the method of cation and anion adsorption for estimating point of zero net charge (PZNC).

Both depths exhibited a net negative charge over the entire pH range investigated. Therefore, the PZNC could not be determined. As explained for PZSE, this is probably due to the presence of organic matter, quartz and other low PZC minerals. The 20-40 cm depth had slightly lower CEC and AEC values, although they were similar to the 0-20 cm depth values.



**Figure 7.** Ion adsorption curves for the 0-20 cm depth



**Figure 8.** Ion adsorption curves for the 20-40 cm depth

CEC and AEC values for each studied depth are given in Table 5. Cation exchange capacity values ranged from 2.4cmol<sub>c</sub>/kg at pH 3.10 in the 20-40 cm depth to 6.45cmol<sub>c</sub>/kg at pH 5.96 in the 0-20 cm depth. Anion exchange capacity values ranged from 0.33cmol<sub>c</sub>/kg at pH 5.96 in the 0-20 cm depth to 1.39cmol<sub>c</sub>/kg at pH 3.32 also in the 0-20 cm depth. CEC and AEC values at native pH are similar to those reported by Rivera (1995) on another Oxisol from Puerto Rico (Bayamón series) that showed nitrate adsorption capacity.

**Table 5.** Measured CEC and AEC at different pH levels for the 0-20 cm and the 20-40 cm depths

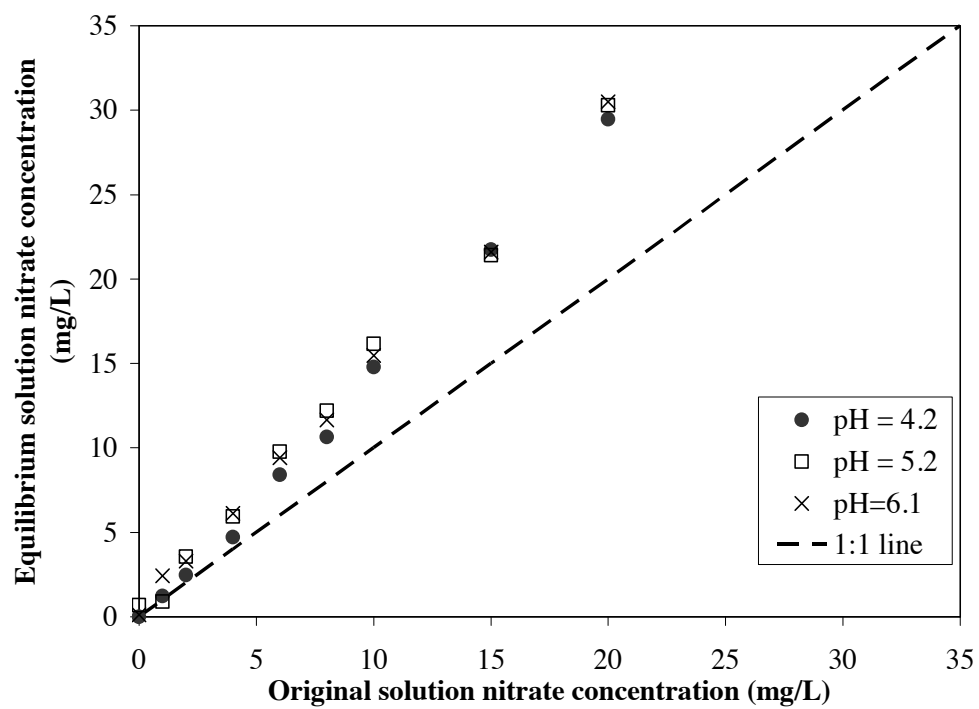
Depth (cm)	pH	CEC (cmol <sub>c</sub> /kg)	AEC (cmol <sub>c</sub> /kg)
0-20	3.32	2.68	1.39
0-20	3.46	2.72	1.31
0-20	3.78	2.79	1.12
0-20	4.24	3.09	0.92
0-20	4.55	3.65	0.74
0-20	4.98	4.13	0.63
0-20	5.41	5.07	0.50
0-20	5.96	6.45	0.33
20-40	3.10	2.44	1.12
20-40	3.32	2.52	0.89
20-40	3.56	2.61	0.71
20-40	4.07	3.00	0.61
20-40	4.21	3.08	0.51
20-40	4.52	3.55	0.50
20-40	4.78	4.02	0.48
20-40	5.10	5.01	0.42

## 4.2 Retention study

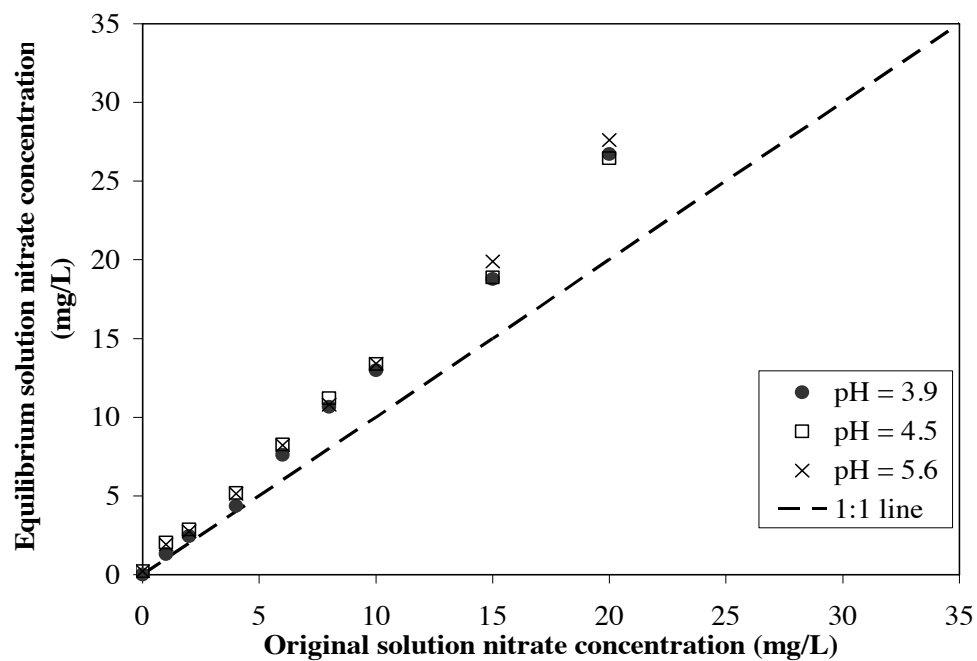
Batch studies were performed to assess the nitrate adsorption capacity of Coto clay at the Isabela Experiment Station. All the properties discussed in the characterization section are integrated and their effect on  $\text{NO}_3^-$  adsorption can be evaluated by this approach.

Observed values show that there was no positive  $\text{NO}_3^-$  adsorption by Coto clay at the studied depths. As with the charge analyses, this might reflect the effect of low PZC minerals, organic matter and adsorbed phosphates and sulfates present in Coto clay.

After the equilibration period, greater amounts of nitrate were found in the equilibrium solution compared to the original solution (Figures 9 and 10; also see Appendix C for tabular data). 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). This may suggest desorption of residual nitrate, negative adsorption caused by anion exclusion, and/or microbial or enzyme activity. Although repeated washing with 0.1 N KCl was performed, usually 2 N KCl is used to ensure total nitrate extraction, and some residual nitrate may have washed off the soil during isotherm studies.



**Figure 9.** Original vs. equilibrium nitrate solution concentration in retention study; 0-20cm depth



**Figure 10.** Original vs. equilibrium nitrate solution concentration in retention study; 20-40cm depth

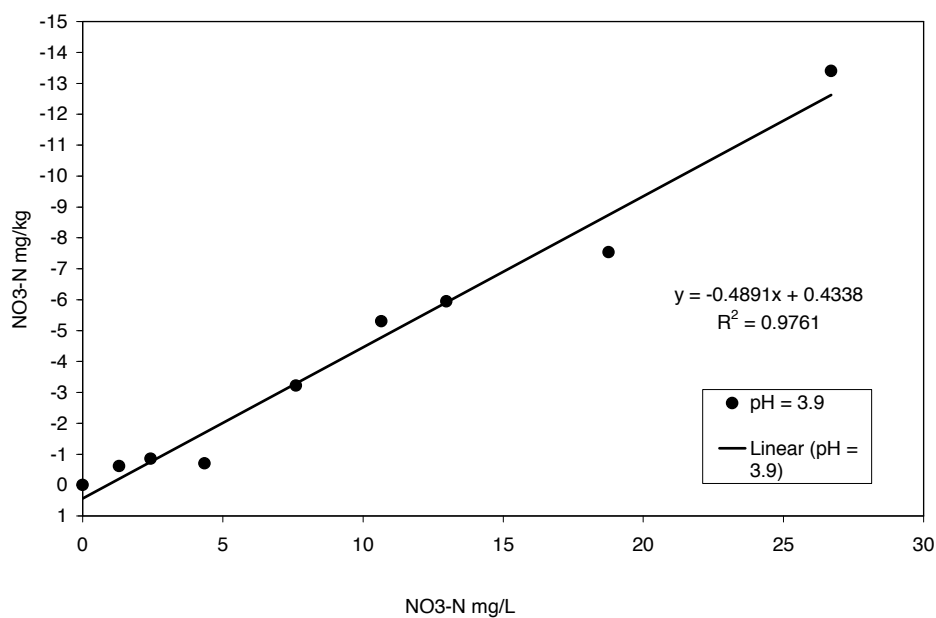
Higher than expected concentrations may also be the result of microbial or enzyme activity. Kowalenko and Yu (1996) reported the occurrence of microbial activity in soil extractions during adsorption measurements done by an equilibration experiment similar to the one used in this experiment. As happened in our study, they found that more nitrate was recovered in the  $\text{NO}_3^-$  equilibrium solutions than had been added. They also reported that the use of toluene as a microbial inhibitor did not necessarily render better results. They suggested that other inhibitors should be tested for effectiveness. Although possible, the effect of microbial activity on the increased nitrate concentrations is believed to be minimal.

Negative adsorption might be another reason for the increased nitrate solution concentration after equilibrium. Sposito (1984) states that the effect of negative adsorption can be observed in a region of depletion of the anion at the soil-solution interface, at surfaces possessing negative charge. This results in a higher concentration of anions in the bulk solution. Specifically adsorbed anions can render oxide surfaces more negative, so even with high iron oxide content, the presence of phosphate and sulfate may be an overriding factor in determining the charge of soil surfaces.

Figure 11 shows the nitrate adsorption isotherm for the 20-40 cm depth at the native pH (see Appendix D for all isotherms). The isotherms clearly show a negative linear trend and were characterized in terms of the



linear partition equation (equation 3). Linear partition coefficients,  $K_p$ , and correlation coefficients ( $R^2$ ) are presented in table 6. The isotherms also point to negative adsorption as the reason for the excess  $\text{NO}_3^-$  in the equilibrium solution, since nitrate measured in excess of that applied increased in a constant manner.



**Figure 11.** Adsorption isotherm for the 20-40 cm depth, at native pH

**Table 6.** Linear partition coefficients,  $K_p$ , and correlation coefficients,  $R^2$ , for adsorption isotherms

Depth (cm)	pH	$K_p$	$R^2$
0-20	4.2	-0.66	0.99
	5.1	-0.66	0.98
	6.2	-0.65	0.99
20-40	3.9	-0.49	0.98
	4.5	-0.45	0.97
	5.6	-0.52	0.99

In any case, data from the retention study shows that no nitrate was positively adsorbed by the Coto clay. Little nitrate adsorption, if any, was expected to occur following the results from the soil characterization. Indeed, results show nitrate repulsion (anion exclusion) may cause negative adsorption.

### 4.3 Field results

Environmental factors, combined with field management, play an important role in the behavior of nitrogen in the soil. To integrate these factors and to support the laboratory study results two field studies were established at the Isabela Experiment Station.

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. In the second year (2003) pH level analyses, no spatial variation was observed. Plots with no lime show pH levels averaging 4.6, while limed plots reached an average pH of 6.5, as expected.

#### *Nitrogen in the soil*

Preliminary statistical analyses showed that there was no block effect on ammonium and nitrate concentrations. Therefore, sampling dates were used as blocks for statistical purposes, instead of the blocks established in the field. An analysis of variance (ANOVA) was performed for each 20 cm depth interval to evaluate the effect of the treatments on  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations.

No significant variation on either  $\text{NO}_3^-$  or  $\text{NH}_4^+$  concentrations was observed between the lime and no lime treatments in either season. This

suggests that the soil in this study does not have enough anion adsorption capacity at its native pH to adsorb nitrate. Both charge analyses and retention studies had suggested Coto clay would not adsorb nitrate at its native pH and natural conditions, and the field data confirms this conclusion.

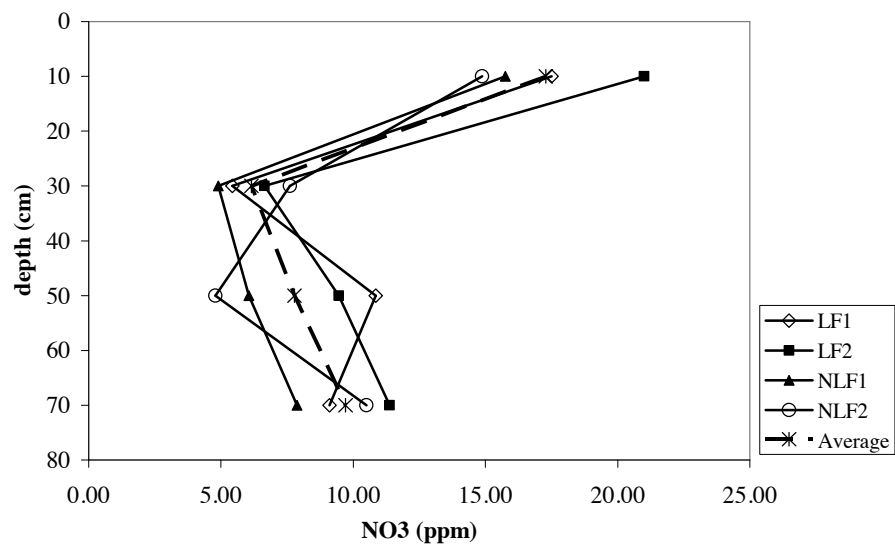
No significant difference was observed between the fertigation treatments either. This could be explained by the fact that plots for both fertigation treatments actually received N on a weekly basis in the form of  $\text{KNO}_3$ . The difference was based solely on urea applications, and this might not have been enough to translate into an actual difference in results for nitrate and ammonium concentrations in the soil.

Nitrate concentrations at different depths, by sampling date, are presented in figures 12 through 27. These figures show that  $\text{NO}_3^-$  movement through the soil profile does not follow a particular pattern by treatment on either year. However, higher concentrations of both parameters were observed at the 0-20 cm interval. Nitrate and ammonium concentrations did not show significant difference between depths over 20 cm (Table 7).

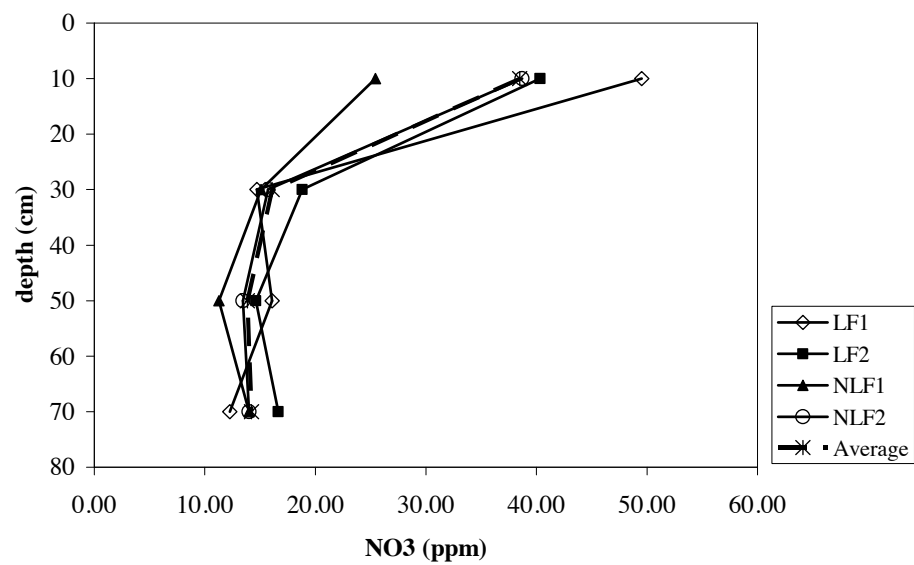
**Table 7.** Average soil nitrate-N concentrations (mg/kg) at different soil depths, by lime level and by year.

