LIMING EFFECTS ON NITRATE ADSORPTION IN SOILS WITH VARIABLE CHARGE CLAYS AND IMPLICATIONS FOR GROUND WATER CONTAMINATION

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ABSTRACT

The present research sought to determine the extent and distribution of nitrate accumulation in the subsoils of central Oahu, and to measure the consequences of surface applied amendments on nitrate mobility. Deep bore holes collected from pineapple fields in central Oahu were analyzed for nitrate and nitrate adsorption, and a lime incubation experiment and column study were conducted

Three and one half to 11 T/ha of nitrate-N have been measured in subsoils and the deep, saprolitic vadose zones of pineapple fields located in central Oahu, Hawai'i. Nitrate adsorption isotherms confirmed the high nitrate retention capacity of the materials in the subsoil and saprolite. Since large areas of former sugarcane land are being converted to diversified crops requiring amendments to reduce acidity, a lime incubation study was conducted on soils from former sugarcane land to investigate the effect of lime on nitrate adsorption. When lime was added to acid subsoils, nitrate retention was decreased by up to one half of the native adsorption capacity. A leaching experiment found that surface applied lime and gypsum increased nitrate mobility through soil columns 50 cm in length. The data indicate that large quantities of nitrate have accumulated in the subsoil overlying the Pearl Harbor aquifer. Mobility of nitrate through the subsoil is retarded, but a laboratory column study shows that nitrate mobility can be increased by adding lime and gypsum to the surface soil. Field studies need to be conducted to evaluate the potential for ground water contamination as a result of surface applied amendments.

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INTRODUCTION

In the temperate regions of the world nitrate contamination of groundwater resources has been extensively researched (Keeney, 1984; Hallberg, 1989; Power and Shepers, 1989; Jeurgens-Gschwind, 1989: Spalding and Exner, 1993). Nitrate is a highly mobile solute and it has been determined the most pervasive contaminant of groundwater resources in a recent publication by the National Research Council devoted to groundwater vulnerability (NRC, 1993). Research over the last decade indicates that groundwater resources in areas under intensive agriculture often exhibit levels of nitrate (NO_3-N) well in excess of the maximum contaminant level (MCL) of 10 mg N L^{-1} set by the U.S. Environmental Protection Agency (EPA). The rising NO_3-N levels have been correlated to fertilization rates and fertilization history of agricultural areas (Fried, 1991; Spalding and Exner, 1991; Hallberg, 1989; Jeurgens-Gschwind, 1989). In the United States, data gathered at the state level show that over 20% of all private wells in the agriculturally-intensive grain belt of the midwestern states exhibit nitrate levels in excess of the MCL. Furthermore, data collected by the United States Department of Agriculture project that 37% of all counties in the continental United States will have a nitrate contamination problem in the near future (Hallberg, 1989). In response to these alarming findings, scientists in the industrialized nations have devoted much time and money to help alleviate the problem and prevent further environmental damage.

Up until the recent past, contamination of groundwater resources on the island of Oahu in Hawai'i was not a primary concern. Indeed, the high quality of the groundwater on Oahu, the most populous and economically important island in the state, has long been a source of pride for its 800,000 plus citizens (NRC, 1993). During the 1970's, however, a series of highly publicized chemical spills leading to the detection of toxic chemicals in the groundwater alerted the public and state institutions to the vulnerability of the groundwater (Lau and Mink, 1987). More recently, the State Department of Health has determined nonpoint source pollutants as having "the most detrimental effects" to the groundwater and assigned nonpoint source pollution from agriculture as a primary culprit (Department of Health, 1994).

While nitrate contamination of groundwater resources from high input agriculture practices is an established phenomenon in the continental U.S., on Oahu nitrate levels in the groundwater have been relatively low even though predominant plantation crops like sugarcane and pineapple have been heavily fertilized with nitrogen for more than a century. A number of explanations for the low incidence of nitrate in Oahu's groundwater have been proposed. Miller (1988) suggests that solute mobility in the unsaturated zone is restricted by the very low saturated conductivities associated with subsoil minerals. Furthermore, the water table lies at great depths below the agricultural fields. Another possible explanation for the lack of nitrate in the groundwater may be attributed to the nature of the soils overlying the aquifer. Contrary to neutral pH soils common in the temperate regions of the world, the highly weathered acid soils mantling large areas of agricultural land on Oahu have the unique ability to adsorb large quantities of nitrate ions due to the nature of the electrical charge associated with their clay surfaces. This charge is variable and is dependent on soil pH. Under acid conditions the clay surfaces acquire increasing amounts of positive charge. As soil pH increases the surface charge shifts and becomes more negative.