Depth (cm)	Lime		No Lime	
	2002	2003	2002	2003
0 - 20	27.2	21.8	21.2	22.1
20 - 40	14.3	13.0	12.3	11.4
40 - 60	14.2	14.2	11.3	12.4
60 - 80	10.6	12.4	10.4	11.9

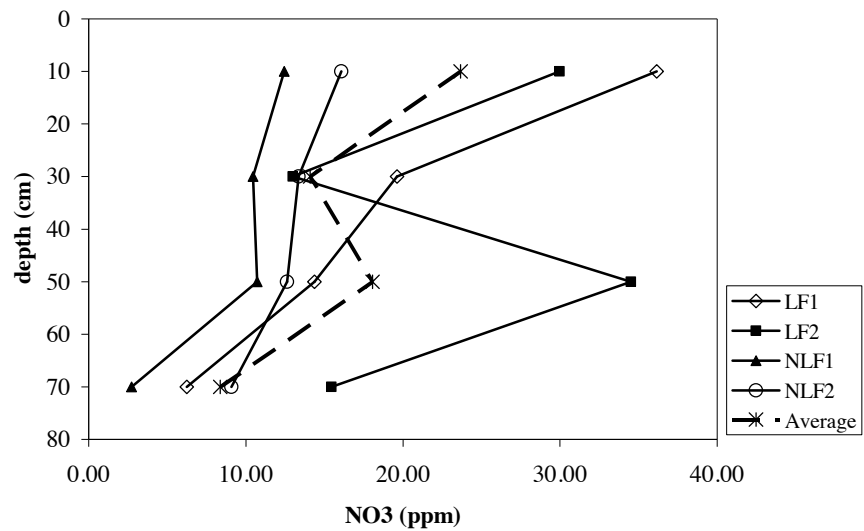
The top 20 cm of the soil is where fertilizer, therefore nitrogen, is directly applied, and it also contains a higher organic matter content. As water moves through the soil profile, the nitrate applied will move to those places percolation water reaches (when there is no nitrate adsorption). The amount of water applied and the frequency of irrigation were adequate to prevent significant movement of water out of the root zone. Since less water reaches the lower depths, owing to uptake by plant roots, less nitrogen will also reach them. This may explain higher nitrogen concentrations in the 0-20 cm depth.



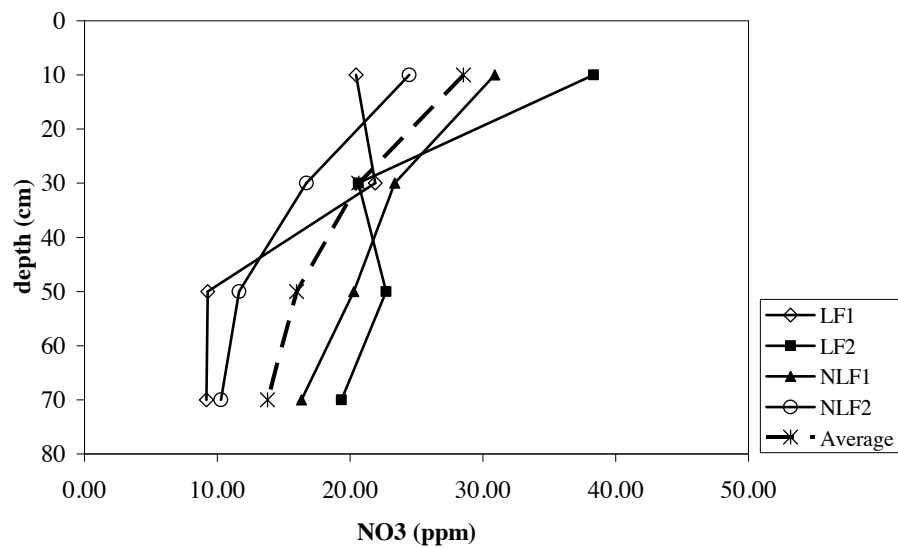
**Figure 12.** Nitrate-N concentration by depth, 3-27-02



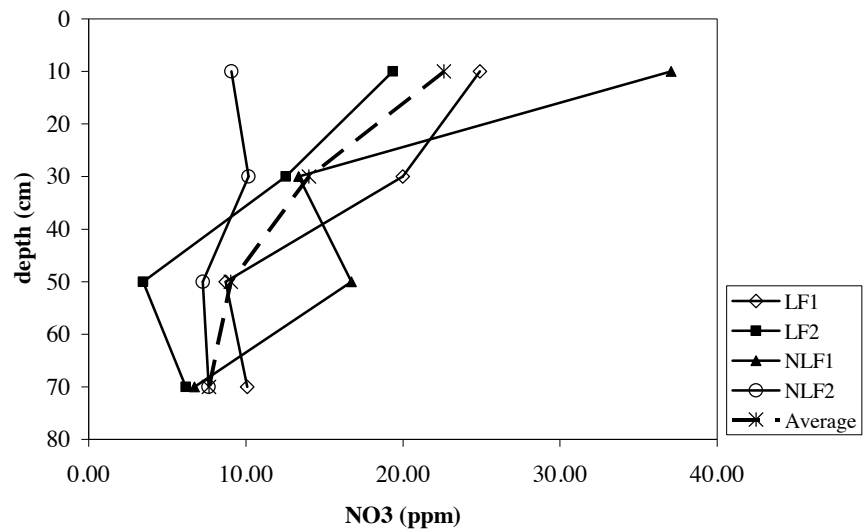
**Figure 13.** Nitrate-N concentration by depth, 4-12-02



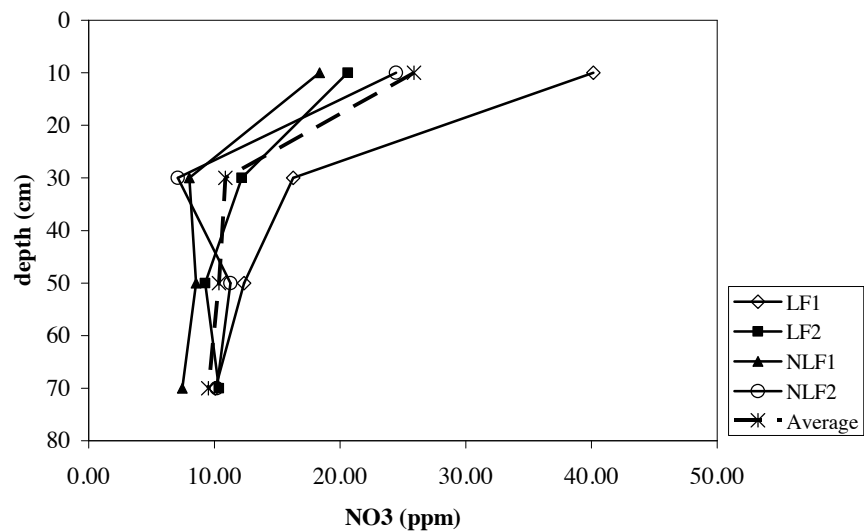
**Figure 14.** Nitrate-N concentration by depth, 4-26-02



**Figure 15.** Nitrate-N concentration by depth, 5-10-02

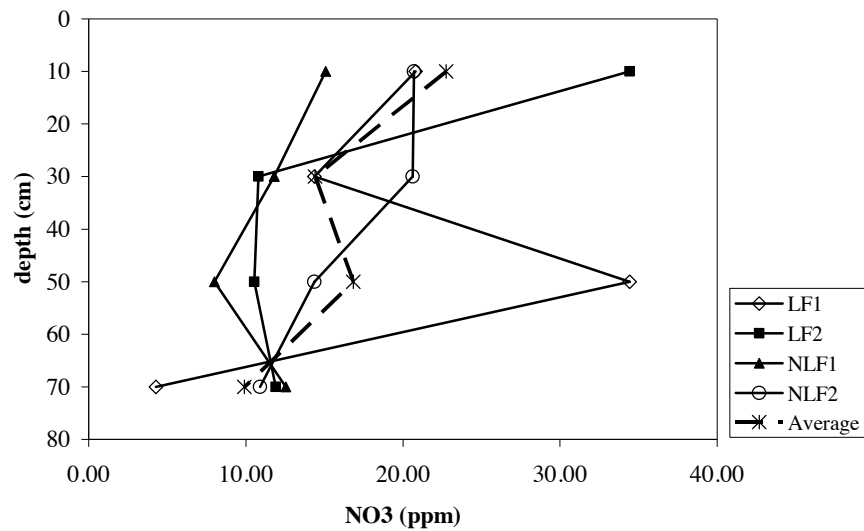


**Figure 16.** Nitrate-N concentration by depth, 5-24-02

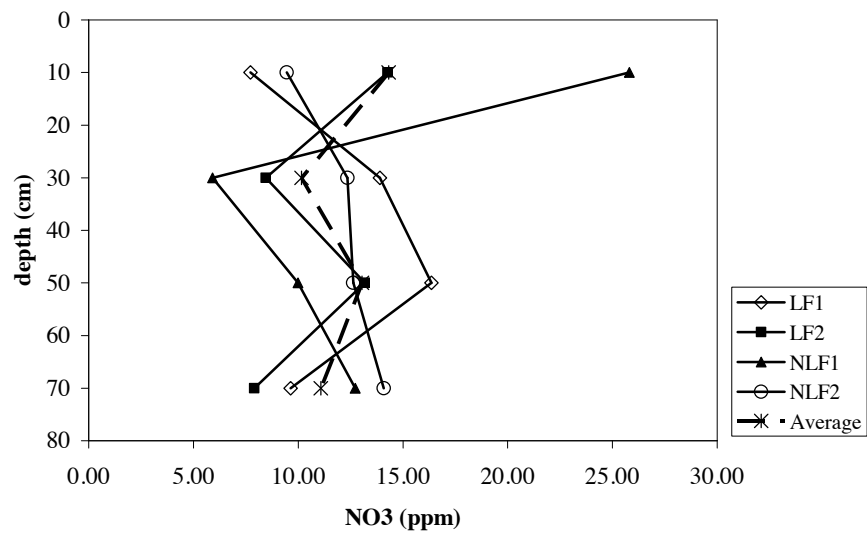


**Figure 17.** Nitrate-N concentration by depth, 6-7-02

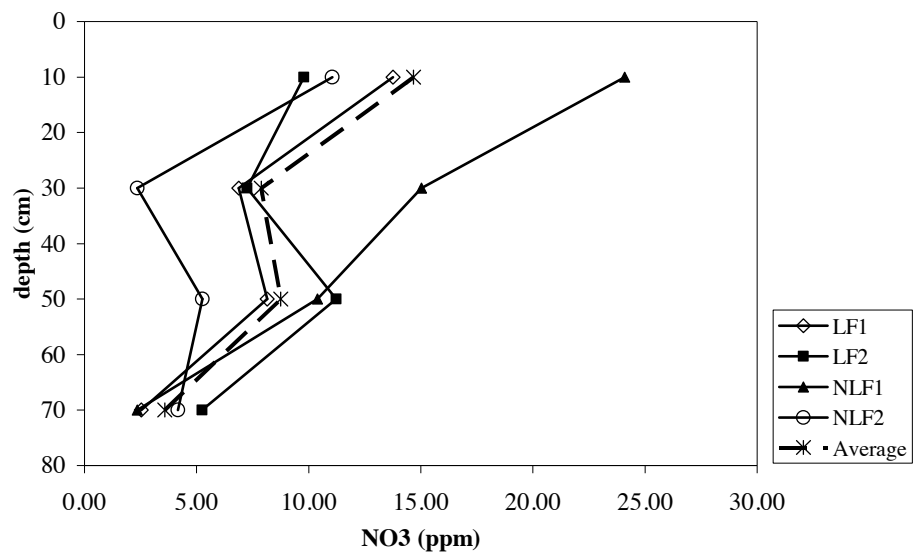




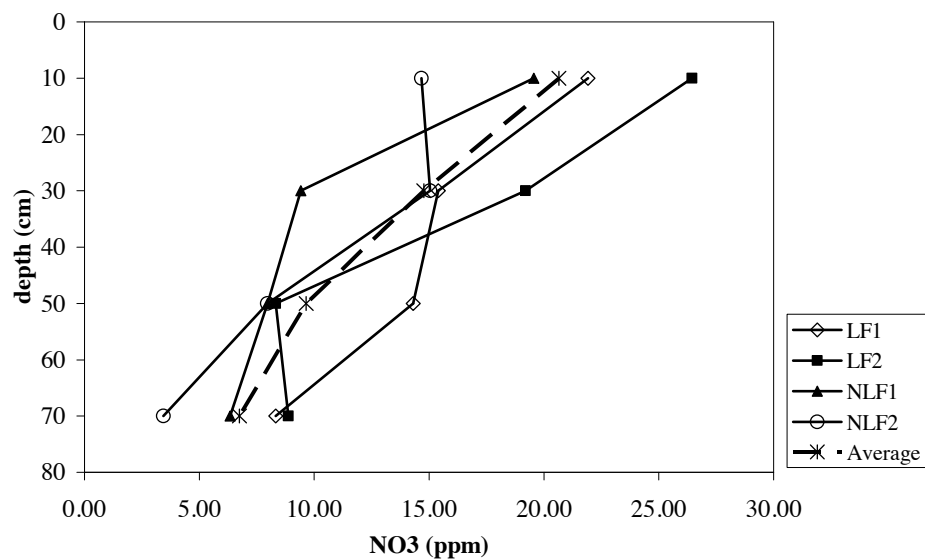
**Figure 18.** Nitrate-N concentration by depth, 6-21-02



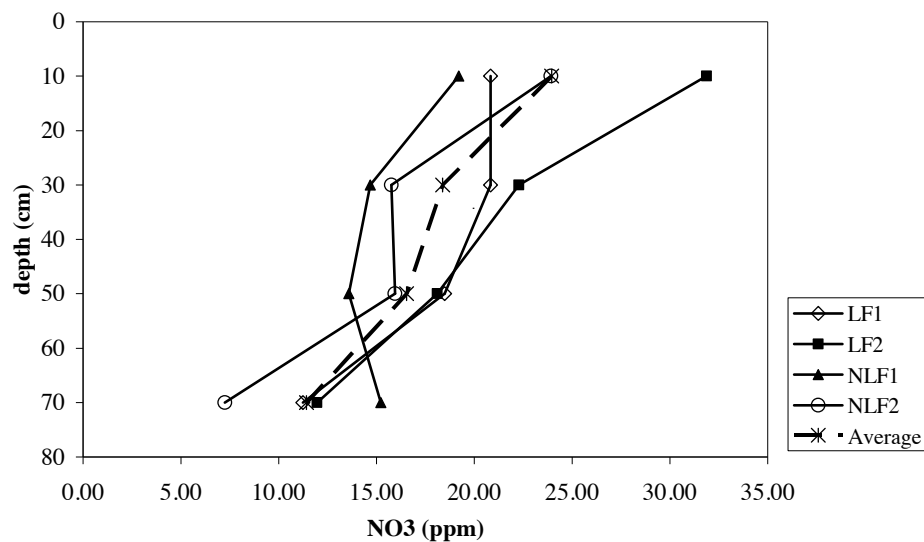
**Figure 19.** Nitrate-N concentration by depth, 7-8-02



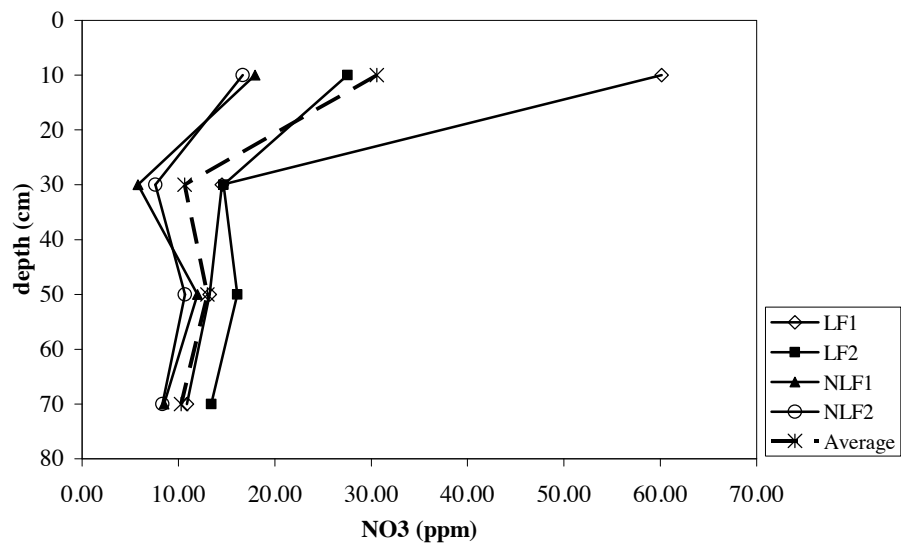
**Figure 20.** Nitrate-N concentration by depth, 2-18-03



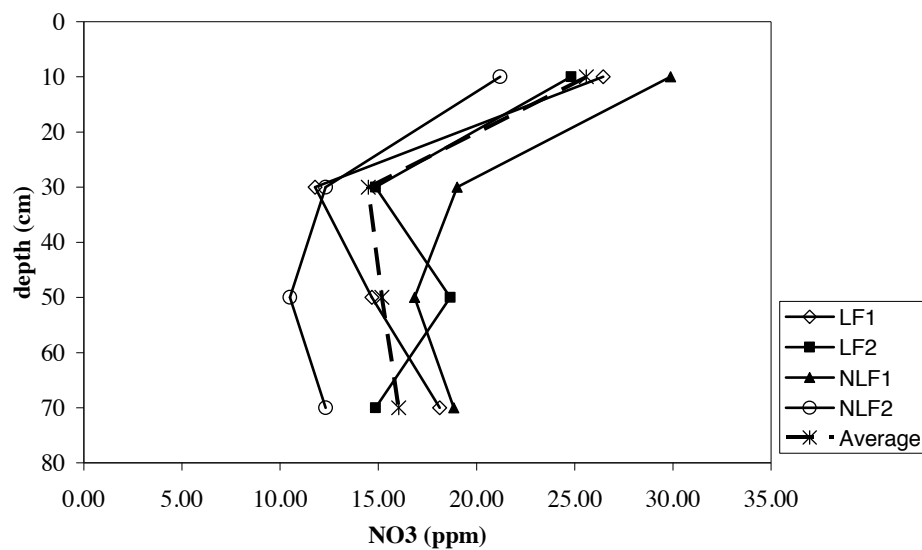
**Figure 21.** Nitrate-N concentration by depth, 3-04-03



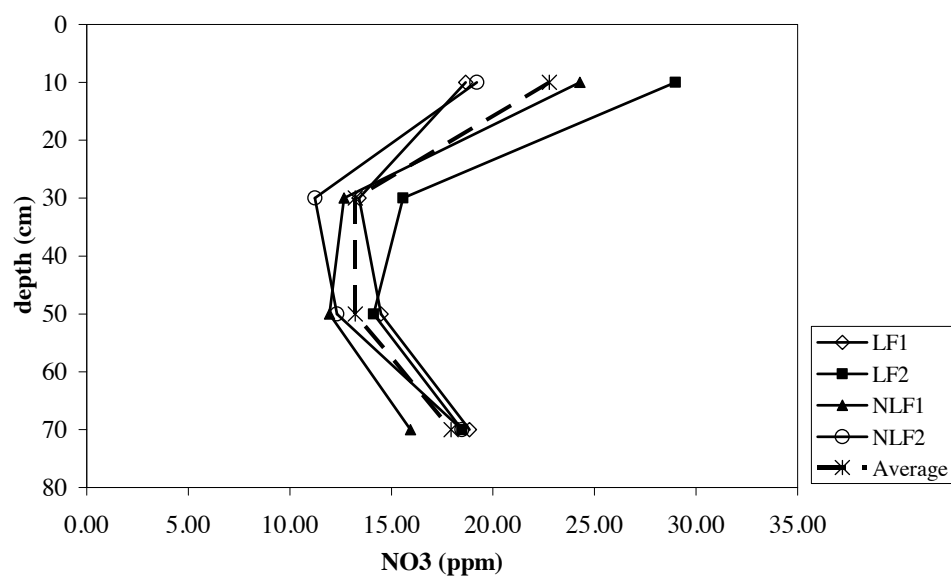
**Figure 22.** Nitrate-N concentration by depth, 3-17-03



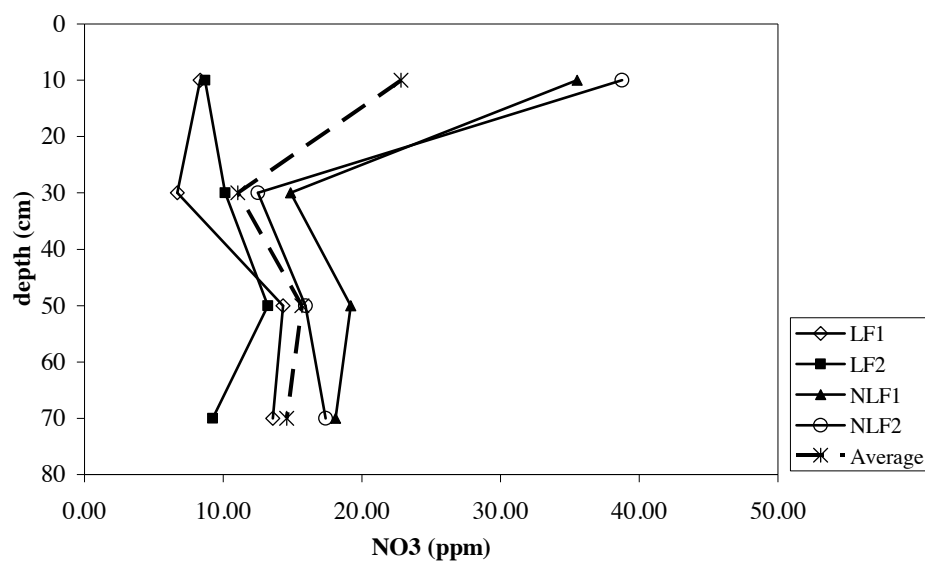
**Figure 23.** Nitrate-N concentration by depth, 3-31-03



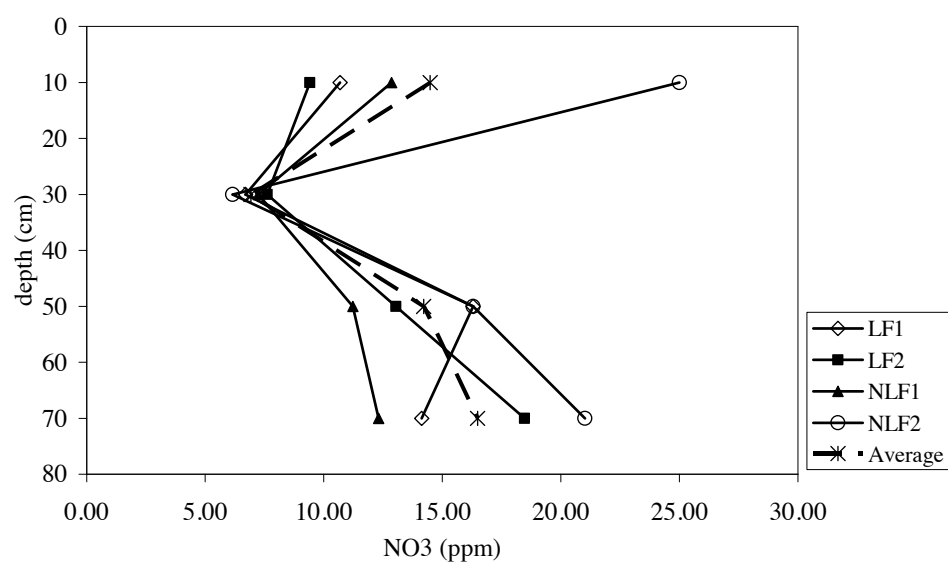
**Figure 24.** Nitrate-N concentration by depth, 4-14-03



**Figure 25.** Nitrate-N concentration by depth, 4-28-03



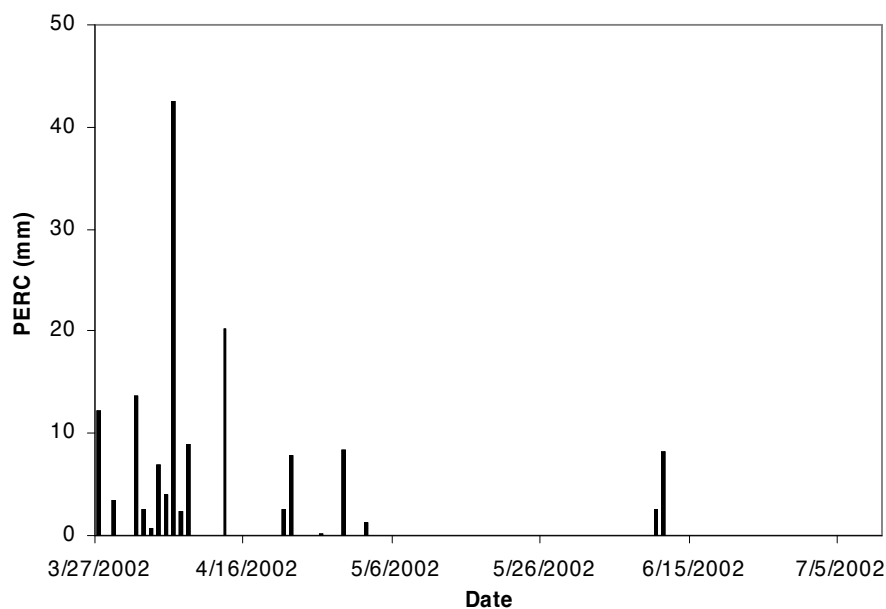
**Figure 26.** Nitrate-N concentration by depth, 5-14-03



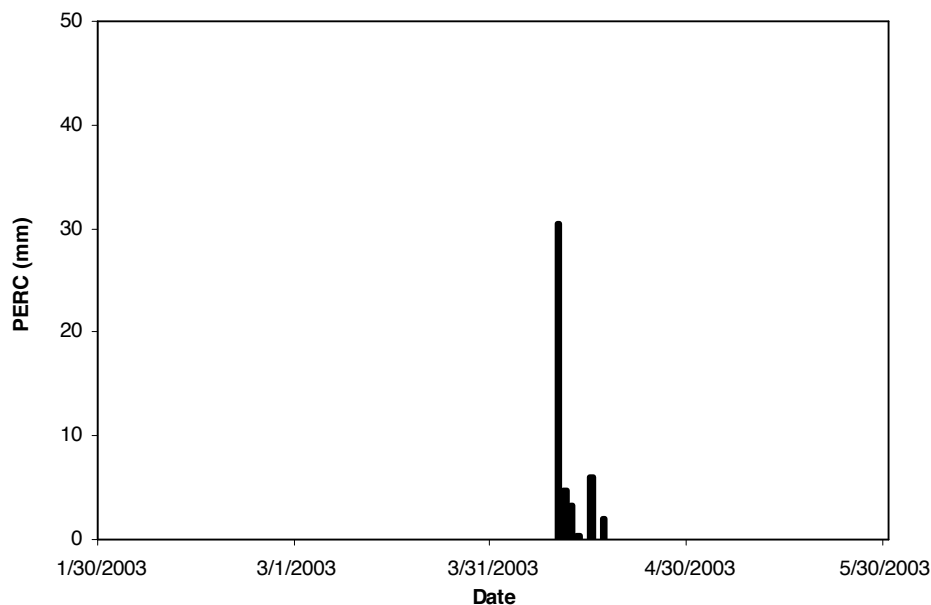
**Figure 27.** Nitrate-N concentration by depth, 5-30-03

#### 4.4 N leaching

For the first approach used for estimating nitrogen losses by leaching, measured bulk density ( $\rho_b$ ) for the 60-80 cm depth was  $1.29 \text{ g/cm}^3$  (see also Appendix F: Harmsen et al., 2003). Results from the water balance performed to calculate percolation (PERC) are shown in Figures 28 and 29. These show the events of percolation and their estimated magnitude for the 2002 and the 2003 seasons, respectively (see Appendix E for weather data used). The percolation events presented in these figures were mainly associated with large rainstorms.

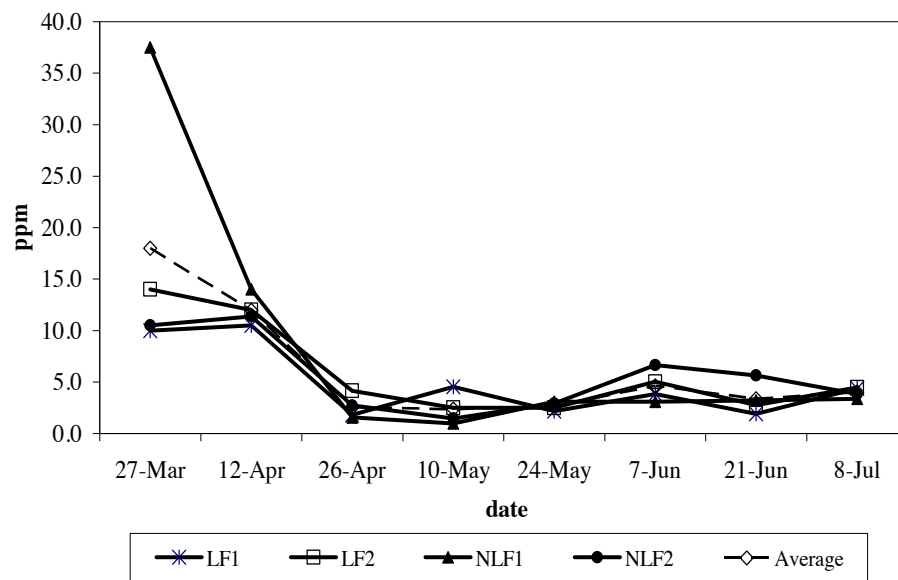


**Figure 28.** Estimated percolation past the root zone during the 2002 season

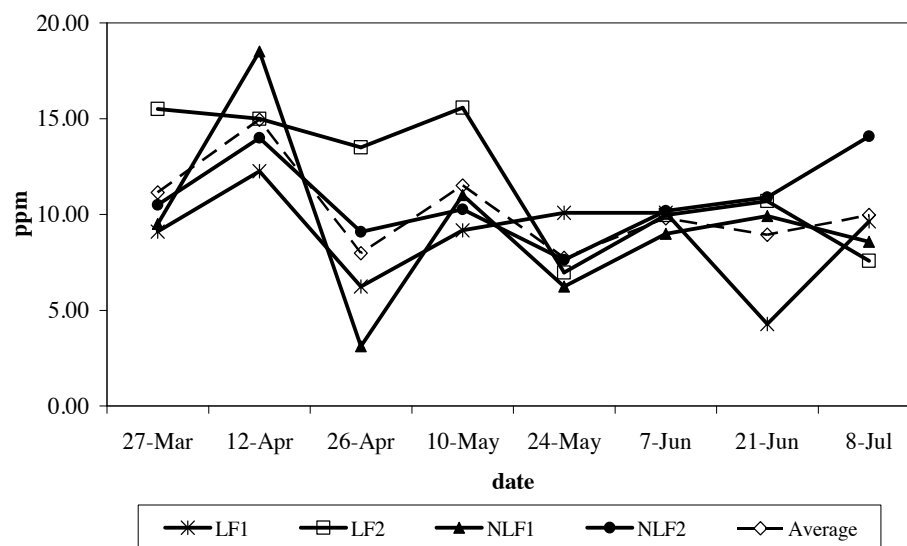


**Figure 29.** Estimated percolation past the root zone during the 2003 season

For these percolation events, leached  $\text{NH}_4^+$  and  $\text{NO}_3^-$  estimates were obtained using equations 7 and 8. Values for ammonium and nitrate were obtained by linearly interpolating between sampling dates. Soil nitrogen concentrations in the 60-80 cm depth interval are presented in Figures 30 through 33. Estimated nitrogen leaching for seasons 1 and 2 are presented in Tables 8 and 9, respectively. Dates with high  $\text{NH}_4$  concentrations in the 60-80 cm depth (Figures 30 and 32) seem to correspond to deep percolation events in both seasons. However,  $\text{NO}_3$ , which was the main form of nitrogen present below the root zone, does not seem to follow any particular trend.