For the last century, plantation agriculture on Oahu has thrived despite these acidic soils because the primary crops, pineapple and to a lesser extent sugarcane, are acid tolerant. Recently, however, the profitability of growing sugarcane and pineapple in Hawaii has decreased dramatically and the conversion of former plantation land to sustainable diversified agriculture is becoming an increasingly attractive alternative. Diversified crops are predominantly acid-intolerant and this transformation will require the addition of lime to the soil to reduce soil acidity. The reduction of soil acidity may result in a sudden desorption of large quantities of subsoil nitrate due to the unique chemistry of these soils. The potential for such a sudden release of nitrate of this magnitude and the associated impact on ground water quality is worthy of critical assessment.

CHAPTER ONE

BACKGROUND

Nitrate and Human Health

Nitrogen in the environment exists primarily in its oxidized form as nitrate (NO_3^-). It and ammonium (NH_4^+) are the two primary forms of inorganic N available for plant uptake. While nitrate is the plant nutrient required in the greatest quantities, it has detrimental effects in humans at high concentrations. At concentrations greater than 45 mg NO_3^-/l, nitrate has been known to induce a potentially lethal condition known as methemoglobinemia ('blue baby' syndrome) in infants. The toxicity of nitrate in infants is a result of the reduction of nitrate to nitrite under alkaline conditions in the stomach. Nitrite reacts with hemoglobin to decrease its capacity to transport oxygen and causes the asphyxiation of the baby. This condition is extremely rare. Walton (1951) reported 320 cases of the condition in infants between 1939 and 1950. A world wide survey completed in 1962 stated that only 1060 cases had been reported. A recent outbreak in Hungary resulted in 1353 reported cases between 1976 and 1982 (Addiscott *et al*. 1991). The primary cause of methemoglobinemia has been attributed to high levels of nitrate in the drinking water. Data gathered by Walton (1951) showed that no cases of the condition were reported in babies exposed to less than 10 ppm NO_3-N in the drinking water, 2.3% in cases exposed to water with between 10 and 20 ppm and 17% in cases where babies drank water with 20 to 40 ppm NO_3-N. Based on these data the Environmental Protection Agency established a limit of 10 ppm NO_3-N in drinking water (Mirvish, 1991). Nitrite reactions in the stomach have also been linked to stomach cancer in humans. However, conclusive evidence for this link does not exist in the literature (Mirvish, 1991; Forman, 1991; Addiscott *et al*, 1991).

The Hydrogeology of the Pearl Harbor Aquifer

Groundwater is the principal source of water for more than 90% of the population in the Hawaiian Islands (Au, 1991). On Oahu, the Pearl Harbor aquifer is the largest source of water supplying the population with approximately half its potable water (Miller *et al*, 1988). The aquifer lies below the predominantly agricultural Wahiawa plateau which is flanked by the Koolau mountain range to the east and the Waianae mountains to the west. Recharge of the Pearl Harbor aquifer comes primarily from rainfall in the Koolau mountains. Rainfall in the Waianae mountains and over central Oahu contributes to a lesser extent. Extensive irrigation of the agricultural areas in central Oahu is an additional source of recharge (Hufen *et al*, 1980).

The water table lies between 100 and 300 meters below the surface at the higher elevations (Miller, 1987). This depth decreases with decrease in elevation closer to the Ewa plain and Pearl Harbor. There are four distinct layers above the aquifer: a thin layer of surface soil, the subsoil, a relatively thick saprolite region comprised of weathered parent material and a thick layer of basaltic parent material (Fig. 1). The surface soil is a thin layer corresponding to the tillage zone which is high in organic matter and biological activity. Most plants concentrate their roots in this region. Bulk density and clay content increase in the subsoil with parallel decrease in root proliferation and biological activity. The subsoil grades into saprolite which consists primarily of secondary minerals weathered from the parent rock.