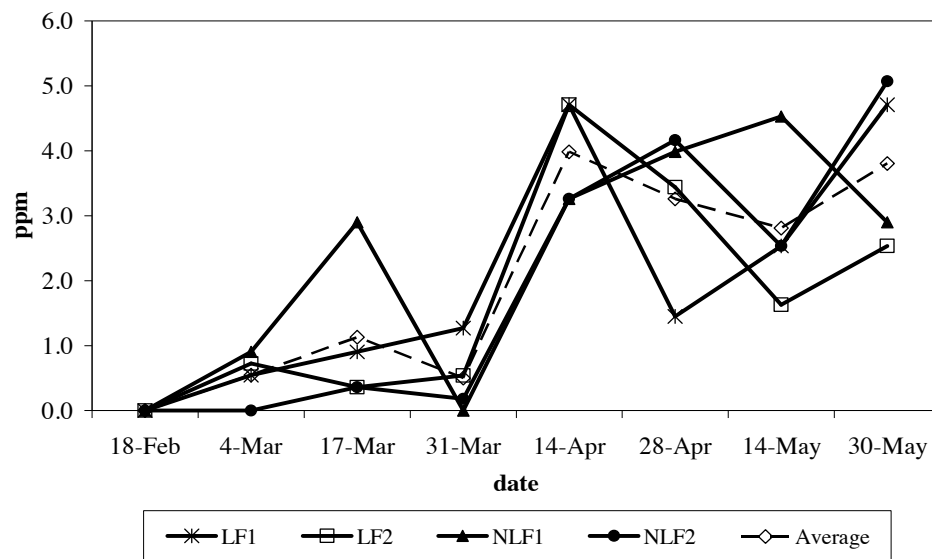


**Figure 30.** NH<sub>4</sub>-N concentrations (mg/kg) at the 60-80 cm depth, 2002

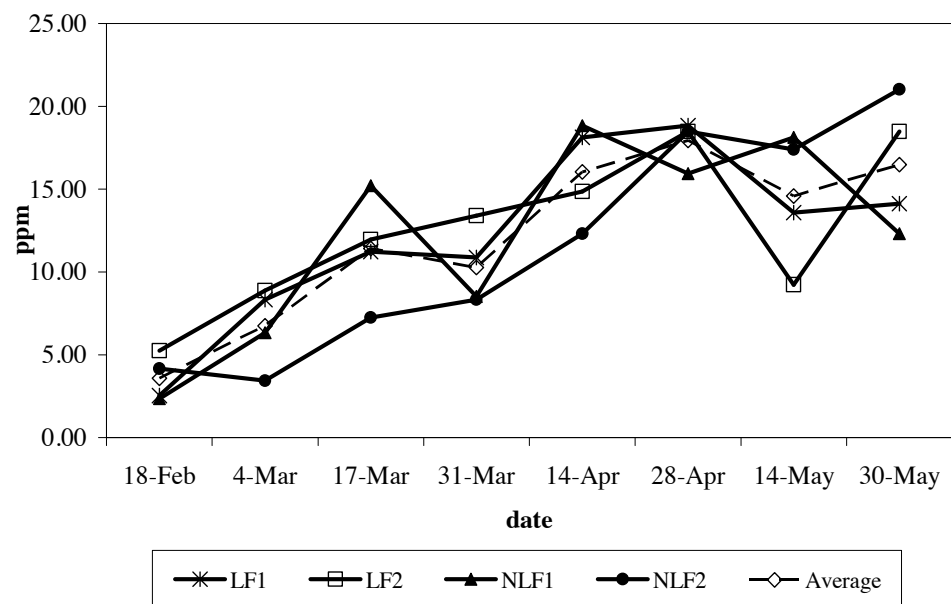


**Figure 31.** NO<sub>3</sub>-N concentrations (mg/kg) at the 60-80 cm depth, 2002





**Figure 32.** NH<sub>4</sub>-N concentrations (mg/kg) at the 60-80 cm depth, 2003



**Figure 33.** NO<sub>3</sub>-N concentrations (mg/kg) at the 60-80 cm depth, 2003

**Table 8.** Nitrate-N and ammonium-N leached during the 2002 season

	Units	LF1	LF2	NLF1	NLF2	Average
NO <sub>3</sub> -N	kg/ha	36	50	47	42	44
NH <sub>4</sub> -N	kg/ha	10	13	21	11	14
Total N	kg/ha	46	63	67	54	58
Total <sup>a</sup>	%	21	28	30	24	26

<sup>a</sup> = % of nitrogen leached from total nitrogen applied as fertilizer

**Table 9.** Nitrate-N and ammonium-N leached during the 2003 season

	Units	LF1	LF2	NLF1	NLF2	Average
NO <sub>3</sub> -N	kg/ha	34	32	34	24	31
NH <sub>4</sub> -N	kg/ha	2	3	2	3	3
Total N	kg/ha	36	35	36	27	34
Total <sup>a</sup>	%	16	16	16	12	15

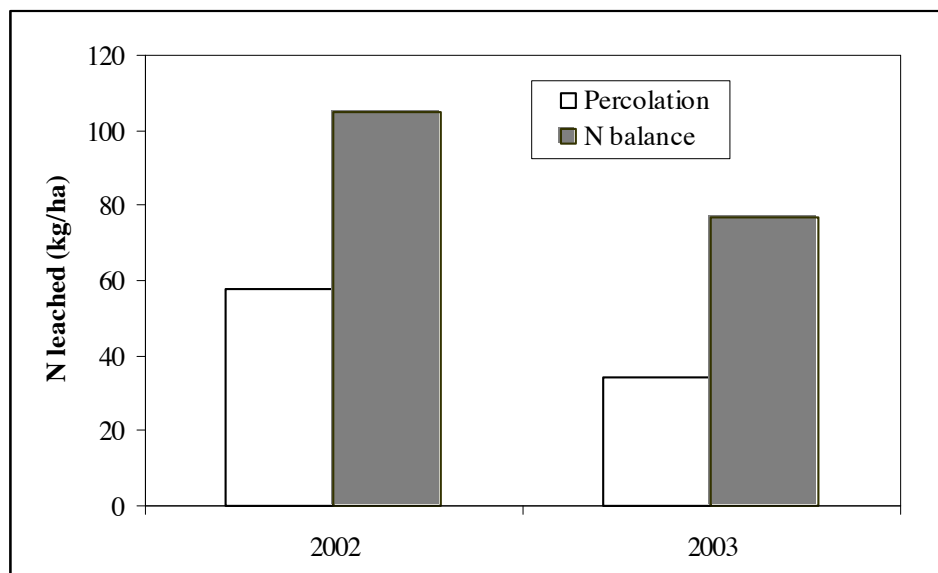
<sup>a</sup> = % of nitrogen leached from total nitrogen applied as fertilizer

Estimated nitrogen leaching for 2002 ranged from 46 to 67 kg/ha, with an average of 58 kg/ha. This represents 26% of the total amount of nitrogen applied as fertilizer (225 kg/ha). For the second season, estimates ranged from 27 to 36 kg/ha, with an average of 32 kg/ha. This represents 15% of the total applied as fertilizer. The difference is due to a higher amount of percolation events occurring in the first season than in the second season. The amount of nitrate-N lost on April 6, 2002 and April 10, 2003 (the largest rainfall events for each season respectively) was 19.6 kg/ha and 20.1 kg/ha, respectively.

For years 1 and 2 this represented 34% and 60% of the total N lost by leaching during the two seasons, respectively.

There is a marked difference in the percentages of ammonium and nitrate from the total nitrogen leached between seasons. For 2002, out of the 58 kg/ha of N leached, 24% was  $\text{NH}_4\text{-N}$  and 76% was  $\text{NO}_3\text{-N}$ . On 2003, only 9% of the 34 kg/ha estimated nitrogen lost was as ammonium and 91% was lost as nitrate. The higher % of  $\text{NH}_4\text{-N}$  was probably due to a lower chance of nitrification. Since percolation events were scattered throughout the first season, more of the  $\text{NH}_4^+$  from urea applied was moved to lower depths before it had a chance to be converted to  $\text{NO}_3^-$ .

The second approach used to estimate nitrogen leaching from the field was a nitrogen (N) balance. The results for the components of equation 10 were calculated during the study and are presented in Table 10, with Figures 35 and 36 presenting nitrogen uptake trends during season 1 and 2, respectively. The product of these factors results is the estimated nitrogen leaching for each season. This estimation shows less N loss on the second season, which is consistent with results from the percolation method. Nevertheless, Figure 34 demonstrates that, when compared, estimated losses with the balance approach were almost twice the amount estimated with the percolation approach.



**Figure 34.** Comparison of estimated N losses by leaching by season; percolation method vs. N balance method

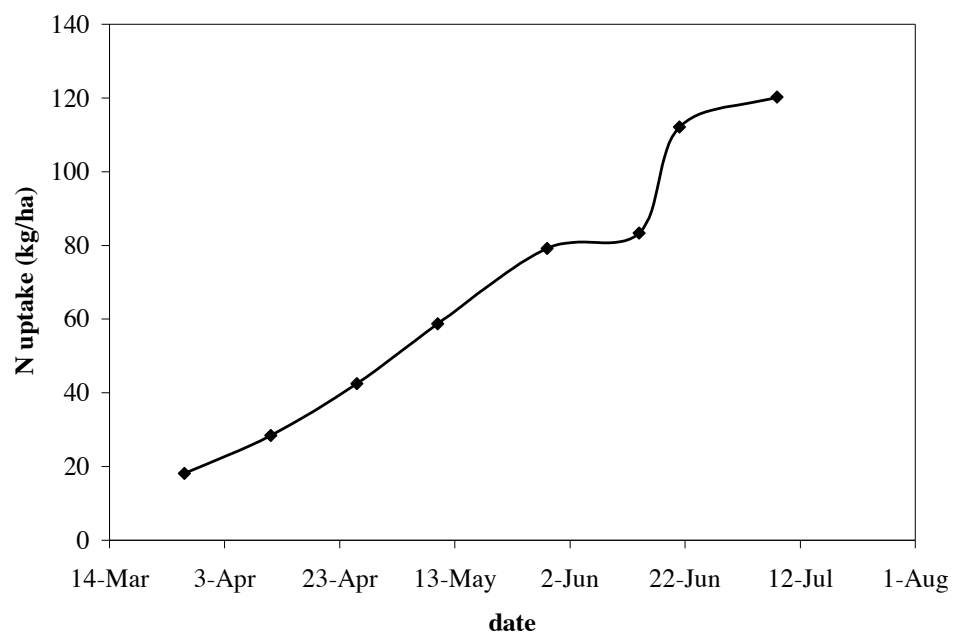
There are sources of uncertainty in both methods. The percolation estimates, for instance, do not account for potential leaching by unsaturated flow. All the leaching was assumed to occur under saturated conditions. However, downward movement of water, along with nitrate, is possible, and probable, under unsaturated conditions. This might have resulted in underestimation of N leaching. Also, nitrogen concentrations between sampling dates were derived by linear interpolation. Estimates do not consider the fact that concentrations, which changed as much as 15 kg/ha in the 60-80 cm interval, do not change linearly between sampling dates.

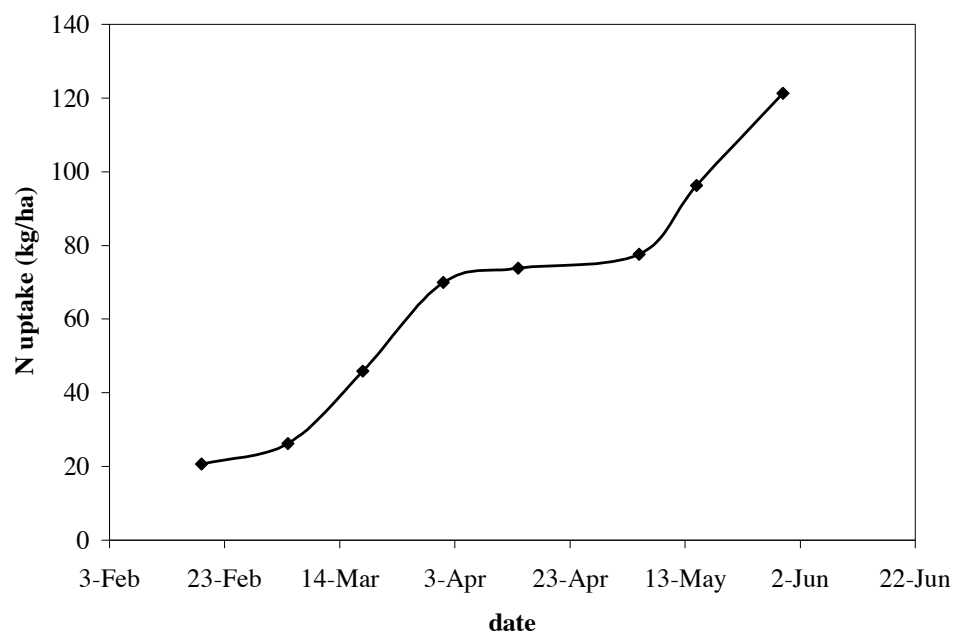
Another source of uncertainty for the percolation method is that it does not take into account that nitrate velocity will increase due to the negative adsorption suggested by the retention study. Anion repulsion by the negatively charged soil surfaces will force nitrate into large pore centers, where the velocity is higher. Sposito (1984) has described a method to determine the exclusion volume (volume of water depleted of anions) and the mobile volume (in which the anion is concentrated). This result could be used in an equation described by Gvirtzman and Gorelick (1991) to estimate the transport velocity of  $\text{NO}_3^-$  in this system. Nevertheless, some of the parameters were not determined in this study.

When using the balance method, all nitrogen lost was assumed to have been leached. Losses by volatilization were assumed to be negligible, since plastic mulches were used in the field, and pH was maintained in the acid to neutral levels. Net mineralization and denitrification were not considered either. To determine plant uptake, only shoots and leaves were analyzed. Nitrogen in fruit, which was harvested, or in the roots, which were left in the soil, was not accounted for. These factors might have contributed to an overestimation of N loss by leaching under the N balance. Real nitrogen losses by leaching should be somewhere between the two estimates calculated in this study.

**Table 10.** Components of the nitrogen balance for both seasons (kg/ha)

	2002	2003
$N_i$	1,822	1,795
$N_a$	225	225
$N_{up}$	120	121
$N_f$	1,822	1,822
$N_l$	105	77

**Figure 35.** Nitrogen uptake by plants during the 2002 season



**Figure 36.** Nitrogen uptake by plants during the 2003 season

## *Chapter 5*

### **SUMMARY AND CONCLUSIONS**

Nitrogen retention characteristics of Coto clay at Isabela, PR, were evaluated by performing a soil characterization, a retention study, and a field experiment. Physical, chemical and mineralogical properties describe the system and provide an idea of possible nitrogen behavior in the soil. Adsorption isotherms developed in the retention study describe the sorption behavior of nitrate at different pH levels and  $\text{NO}_3^-$  concentrations. The distribution of ammonium and nitrate through the soil profile at different pH and fertigation levels describes the behavior of nitrogen in the field and was used to predict N leaching from this soil.

The results obtained in this study suggest:

1. Although the soil at the study site has an acid native pH and contains variable charge minerals, as well as iron oxides, the charge analyses showed a net negative charge on the soil surface. Phosphate and sulfate render soil surfaces more negative. Their presence in this soil, as well as organic matter content, may explain that, although the soil did present some anion exchange capacity, the net surface charge was consistently negative.



2. The retention study demonstrated that Coto clay, under the conditions prevailing in this study, does not retain nitrate through the soil profile. Adsorption isotherms show a negative linear trend, indicating negative adsorption and suggesting anion repulsion and exclusion behavior.

3. Ammonium and nitrate concentrations in the field did not vary significantly between liming or fertigation treatments. This confirms laboratory results that Coto clay has no nitrate adsorption capacity, even at its low native pH.

4. When estimating nitrogen leaching with the percolation method, leaching occurred primarily on events associated with large rainstorms. Nevertheless, irrigation scheduling should be an important part of a crop management plan, since unsaturated fluid flow will also carry nitrogen away from the root zone. The nitrogen balance method resulted in larger estimates of leached nitrogen than the percolation approach. A more detailed balance should be performed to account for N in fruit and roots, which will result in a more realistic estimate.

5. Performing a column study should provide enough information for estimating an exclusion volume due to anion repulsion and for predicting nitrate transport velocity in this soil. This could be incorporated into a model to predict  $\text{NO}_3^-$  leaching and its potential for groundwater contamination when developing a management plan for Coto clay.

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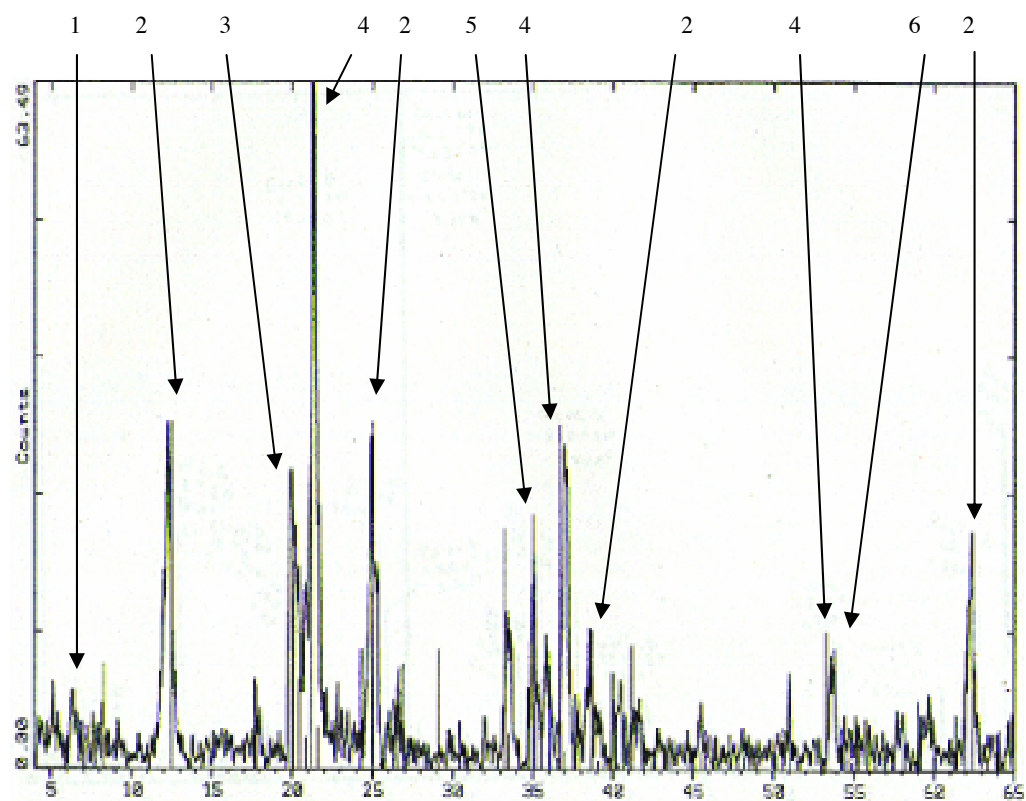
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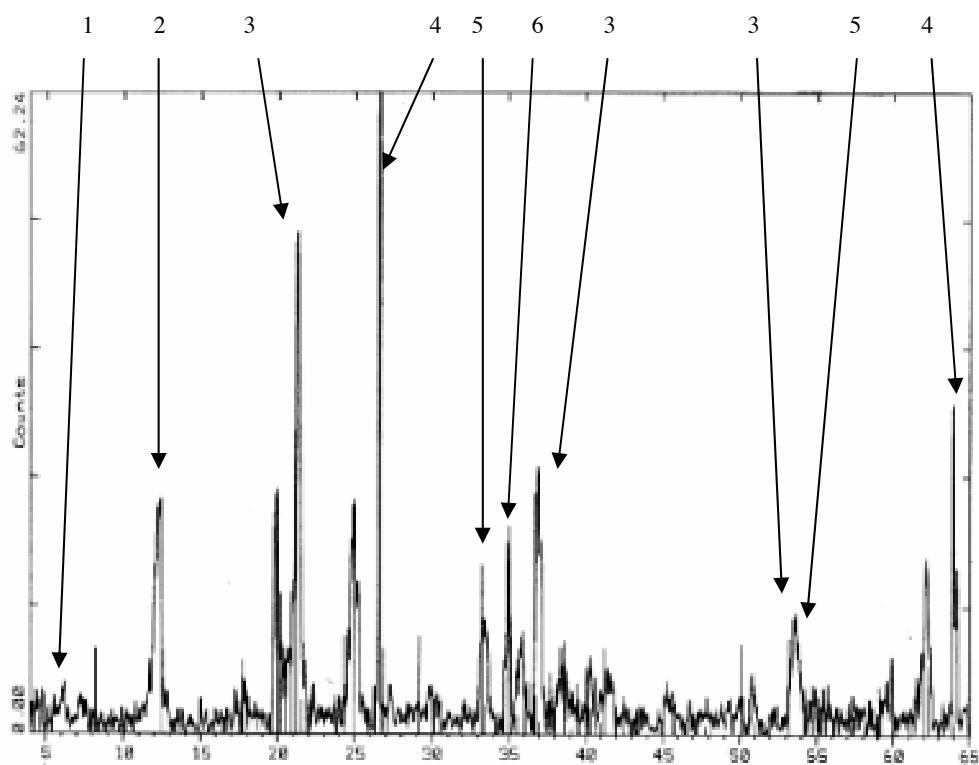
## **APPENDICES**

**Appendix A.** X-ray diffractograms obtained with mineralogy analyses



- |              |             |
|--------------|-------------|
| 1- chlorite  | 4- goethite |
| 2- kaolinite | 5- illite   |
| 3- gibbsite  | 6- hematite |

X-ray diffractogram of the 0-20 cm depth, 2 $\theta$  scale



- |              |             |
|--------------|-------------|
| 1- chlorite  | 4- quartz   |
| 2- kaolinite | 5- hematite |
| 3- goethite  | 6- illite   |

X-ray diffractogram of the 20-40 cm depth, 2θ scale

**Appendix B.** Pictures of field experiment



**Picture 1.** Experiment site, at planting



**Picture 2.** Grown pepper plants.

**Appendix C.** Tabular data from the retention study



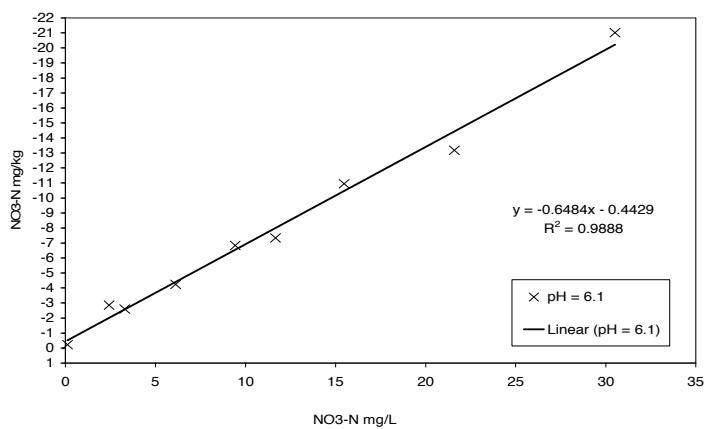
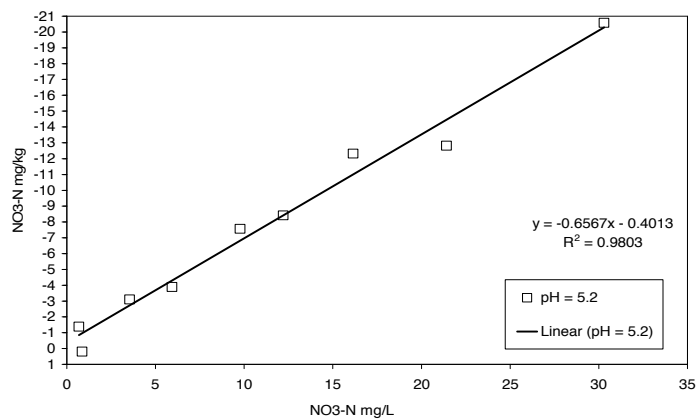
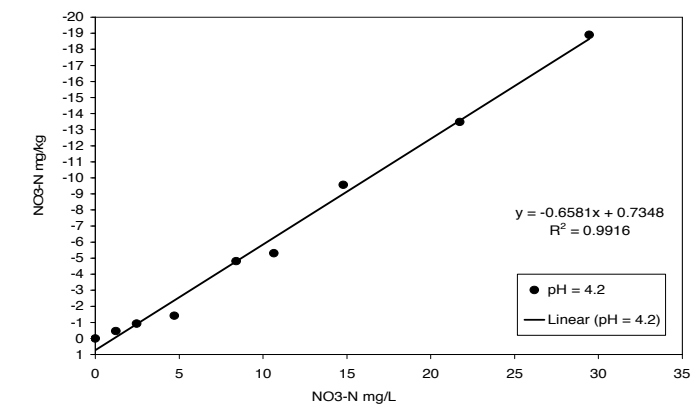
Comparison of NO<sub>3</sub><sup>-</sup> concentration in original solution vs. equilibrium concentration

NO <sub>3</sub> sol. (mg/L)	Depth (cm)	Lime (g/kg)	eq. NO <sub>3</sub> (mg/L)	Difference (added - eq.)
0	0 - 20	0	0.00	0.00
		2	0.69	-0.69
		4	0.11	-0.11
	20 - 40	0	0.00	0.00
		2	0.22	-0.22
		4	0.22	-0.22
1	0 - 20	0	1.23	-0.23
		2	0.91	0.09
		4	2.43	-1.43
	20 - 40	0	1.30	-0.30
		2	2.03	-1.03
		4	1.92	-0.92
2	0 - 20	0	2.46	-0.46
		2	3.55	-1.55
		4	3.30	-1.30
	20 - 40	0	2.43	-0.43
		2	2.86	-0.86
		4	2.75	-0.75
4	0 - 20	0	4.71	-0.71
		2	5.94	-1.94
		4	6.12	-2.12
	20 - 40	0	4.35	-0.35
		2	5.18	-1.18
		4	5.14	-1.14
6	0 - 20	0	8.41	-2.41
		2	9.78	-3.78
		4	9.42	-3.42
	20 - 40	0	7.61	-1.61
		2	8.26	-2.26
		4	8.22	-2.22

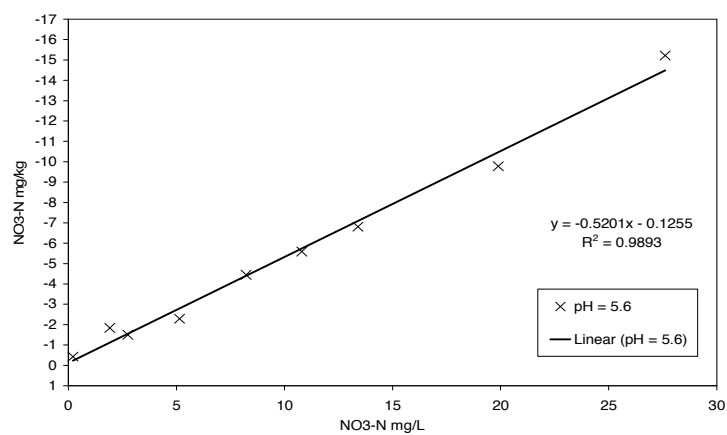
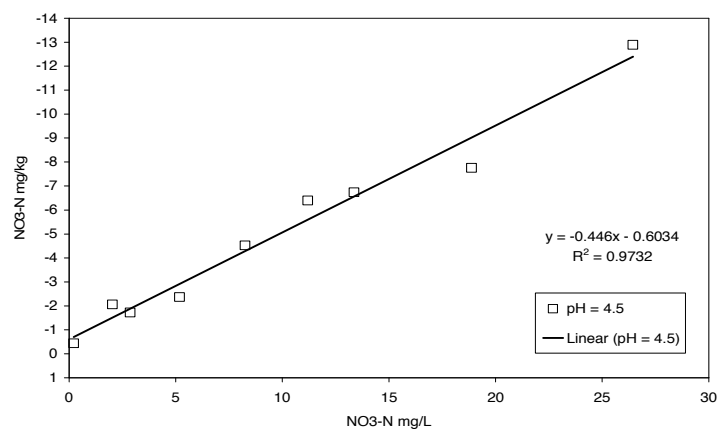
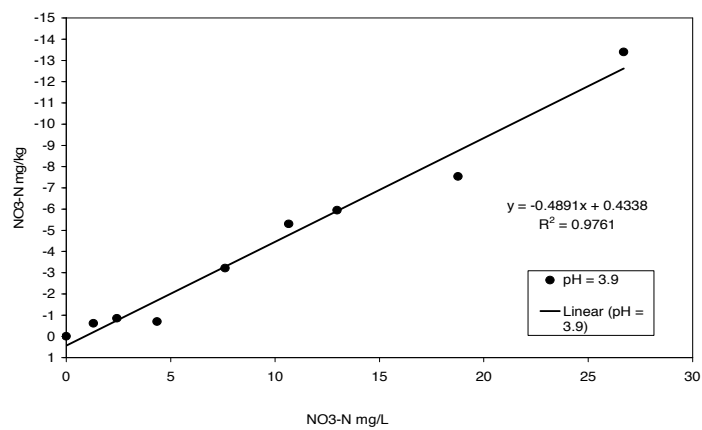
Comparison of NO<sub>3</sub><sup>-</sup> concentration in original  
solution vs. equilibrium concentration (cont.)

NO <sub>3</sub> sol. (mg/L)	Depth (cm)	Lime (g/kg)	eq. NO <sub>3</sub> (mg/L)	Difference (added - eq.)
8	0 - 20	0	10.65	-2.65
		2	12.21	-4.21
		4	11.67	-3.67
	20 - 40	0	10.65	-2.65
		2	11.20	-3.20
		4	10.80	-2.80
10	0 - 20	0	14.78	-4.78
		2	16.16	-6.16
		4	15.47	-5.47
	20 - 40	0	12.97	-2.97
		2	13.37	-3.37
		4	13.41	-3.41
15	0 - 20	0	21.74	-6.74
		2	21.41	-6.41
		4	21.59	-6.59
	20 - 40	0	18.77	-3.77
		2	18.88	-3.88
		4	19.89	-4.89
20	0 - 20	0	29.45	-9.45
		2	30.29	-10.29
		4	30.51	-10.51
	20 - 40	0	26.70	-6.70
		2	26.45	-6.45
		4	27.61	-7.61

**Appendix D.** Nitrate adsorption isotherms



Adsorption isotherms for the 0-20 cm depth



Adsorption isotherms for the 20-40 cm depth

**Appendix E.** Weather data used to estimate percolation

Date	Wind speed	Tmin	Tmax	Min. Rel. Humidity	Max. Rel. Humidity	Rainfall	Solar Radiation	Eto	Kc	Epan
	mi/hr	F	F	%	%	in	MJ/m2- day	mm/day		mm
3/1/02	17.77	67	81	58	100	0.11	15.70	15.81	0.6	missing
3/2/02	11.70	69	82	60	96	0.05	21.87	21.92	0.6	missing
3/3/02	8.93	68	81	62	100	0.08	18.74	18.82	0.6	missing
3/4/02	16.06	69	83	42	94	0	22.54	22.54	0.6	missing
3/5/02	15.42	68	81	47	95	0	25.38	25.38	0.6	missing
3/6/02	17.97	66	81	54	89	0	22.77	22.77	0.6	missing
3/7/02	11.64	69	83	57	91	0.01	21.43	21.44	0.6	missing
3/8/02	17.20	69	82	75	100	0.8	13.98	14.78	0.6	missing
3/9/02	14.55	68	84	71	100	0.7	18.14	18.84	0.6	missing
3/10/02	14.76	69	82	73	100	0.11	16.20	16.31	0.6	missing
3/11/02	16.32	68	84	63	100	0	24.80	24.80	0.6	missing
3/12/02	16.26	70	83	59	98	0	24.33	24.33	0.6	missing
3/13/02	16.55	70	86	60	97	0	18.80	18.80	0.6	0.12
3/14/02	14.85	66	83	56	100	0	26.19	26.19	0.6	0.06
3/15/02	17.87	65	83	65	98	0.01	23.44	23.45	0.6	0.05
3/16/02	18.90	68	83	62	100	0	24.97	24.97	0.6	0.20
3/17/02	17.42	68	83	63	100	0	24.67	24.67	0.6	0.13
3/18/02	15.01	70	84	53	98	0	24.06	24.06	0.6	0.16
3/19/02	17.17	70	83	58	96	0	25.34	25.34	0.6	0.15
3/20/02	16.72	68	83	51	94	0	26.66	26.66	0.6	0.19
3/21/02	16.34	69	84	56	94	0	22.22	22.22	0.6	0.15
3/22/02	missing	missing	missing	missing	missing	missing	missing	missing	0.6	0.11
3/23/02	9.67	66	86	62	100	1.25	21.66	22.91	0.6	0.13
3/24/02	13.27	68	87	64	100	0	20.07	20.07	0.6	0.03
3/25/02	16.19	70	85	63	100	0	24.07	24.07	0.6	0.09
3/25/02	missing	missing	missing	missing	missing	missing	missing	missing	0.6	0.13
3/26/02	16.64	71	83	64	100	0	24.42	24.42	0.6	0.11
3/27/02	9.94	67	84	66	99	0.07	16.82	16.89	0.6	0.17
3/28/02	4.33	68	87	53	98	0.91	16.79	17.70	0.6	0.04
3/29/02	8.75	68	85	62	100	0.01	22.17	22.18	0.6	0.06
3/30/02	15.64	69	82	66	100	0	23.59	23.59	0.6	0.11
3/31/02	18.30	69	83	68	100	0	25.39	25.39	0.6	0.11
4/1/02	15.92	69	84	65	100	0.7	24.36	25.06	0.6	0.11
4/2/02	15.81	70	83	70	100	0.37	23.33	23.70	0.6	0.10
4/3/02	15.37	72	84	69	100	1.33	16.90	18.23	0.6	0.12
4/4/02	14.17	70	85	71	100	0.87	20.02	20.89	0.6	0.09
4/5/02	6.39	68	88	58	100	6.91	13.29	20.20	0.6	0.00
4/6/02	3.17	69	87	59	100	0.53	12.47	13.00	0.6	0.00
4/7/02	11.17	68	80	79	100	0.82	10.33	11.15	0.6	0.12

Date	Wind speed	Tmin	Tmax	Min. Rel. Humidity	Max. Rel. Humidity	Rainfall	Solar Radiation	Eto	Kc	Epan
	mi/hr	F	F	%	%	in	MJ/m2- day	mm/day		mm
4/8/02	9.62	71	81	66	97	0.06	18.73	18.79	0.6	0.16
4/9/02	11.99	71	79	61	90	0	17.08	17.08	0.6	0.14
4/10/02	19.41	69	79	60	100	0.07	16.63	16.70	0.6	0.13
4/11/02	18.63	66	79	52	100	0.22	23.28	23.50	0.61	0.01
4/12/02	12.94	65	79	63	94	0.01	18.70	18.71	0.62	0.13
4/13/02	missing	missing	missing	missing	missing	missing	missing	missing	0.63	0.01
4/14/02	14.58	68	82	61	96	0	26.72	26.72	0.65	0.11
4/15/02	17.53	71	82	70	100	0.11	14.19	14.30	0.66	0.17
4/16/02	18.79	71	83	70	100	0	15.30	15.30	0.67	0.09
4/17/02	15.43	72	82	73	95	0	20.98	20.98	0.68	0.14
4/18/02	19.55	70	83	58	100	0	25.15	25.15	0.69	0.14
4/19/02	12.28	70	84	69	100	0.54	11.86	12.40	0.7	0.05
4/20/02	6.03	69	76	96	100	0.5	4.78	5.28	0.71	0.02
4/21/02	5.57	69	88	65	100	0.88	14.22	15.10	0.72	0.06
4/22/02	10.48	71	87	71	100	0.27	16.40	16.67	0.74	0.10
4/23/02	14.99	72	84	69	100	0.03	24.75	24.78	0.75	0.14
4/24/02	15.69	71	83	71	100	0.11	21.62	21.73	0.76	0.12
4/25/02	17.26	71	84	72	100	0.02	22.63	22.65	0.77	0.14
4/26/02	16.28	70	84	68	100	0	25.64	25.64	0.78	0.14
4/27/02	12.93	70	84	72	100	0.32	23.60	23.92	0.79	0.15
4/28/02	16.00	71	83	63	100	0.01	26.19	26.20	0.8	0.19
4/29/02	19.23	69	83	66	99	0	24.87	24.87	0.81	0.15
4/30/02	13.77	68	85	62	100	0.01	22.45	22.46	0.82	0.16
5/1/02	12.34	70	85	69	100	2.02	21.99	24.01	0.84	0.09
5/2/02	18.58	70	84	75	100	0	25.50	25.50	0.85	0.18
5/3/02	13.27	71	84	66	100	0	26.66	26.66	0.86	0.21
5/4/02	14.61	72	83	67	95	0	22.03	22.03	0.87	0.18
5/5/02	14.55	71	83	65	98	0.01	23.66	23.67	0.88	0.19
5/6/02	19.15	71	83	71	100	0.09	26.16	26.25	0.89	0.21
5/7/02	16.77	71	84	69	100	0	26.35	26.35	0.9	0.19
5/8/02	18.86	70	83	69	100	0	25.12	25.12	0.91	0.19
5/9/02	16.98	69	84	66	96	0	24.36	24.36	0.93	0.22
5/10/02	15.18	70	84	68	98	0	23.18	23.18	0.94	0.12
5/11/02	11.44	71	85	73	100	0.14	23.65	23.79	0.95	0.26
5/12/02	12.52	72	84	67	98	0	27.59	27.59	0.96	0.18
5/13/02	missing	missing	missing	missing	missing	missing	missing	missing	0.97	0.34
5/14/02	20.42	72	86	60	95	0	25.36	25.36	0.98	0.08
5/15/02	18.23	69	86	62	96	0	24.32	24.32	0.99	0.22
5/16/02	13.90	72	87	64	100	1.26	20.72	21.98	1	0.20



Date	Wind speed	Tmin	Tmax	Min. Rel. Humidity	Max. Rel. Humidity	Rainfall	Solar Radiation	Eto	Kc	Epan
	mi/hr	F	F	%	%	in	MJ/m2- day	mm/day		mm
5/17/02	13.34	71	85	65	100	0	23.23	23.23	1.02	0.19
5/18/02	14.44	70	85	66	100	0.45	21.45	21.90	1.03	0.21
5/19/02	17.30	71	86	70	100	0	20.00	20.00	1.04	0.18
5/20/02	15.51	72	87	65	99	0	21.26	21.26	1.05	0.17
5/21/02	14.58	72	87	71	100	0	23.41	23.41	1.05	0.21
5/22/02	missing	missing	missing	missing	missing	missing	missing	missing	1.05	0.16
5/23/02	9.96	73	94	42	98	0	22.45	22.45	1.05	0.28
5/24/02	6.14	71	94	39	95	0	25.04	25.04	1.05	0.22
5/25/02	14.47	71	87	56	95	0	25.38	25.38	1.05	0.29
5/26/02	13.24	69	85	56	97	0.05	22.40	22.45	1.05	0.18
5/27/02	10.61	72	86	58	97	0.29	15.28	15.57	1.05	0.08
5/28/02	4.57	70	87	66	101	0.31	13.10	13.41	1.05	0.13
5/29/02	5.57	72	88	63	102	0	16.80	16.80	1.05	0.06
5/30/02	4.96	74	87	65	99	0	11.17	11.17	1.05	0.07
5/31/02	5.43	72	91	58	98	0.2	18.15	18.35	1.05	0.15
6/1/02	6.15	73	92	55	101	0.45	24.68	25.13	1.05	0.19
6/2/02	5.80	75	91	58	100	0.22	17.22	17.44	1.05	0.15
6/3/02	3.89	74	90	62	100	1.1	16.85	17.95	1.05	0.14
6/4/02	3.54	72	85	74	100	0.49	8.53	9.02	1.05	0.02
6/5/02	8.88	73	90	55	100	0.01	19.83	19.84	1.05	0.18
6/6/02	2.38	72	91	56	98	0.04	12.51	12.55	1.05	0.08
6/7/02	10.26	70	87	65	99	0.18	17.94	18.12	1.05	0.25
6/8/02	6.82	72	88	65	100	0.1	15.30	15.40	1.05	0.05
6/9/02	12.48	73	86	76	98	0	15.58	15.58	1.05	0.11
6/10/02	10.81	70	88	63	99	0	22.45	22.45	1.05	0.19
6/11/02	16.57	71	87	68	99	0	24.57	24.57	1.05	0.10
6/12/02	14.90	73	87	65	99	0.08	22.71	22.79	1.05	0.32
6/13/02	12.91	72	89	59	100	0.17	24.18	24.35	1.05	0.21
6/14/02	19.27	73	87	65	100	0.01	25.80	25.81	1.05	0.17
6/15/02	17.48	71	87	63	98	0	25.62	25.62	1.05	0.25
6/16/02	14.53	71	89	59	98	0	24.17	24.17	1.05	0.26
6/17/02	13.60	74	86	67	100	0.09	22.12	22.21	1.05	0.14
6/18/02	17.15	75	89	62	99	0	24.06	24.06	1.05	0.20
6/19/02	13.27	75	86	64	96	0	23.87	23.87	1.05	0.20
6/20/02	13.50	72	86	64	98	0	26.23	26.23	1.05	0.18
6/21/02	15.81	71	87	64	96	0.07	19.06	19.13	1.05	missing
6/22/02	14.88	71	88	61	100	0	24.39	24.39	1.05	missing
6/23/02	16.81	72	87	56	99	0	25.01	25.01	1.05	missing
6/24/02	15.90	72	86	66	97	0	20.47	20.47	1.05	missing

Date	Wind speed	Tmin	Tmax	Min. Rel. Humidity	Max. Rel. Humidity	Rainfall	Solar Radiation	Eto	Kc	Epan
	mi/hr	F	F	%	%	in	MJ/m2- day	mm/day		mm
1/28/03	14.20	68	85	59	100	0	16.43	16.43	0.6	missing
1/29/03	17.26	68	84	61	99	0	15.69	15.69	0.6	missing
1/30/03	13.57	67	83	68	100	0.44	13.53	13.97	0.6	missing
1/31/03	5.52	67	85	60	100	0	12.83	12.83	0.6	missing
2/1/03	4.06	67	85	59	100	0	15.98	15.98	0.6	missing
2/2/03	5.80	70	85	69	100	0.04	11.51	11.55	0.6	missing
2/3/03	12.22	71	81	78	100	0.14	10.44	10.58	0.6	missing
2/4/03	19.04	72	81	73	100	0.12	9.40	9.52	0.6	missing
2/5/03	17.64	70	82	72	100	0	15.27	15.27	0.6	missing
2/6/03	16.24	68	84	71	100	0	21.15	21.15	0.6	missing
2/7/03	13.64	69	88	53	99	0	18.74	18.74	0.6	missing
2/8/03	16.49	70	83	70	98	0	18.41	18.41	0.6	missing
2/9/03	16.65	70	86	67	100	0	21.48	21.48	0.6	15.24
2/10/03	14.83	69	84	62	96	0	20.74	20.74	0.6	15.24
2/11/03	15.48	66	84	65	99	0	17.04	17.04	0.6	15.24
2/12/03	15.98	69	85	66	98	0	20.21	20.21	0.6	15.24
2/13/03	15.73	69	84	65	100	0	19.31	19.31	0.6	15.24
2/14/03	16.95	67	84	69	100	0	20.61	20.61	0.6	15.24
2/15/03	13.17	69	85	56	96	0	22.72	22.72	0.6	15.24
2/16/03	12.68	69	84	60	99	0	17.72	17.72	0.6	15.24
2/17/03	15.60	72	86	58	99	0	20.82	20.82	0.6	missing
2/18/03	13.41	67	86	59	100	0	20.09	20.09	0.6	missing
2/19/03	11.48	70	83	70	95	0	18.21	18.21	0.6	15.24
2/20/03	16.89	68	84	67	98	0.04	17.40	17.44	0.6	15.24
2/21/03	13.82	69	86	58	100	0.01	18.17	18.18	0.6	15.24
2/22/03	6.39	66	92	40	100	0	20.73	20.73	0.6	15.24
2/23/03	13.39	66	86	59	95	0	18.60	18.60	0.6	15.24
2/24/03	14.84	64	84	55	94	0	21.85	21.85	0.6	15.24
2/25/03	15.43	66	84	60	98	0	20.84	20.84	0.6	15.24
2/26/03	8.03	65	86	54	98	0	23.58	23.58	0.6	15.24
2/27/03	7.45	66	88	41	94	0	17.66	17.66	0.61	15.494
2/28/03	12.59	65	87	42	97	0	19.72	19.72	0.62	15.748
3/1/03	17.01	68	85	60	96	0	22.11	22.11	0.63	16.002
3/2/03	14.14	68	87	47	98	0	13.44	13.44	0.64	16.256
3/3/03	11.87	65	87	49	98	0	19.79	19.79	0.66	16.764
3/4/03	13.92	68	88	57	100	0	21.23	21.23	0.67	17.018
3/5/03	15.92	68	87	49	95	0	21.25	21.25	0.68	17.272
3/5/03	15.20	67	91	45	98	0	22.36	22.36	0.69	17.526
3/7/03	16.38	69	88	55	98	0	20.37	20.37	0.7	17.78

Date	Wind speed	Tmin	Tmax	Min. Rel. Humidity	Max. Rel. Humidity	Rainfall	Solar Radiation	Eto	Kc	Epan
	mi/hr	F	F	%	%	in	MJ/m2- day	mm/day		mm
3/8/03	17.55	71	85	65	98	0.14	18.37	18.51	0.71	18.034
3/9/03	15.45	70	85	65	100	0	20.95	20.95	0.72	18.288
3/10/03	9.31	67	84	65	100	0.26	13.49	13.75	0.74	18.796
3/11/03	13.33	66	86	59	100	0	16.76	16.76	0.75	19.05
3/12/03	15.71	66	85	57	98	0	23.29	23.29	0.76	19.304
3/13/03	12.72	69	85	55	97	0	25.25	25.25	0.77	19.558
3/14/03	17.06	68	86	50	94	0	21.99	21.99	0.78	19.812
3/15/03	15.54	67	85	59	100	0.28	15.34	15.62	0.79	20.066
3/16/03	10.55	66	87	53	100	0	19.49	19.49	0.8	20.32
3/17/03	7.50	66	88	44	97	0	22.02	22.02	0.81	missing
3/18/03	6.94	67	88	53	98	0	14.92	14.92	0.82	20.828
3/19/03	11.16	70	90	53	97	0	22.60	22.60	0.84	21.336
3/20/03	9.70	70	87	59	98	0	22.26	22.26	0.85	21.59
3/21/03	13.31	71	87	49	99	0	25.96	25.96	0.86	21.844
3/22/03	13.94	71	85	55	98	0	22.83	22.83	0.87	22.098
3/23/03	15.05	70	84	51	100	0.06	21.93	21.99	0.88	22.352
3/24/03	11.82	70	86	54	100	0	20.00	20.00	0.89	22.606
3/25/03	8.60	69	87	56	100	0.54	18.08	18.62	0.9	22.86
3/26/03	9.62	70	86	61	100	0	20.17	20.17	0.91	23.114
3/27/03	8.32	73	86	64	97	0	13.94	13.94	0.93	missing
3/28/03	7.91	70	88	57	96	0.01	18.53	18.54	0.94	23.876
3/29/03	13.26	71	86	60	100	0.39	19.27	19.66	0.95	24.13
3/30/03	17.92	71	84	56	100	0	26.40	26.40	0.96	24.384
3/31/03	18.30	70	85	64	96	0	24.59	24.59	0.97	24.638
4/1/03	6.23	71	86	62	100	0.1	9.45	9.55	0.98	24.892
4/2/03	15.37	70	83	70	100	0.01	16.33	16.34	0.99	25.146
4/3/03	13.76	71	84	68	100	0.41	18.68	19.09	1	25.4
4/4/03	15.61	70	84	72	100	0.06	14.95	15.01	1.02	25.908
4/5/03	6.16	69	88	59	100	1.57	14.11	15.68	1.03	26.162
4/6/03	7.75	72	87	59	100	0.42	19.37	19.79	1.04	26.416
4/7/03	19.25	72	83	73	100	0.19	21.97	22.16	1.05	26.67
4/8/03	17.81	70	83	68	98	0	27.04	27.04	1.05	26.67
4/9/03	4.94	69	87	57	100	1.67	11.59	13.26	1.05	26.67
4/10/03	5.58	68	86	67	100	3.82	12.13	15.95	1.05	26.67
4/11/03	4.20	69	87	62	100	1.26	12.64	13.90	1.05	26.67
4/12/03	3.61	70	89	59	100	1.03	12.47	13.50	1.05	missing
4/13/03	7.47	70	88	61	100	0.94	25.10	26.04	1.05	missing
4/14/03	9.05	70	88	52	100	0.01	14.95	14.96	1.05	26.67
4/15/03	12.17	70	85	65	99	0.62	16.27	16.89	1.05	26.67
4/16/03	5.59	70	91	53	97	0	17.13	17.13	1.05	26.67
4/17/03	3.39	71	79	87	100	1.29	5.86	7.15	1.05	26.67
4/18/03	6.43	71	82	77	100	0	13.31	13.31	1.05	missing

Date	Wind speed	Tmin	Tmax	Min. Rel. Humidity	Max. Rel. Humidity	Rainfall	Solar Radiation	Eto	Kc	Epan
	mi/hr	F	F	%	%	in	MJ/m2- day	mm/day		mm
4/19/03	8.00	70	83	72	100	0	17.04	17.04	1.05	missing
4/20/03	8.73	71	84	71	100	0	18.91	18.91	1.05	missing
4/21/03	9.09	70	84	69	100	0	19.84	19.84	1.05	missing
4/22/03	9.46	71	84	66	100	0.04	20.78	20.82	1.05	missing
4/23/03	7.70	70	85	68	100	0.01	17.32	17.33	1.05	missing
4/24/03	10.04	71	89	67	100	0.07	18.40	18.47	1.05	26.67
4/25/03	17.58	71	85	71	100	0.1	24.73	24.83	1.05	26.67
4/26/03	5.65	69	87	67	100	0.14	14.69	14.83	1.05	26.67
4/27/03	6.72	69	89	57	100	0	23.72	23.72	1.05	26.67
4/28/03	6.82	68	88	60	99	0	25.69	25.69	1.05	26.67
4/29/03	6.70	69	88	58	100	0	25.56	25.56	1.05	26.67
4/30/03	11.93	70	91	52	97	0	25.30	25.30	1.05	26.67
5/1/03	14.04	71	88	66	98	0	23.35	23.35	1.05	26.67
5/2/03	14.40	70	87	61	98	0	25.67	25.67	1.05	26.67
5/3/03	14.06	72	88	64	94	0	24.72	24.72	1.05	26.67
5/4/03	16.05	70	86	56	95	0	25.02	25.02	1.05	26.67
5/5/03	16.80	72	86	63	95	0	26.76	26.76	1.05	26.67
5/6/03	14.06	72	86	62	98	0	26.98	26.98	1.05	26.67
5/7/03	16.33	73	85	65	97	0	25.74	25.74	1.05	26.67
5/8/03	15.30	71	86	64	99	0	26.88	26.88	1.05	26.67
5/9/03	14.76	71	86	64	100	0.17	18.90	19.07	1.05	26.67
5/10/03	15.62	68	89	60	100	0	26.57	26.57	1.05	26.67
5/11/03	15.83	72	86	63	100	0.72	24.87	25.59	1.05	26.67
5/12/03	15.61	70	85	63	98	0	27.61	27.61	1.05	26.67
5/13/03	13.50	70	86	62	100	0.42	24.69	25.11	1.05	26.67
5/14/03	7.74	70	87	60	100	0.75	16.50	17.25	1.05	26.67
5/15/03	15.53	70	85	71	100	0.4	24.98	25.38	1.05	26.67
5/16/03	16.05	71	85	70	100	0	25.58	25.58	1.05	missing
5/17/03	17.97	71	85	69	100	0.72	21.84	22.56	1.05	26.67
5/18/03	16.05	70	85	77	100	0.28	21.42	21.70	1.04	26.416
5/19/03	6.22	74	90	61	100	0.04	13.37	13.41	1.03	26.162
5/20/03	4.02	73	88	65	100	1.2	11.99	13.19	1.03	26.162
5/21/03	3.15	72	85	72	100	0.23	10.12	10.35	1.02	25.908
5/22/03	9.30	73	85	74	100	0.23	14.35	14.58	1.01	25.654
5/23/03	15.45	74	85	76	100	0	18.58	18.58	1	25.4
5/24/03	14.29	75	90	66	100	0.01	16.10	16.11	1	25.4
5/25/03	16.56	73	87	67	100	0	25.27	25.27	0.99	25.146
5/26/03	17.85	72	86	70	97	0	25.54	25.54	0.98	24.892
5/27/03	15.84	73	87	61	97	0	25.94	25.94	0.97	24.638
5/28/03	17.64	70	87	63	99	0	24.06	24.06	0.97	24.638
5/29/03	11.62	71	88	61	96	0	21.97	21.97	0.96	missing
5/30/03	10.23	71	89	58	95	0	23.30	23.30	0.95	missing

**Appendix F.** Evaluation of percolation and nitrogen leaching from a sweet pepper crop grown on an Oxisol in northwest Puerto Rico (Harmsen et al., 2003)

## EVALUATION OF PERCOLATION AND NITROGEN LEACHING FROM A SWEET PEPPER CROP GROWN ON AN OXISOL SOIL IN NORTHWEST PUERTO RICO<sup>1,2</sup>

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### INTRODUCTION

A study was conducted to evaluate the influence of agricultural lime ( $\text{CaCO}_3$ ) on the movement and uptake of inorganic nitrogen for a sweet pepper crop (*Capsicum annuum*) grown on an Oxisol soil (Coto clay) in northwest Puerto Rico. The Coto clay soil, which contains the 1:1 kaolinite mineral, has a low pH (4 to 4.5). The 1:1 type clays are known to possess a net positive charge at low pH, resulting in the adsorption of negatively charged ions such as nitrate. From an environmental standpoint this characteristic of the 1:1 clay is favorable, since nitrate leaching, a major cause of groundwater pollution in many areas, is reduced relative to soils with net negative charge. However, agricultural plants, such as sweet peppers, favor a higher soil pH (approximately 6.5), which can be obtained by the application of agricultural lime. This, however, may have the negative effect of increasing the potential for nitrate leaching, as the net charge on the soil particles becomes positive with increasing pH.

This paper describes the results of a nitrogen leaching analysis for two sweet pepper crop seasons. The analysis was based on multiplying the daily percolation flux through the soil profile by the measured concentration of nitrogen below the root zone. Irrigations were scheduled using the pan evaporation method for estimating crop water requirements. No significant difference in nitrogen leaching was observed for the lime and no-lime treatments. This was attributed to the low nitrate retention capacity of this soil, even a low pH. The average percent of nitrogen leached during the 1<sup>st</sup> and 2<sup>nd</sup> season, relative to the amounts applied, were 26% and 15%, respectively. Leaching events were associated with large rainstorms, suggesting that leaching of N would have occurred regardless of the irrigation scheduling method used.

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<sup>2</sup> Presented at the 39th Annual Meeting of the Caribbean Food Crops Society, 2003. Grenada. Vol. 39.

## TECHNICAL APPROACH

Sweet pepper crops were planted at the UPR Experiment Station at Isabela in northwest PR (Figure 1) during March 2002, and January 2003. Harmsen et al. (2002) provided a detailed description of the experimental layout of the field site.



Figure 1. Location of field site at Isabela, PR.

The soil at the Isabela Experiment Station belongs to the Coto series. It is a very fine kaolinitic, isohyperthermic Typic Eutruxox. These are very deep, well drained, moderately permeable soils formed in sediments weathered from limestone. The available water capacity is moderate, and the reaction is strongly acidic throughout the whole profile. Consistence is slightly sticky and slightly plastic in the Oxic horizons. A strong, stable granular structure provides these soils with a very rapid drainage, despite their high clay content (Keng et al, 1981). Average values of hydraulic properties published for the Coto clay soil near the study area are as follows: air dry bulk density  $1.39 \text{ g/cm}^3$ , porosity 48%, field capacity 30%, wilting point 23%, available water holding capacity (AWHC) 9% (Soil Conservation Service, 1967). The AWHC of this soil is low for clay. Typical values for clay are 15 to 20% (Keller and Bliesner, 1990). A small value of AWHC means that there is a greater potential for leaching since the soil moisture content associated with the field capacity is more easily exceeded.

The experimental site of 0.1 ha was divided into four blocks, each block divided into four plots, one for each treatment, for a total of sixteen plots. The plots measure  $67 \text{ m}^2$ . The treatments included two lime levels (lime and no lime) and two fertigation frequencies (F1 and F2). Each plot had four beds covered with plastic (silver side exposed) with two rows of sweet pepper plants per bed. The transplanted sweet peppers were grown in rows 91 cm apart, 30 cm apart along rows, with beds 1.83 meter on center. This gave a plant population of approximately 37,000 plants per hectare. There was an initial granular application of triple super-phosphate of 224 Kg/ha and 80 Kg/ha of 10-10-10 fertilizer. Peppers were planted from March 11th through March 13<sup>th</sup>, 2002 and January 27 through January 31<sup>th</sup>, 2003.  $\text{KNO}_3$  and urea were injected through the drip irrigation system throughout the season at different frequencies (weekly [F1] or bi-weekly [F2]). The total nitrogen applied during the season was 225 Kg/ha. After transplanting, soil samples were taken bi-weekly at 20 cm increments, down to an 80 cm depth from each plot to be analyzed for moisture content and nitrogen concentration. Each date in which soil samples were

collected, whole plants were harvested for growth data. Periodic pesticide applications were made to control weeds and insects affecting crop growth.

### Water Balance

A water balance approach was used in this study to estimate percolation past the root zone. The water balance is shown in the following equation:

$$\text{PERC} = R - \text{RO} + \text{IRR} - \text{ET}_c + \Delta S \quad (1)$$

where PERC is percolation below the root zone, R is rainfall, IRR is irrigation, RO is surface runoff,  $\text{ET}_c$  is crop evapotranspiration, and  $\Delta S = S_1 - S_2$ , where  $S_1$  and  $S_2$  are the water stored in the soil profile at times 1 and 2, respectively. The units of each term in equation 1 are in mm of water per day. Rainfall (R) was obtained from a tipping bucket-type rain gauge located on the Experiment Station property. The rain gauge was located within a weather station complex located approximately 0.4 km from the study area. The weather station consisted of a 10 meter (high wind resistant) tower with lighting protection, data logger and radio communication system, and sensors to measure the following parameters: wind direction and speed, temperature, relative humidity, barometric pressure, cumulative rainfall, and solar radiation (Zapata et al., 2001). Irrigation (IRR) was applied through a drip irrigation system. The inline-type emitters produced a flow of 1.9 liters per hour per emitter at a design pressure of 10 pounds per square inch (psi). Emitters were spaced every 30 cm. Irrigations (IRR) were scheduled based on the estimated evapotranspiration rate as determined from the following equation:

$$\text{IRR} = \text{ET}_{\text{pan}} = (K_c K_p E_{\text{pan}}) \quad (2)$$

where  $\text{ET}_{\text{pan}}$  is the pan evaporation-derived evapotranspiration,  $K_c$  is the evapotranspiration crop coefficient for sweet peppers (FAO Paper No. 56, Allen et al., 1998), which varied daily;  $K_p$  is the average annual value of the pan coefficient equal to 0.78 for Isabela, PR (Gonzales and Goyal, 1989). A cumulative water meter was used to control the gallons of irrigation water applied.

The evapotranspiration term in equation 1 was estimated from the following equation:

$$\text{ET}_c = K_c \text{ET}_o \quad (3)$$

where  $K_c$  is the crop coefficient (dimensionless) and  $\text{ET}_o$  (mm/day) is the reference evapotranspiration obtained using the Penman-Monteith equation, given below (Allen et al., 1998):



$$ET_o = \frac{0.408 \Delta (R_n - G) + \gamma \left( \frac{900}{T + 273} \right) u_2 (e_s - e_a)}{\Delta + \gamma (1 + 0.34 u_2)} \quad (4)$$

where  $\Delta$  is the slope of the vapor pressure curve ( $\text{kPa } ^\circ\text{C}^{-1}$ ),  $R_n$  is net radiation ( $\text{MJ m}^{-2} \text{d}^{-1}$ ),  $G$  is the soil heat flux density ( $\text{MJ m}^{-2} \text{d}^{-1}$ ),  $\gamma$  is the psychrometric constant ( $\text{kPa}^{-1}$ ),  $T$  is mean daily air temperature at 2 m height ( $^\circ\text{C}$ ),  $u_2$  is wind speed at 2-m height,  $e_s$  is the saturated vapor pressure ( $\text{kPa}^{-1}$ ) and  $e_a$  is the actual vapor pressure ( $\text{kPa}^{-1}$ ). Equation 4 applies specifically to a hypothetical reference crop with an assumed crop height of 0.12 m, a fixed surface resistance of  $70 \text{ sec m}^{-1}$  and an albedo of 0.23. Data required by equation 4 were obtained from the weather station located near the study area. Wind speeds obtained from the 10 m high tower were adjusted to the 2 m wind speed, required by the Penman-Monteith method, by means of an exponential relationship. Initial values of the crop coefficient were obtained from the literature for sweet pepper for the initial, mature and end crop stages (FAO Paper No. 56). Adjustments of  $K_c$  were made during the calibration of equation 1 as described later in this section.  $ET_o$  was estimated on a daily basis using a spreadsheet program. The calculation methodology is described by Allen, et al. (1998).

The values of  $S$  in equation 1 and 2 were obtained from the following general formula:  $S = \theta_v * Z$ , where  $\theta_v$  is the vertically averaged volumetric soil moisture content over the depth  $Z$ , obtained by multiplying the moisture content, mass-basis ( $\theta_m$ ), by the soil bulk density and dividing by the density of water. The soil bulk densities were obtained from undisturbed soil cores.

Between sampling dates when measured values of  $\theta_v$  were not available, daily values were estimated using equation 1 along with information about the moisture holding capacity of the soil. In this method, if the water added to the profile by rainfall or irrigation exceeds the soil moisture holding capacity (or field capacity), then the excess water was assumed to be equal to PERC and the moisture content was set equal to the field capacity on that day. This approach has previously been used for irrigation scheduling (Shayya and Bralts, 1994), waste landfill leachate estimation (Fenn et al., 1975) and estimation of aquifer recharge rates (Thornthwaite and Mather, 1955; Papadopoulos & Associates, Inc. and MathSoft, Inc. 1994). In this study, the effective field capacity of the soil was determined in-situ by saturating the soil and obtaining the soil moisture content within 48 hours.

Calibration of the water balance equation was accomplished by adjusting the ratio of runoff to rainfall (RO/R) within reasonable limits, until the measured and estimated soil moisture content were in reasonable agreement.  $1 - \text{RO/R}$  represents the fraction of rainfall that infiltrates into the soil bed. This contribution of water can occur in several ways for the plastic covered bed-type system used in this study. Rainfall may enter directly through the holes in the plastic made for the plants. Rainfall that runs off of the plastic into the furrow or that falls directly into the furrow may also be absorbed into the beds. Under flood conditions, which occurred on several occasions during the two crop seasons, water could have entered the beds under a positive water pressure. For non-flooding rainfall events, soil water may move from the furrows into the beds by means unsaturated flow, which is controlled by the pore water pressure gradient between the furrow and the bed.

### Nitrogen Leaching

Nitrogen leaching (nitrate and ammonium) was estimated by multiplying the daily value of PERC by the concentration of nitrogen within the 60 to 80 cm depth of soil. This vertical interval was considered to be below the root zone, since plant roots were not observed within this interval any time throughout the two seasons. The following equation was used to estimate nitrate and ammonium leaching, respectively:

$$L_{NO_3} = 0.01 \rho_b NO_3 PERC / \theta_{vol} \quad (5a)$$

$$L_{NH_4} = 0.01 \rho_b NH_4 PERC / \theta_{vol} \quad (5b)$$

where  $L_{NO_3}$  and  $L_{NH_4}$  are the kg of nitrate and ammonium leached below the root zone per hectare,  $NO_3$  and  $NH_4$  are the nitrate and ammonium soil concentration in mg/kg in the 60 to 80 cm depth interval, PERC is the percolation rate in mm, and  $\rho_b$  and  $\theta_{vol}$  are the bulk density ( $gm/cm^3$ ) and volumetric moisture content ( $cm^3/cm^3$ ) in the 60 to 80 cm depth interval. Equations 5a and 5b were used on a daily basis. Each measured value of soil concentration used in equation 5a and 5b were based on the average of four replications. Values of  $NO_3$  and  $NH_4$  between sampling dates were linearly interpolated.

### RESULTS AND DISCUSSION

The Coto clay soil was analyzed for various physical and hydraulic properties (Table 1). The soil has a relatively high sand content and high hydraulic conductivity in the 0-20 cm interval, which accounts for its high water intake capacity. We observed on several occasions the rapid infiltration of water after large rainfall events. In fact, the value of hydraulic conductivity for the 0-20 cm interval is similar to sand, which averages 900 cm/day (Freeze and Cherry, 1979). Bulk density, porosity, hydraulic conductivity, moisture content at 0.33 and 15 bars pressure, and AWHC were obtained from undisturbed cores in the laboratory.

Measured soil pH was between 4 and 5. Laboratory incubation tests were performed to determine the proper amount of lime needed to be applied to the soil to increase the pH to around 6.5 in the limed treatments; this amount was 7.4 tons lime/ha. The first year the pH did not respond as expected in the limed plots, and therefore, this may have contributed to there being no significant difference observed in the estimated nitrate losses by leaching between the lime and no-lime treatments. The second year the amount of lime applied to the limed treatments was doubled (14.8 tons lime/ha) and pH levels rose as expected.

Figure 2 shows a comparison of the evapotranspiration derived from pan and Penman-Monteith methods during Year 2.  $ET_{pan}$  was observed to have higher variability than  $ET_c$ . For reference, Figure 2 also shows the  $ET_c$  based on long-term average climate data for Isabela, PR. The seasonal ET for the methods of pan, Penman-Monteith and Penman-Monteith based on long-term data were 447 mm, 402 mm and 511 mm, respectively.

Table 1. Physical and hydraulic properties of Coto clay in the 0-20, 20-40, 40-60 and 60-80 cm depth intervals.

Depth	% Sand <sup>1</sup>	% Silt <sup>1</sup>	% Clay <sup>1</sup>	Soil Classification	Bulk Density	Porosity
0-20 cm	35.10	19.35	45.55	silty clay	1.36	0.49
20-40 cm	28.72	1.85	69.43	clay	1.36	0.49
40-60 cm	22.50	5.00	72.50	clay	1.31	0.51
60-80 cm	20.00	5.80	74.20	clay	1.29	0.51
Depth	Hydraulic Conductivity (cm/day)	In-Situ Field Capacity Year 1 Site	In-Situ Field Capacity Year 2 Site	Moisture Content at 0.33 bar Pressure	Moisture Content at 15 bar Pressure	Available Water Holding Capacity (AWHC)
0-20 cm	1210.06	0.33	0.44	0.44	0.39	0.05
20-40 cm	316.99	0.33	0.37	0.37	0.27	0.10
40-60 cm	70.10	0.37	0.36	0.36	0.31	0.05
60-80 cm	12.19	0.37	0.38	0.38	0.30	0.08

<sup>1</sup> Soil texture data for the 40-60 cm and 60-80 cm were obtained from Soil Conservation Service(1967). All other data were measured during the project.

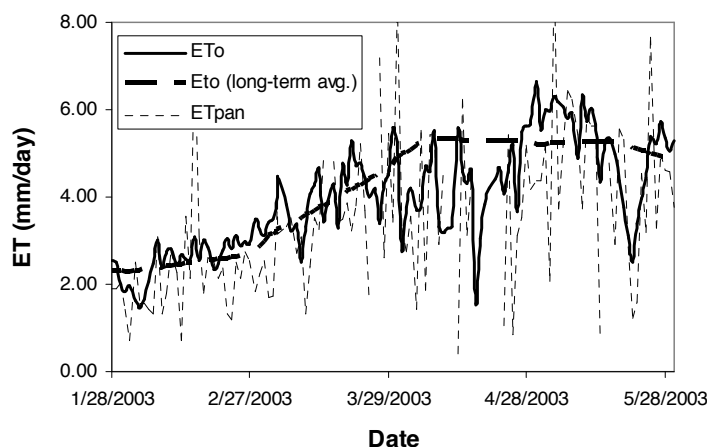


Figure 2. Daily values of evapotranspiration for a sweet pepper crop between January 27<sup>th</sup> to June 12<sup>th</sup>, 2003 at Isabela, PR. Evapotranspiration was derived from the pan evaporation and Penman-Monteith methods.

The water balance equation (Eqn. 5) was calibrated for the site conditions. Figure 3 shows the simulated and measured average soil moisture content for Year 1 and Year 2. The measured moisture contents shown in Figure 3 represent the vertically averaged moisture content over all sixteen plots. The minimum and maximum measured soil moisture content is also shown in Figure 3. Vertically averaged values of the in-situ-measured field capacity equal to 0.39 and 0.35 were used in the Year 1 and Year 2 analyses, respectively (averages

from Table 1). It was necessary to use a value of  $RO/R = 0.25$  reasonable agreement between the estimated and measured soil moisture content. During Year 1, the beginning of the season was quite wet. On April 6, 2002, a 176 mm rainfall occurred, which caused severe flooding of the study area. During Year 2, a rainy period occurred during April 5<sup>th</sup> through April 18<sup>th</sup> with flooding observed in the field plots. The largest rainfall of the season occurred on April 10, 2003 equal to 97 mm.

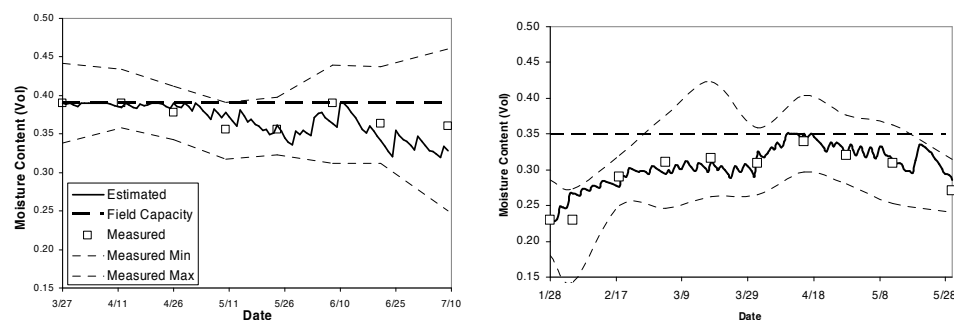


Figure 3. Estimated and measured volumetric soil moisture content between March 27<sup>th</sup> and July 9<sup>th</sup> 2002 and January 27<sup>th</sup> and June 12<sup>th</sup>, 2003.

According to the procedure for described above, percolation occurred on those days when the estimated moisture content exceeded the field capacity moisture content (0.39 for Year 1 and 0.35 during Year 2). On those days, the water in excess of the field capacity was assigned to PERC and the moisture content set equal to the field capacity. This can be seen in Figure 3 for those days in which the moisture content curve touched the dashed horizontal line associated with the field capacity moisture content. Figure 4 shows the estimated percolation during the Year 1 and Year 2. During the April 6, 2002 rainfall event of 175 mm, 43 mm were converted to percolation. During the April 10<sup>th</sup>, 2003 rainfall event of 97 mm, 31 mm were converted to percolation. Recall that only 25 percent of the rainfall was allowed to infiltrate, which was equal to 44 mm on April 6, 2002 and 24 mm on April 10, 2003. In the latter case 18 mm of irrigation was also applied, which together (24 mm + 18 mm) equaled 42 mm. In this case 31 mm was lost to percolation and 11 mm was stored in the root zone. Table 2 shows the Year 1 and Year 2 seasonal components of the water balance.

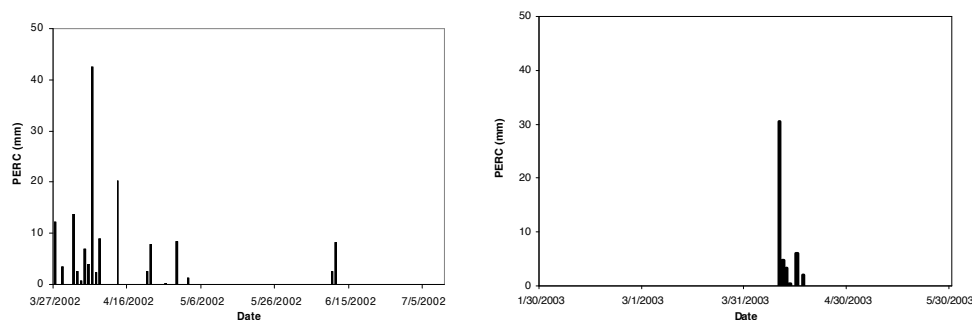


Figure 4. Estimated percolation past the root zone during the Year 1 and Year 2 seasons.

Table 2. Components of the seasonal water balance for Years 1 and 2.

	<b>Year 1 (2002)</b>	<b>Year 2 (2003)</b>
<b>R-RO</b>	175	136
<b>IRR</b>	350	411
<b>ET<sub>c</sub></b>	416	441
<b>ΔS</b>	50	-52
<b>PERC</b>	159	54

Table 3 compares the Year 1 and Year 2 results of the nitrogen leaching analysis. The leached nitrate and ammonium estimates were obtained from equations 5a and 5b, respectively. Figure 5 shows the nitrate concentrations in the 60 – 80 cm depth interval during the Year 1 season. During Year 1 the range of estimated nitrogen leached was between 36 and 67 kg/ha. During Year 2, the range of estimated nitrogen leached was between 27 and 36 kg/ha. Interestingly, the amount of nitrate lost (average of all treatments) on April 6, 2002 and April 10, 2003 was 19.6 kg/ha and 20.1 kg/ha, respectively. For years 1 and 2 this represented 34% and 60% of the total N lost by leaching during the two seasons, respectively. Figure 6 shows the estimated percent of nitrogen (i.e., nitrate plus ammonium) leached relative to N applied (225 kg/ha) during the Year 1 and Year 2 seasons for the four experimental treatments.

Table 3. Nitrate, ammonium and nitrate plus ammonium (Total) leached during Year 1 and 2 for the four experimental treatments.

	Units	2002				2003			
		LF1	LF2	NLF1	NLF2	LF1	LF2	NLF1	NLF2
NO <sub>3</sub>	kg/ha	36	50	47	42	34	32	34	24
NH <sub>4</sub>	kg/ha	10	13	21	11	2	3	2	3
Total	kg/ha	46	63	67	54	36	35	36	27
Total	kg/ha	21	28	30	24	16	16	16	12

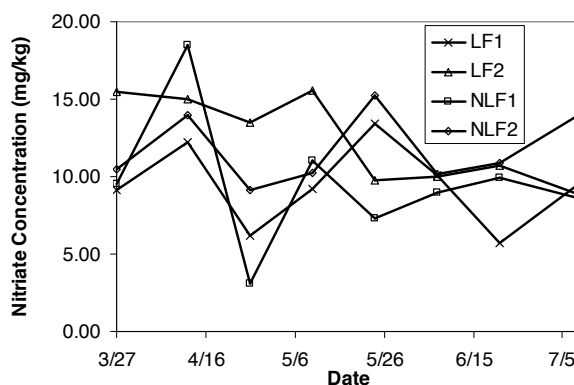


Figure 5. Year 1 Soil nitrate concentrations in the 60 – 80 cm depth interval. Values between the sampling dates were obtained by linear interpolation.

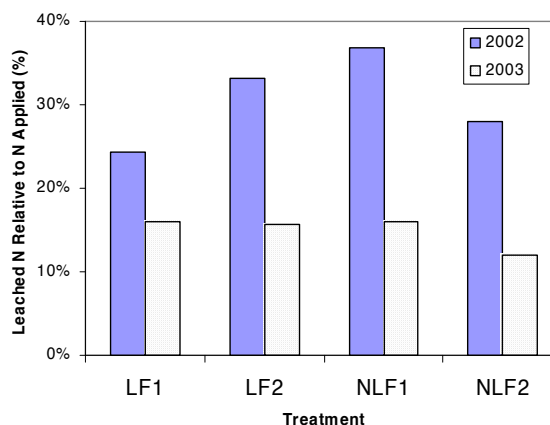


Figure 5. Estimated nitrogen leached during the Year 2 season. LF1 is the Lime-Fertigation 1 treatment, LF2 is the Lime-Fertigation 2 treatment, NLF1 is the No-Lime-Fertigation 1 treatment, NFL2 is the No-Lime-Fertigation 2 treatment.

The smallest amount of nitrogen leaching occurred in the LF1 treatment in 2002 and the NLF2 treatment during the second year. There is no clear difference between either the lime or fertigation treatments. Ammonium leaching was typically much lower than nitrate leaching (Table 3) except in the case of treatment NLF1 in 2002, in which 21 kg/ha ammonium was leached as compared to 47 kg/ha nitrate. The fact that no clear difference was observed between nitrogen leaching for the two lime treatments is consistent with laboratory studies currently being conducted on the Coto clay soil at the University of Puerto Rico Mayaguez Campus, which indicates that the pH at which this soil will possess a net positive charge ( $< 4$ ) is below the native pH measured in the field (around 4.3).

### METHOD LIMITATIONS

There are several sources of uncertainty in the estimates of nitrogen leaching, which include:

- Between sampling dates, soil nitrogen concentrations were derived by linear interpolation. Nitrogen concentrations were measured every two weeks. In some cases, the average nitrate concentration was observed to change as much as 15 mg/kg in the 60 – 80 cm depth interval. The estimated nitrogen leaching would be in error if these concentrations did not change linearly between sampling dates.
- The method of estimating percolation in this study does not account for the leaching that can potentially occur by unsaturated flow. All leaching was assumed to occur when the moisture content of the soil exceeded the soil field capacity. However, significant downward gradients can exist which would result in unsaturated flow. Although not presented in this paper, continuous soil pressure data obtained from vertically spaced tensiometers indicated downward hydraulic gradients throughout most of the season.

### SUMMARY AND CONCLUSIONS

This paper described the results of a nitrogen leaching analysis for two sweet pepper crop seasons. The study was conducted on an Oxisol soil in NW Puerto Rico. The analysis was based on multiplying the daily percolation flux through the soil profile by the measured concentration of nitrogen below the root zone. Irrigations were scheduled using the pan evaporation method for estimating crop water requirements. Estimated percolation in 2002 was three times greater than occurred in 2003, whereas the nitrogen leached during 2002 was only slightly greater than two times the nitrogen leached during 2003.

No clear difference in nitrogen leaching was observed for the lime and no-lime treatments. This result is consistent with on-going studies of the Coto clay, which indicate that this soil has little to no capacity to retain nitrate. The average percent of nitrogen (nitrate plus ammonium) leached during the 1<sup>st</sup> and 2<sup>nd</sup> season, relative to the amounts applied, were 26% and 15%, respectively. Leaching events were associated with large rainstorms, suggesting that leaching of N would have occurred regardless of the irrigation scheduling method used. During the first and second seasons, respectively, 34% and 60% of the total N lost by leaching occurred during a single day (April 6 in 2002 and April 10 in 2003) when flooding was observed in the study areas.

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