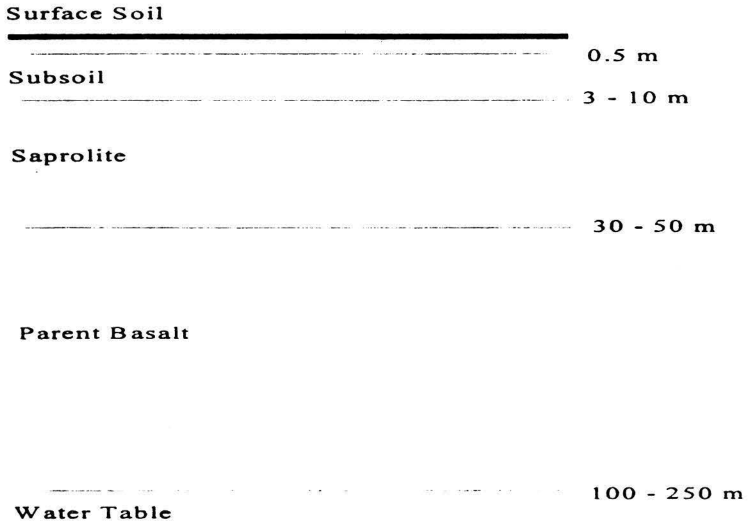

Figure 1. Idealized geologic profile of the unsaturated zone of central Oahu. Not drawn to scale. (*Source, Miller, 1987*).

The water table is overlain by a thick layer of parent basalt. Permeability is high in the surface soils, decreases in the subsoil and saprolite region due to high microporosity, and then increases in the parent basalt. A detailed description of the hydrologic characteristics can be found in Miller (1987).

Eight soil orders are present on the island of Oahu (Fig. 2). Seven of the eight orders exist in the Pearl Harbor watershed (Table 1). At the upper elevations the watershed is dominated by the Oxisols and Ultisols. These soils are weathered, acid, well aggregated and composed primarily of kaolinite and oxides of aluminum and iron. Inceptisols are found on the slopes of the Waianae range in the Kunia region. They are similar to the Oxisols mineralogically with two important differences: 1) they are less

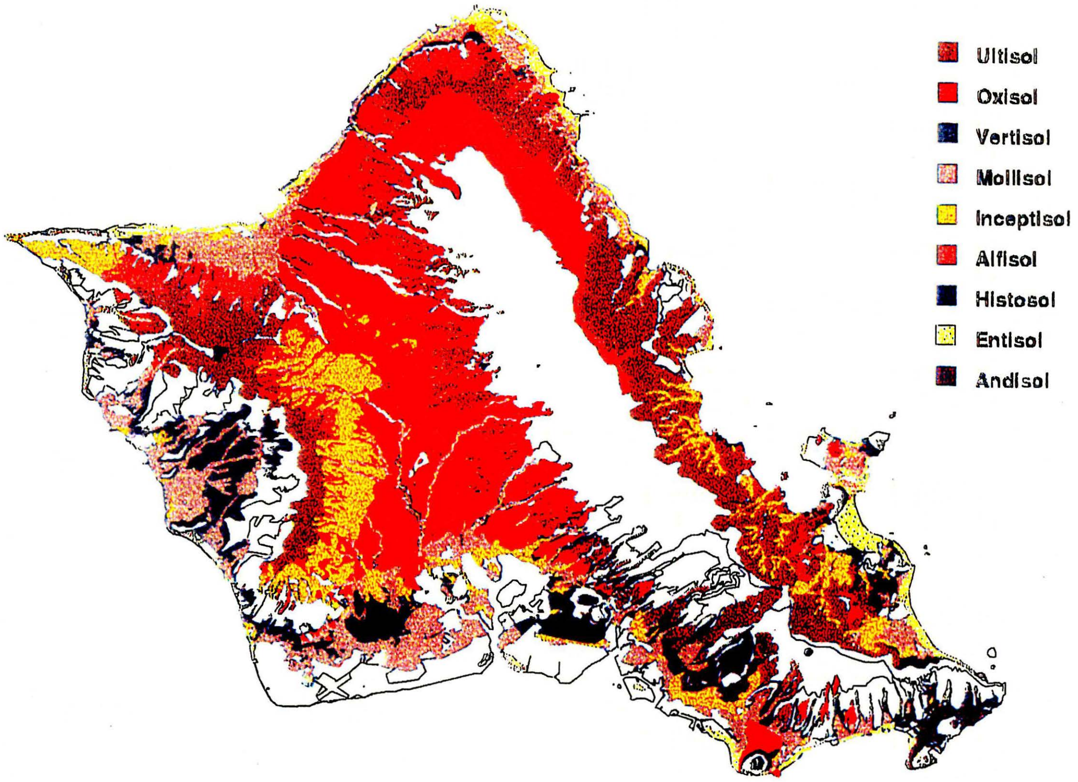

Figure 2. Soil orders found on the island of Oahu. The map was developed from Soil Survey map of Oahu using ARCINFO computer software.

acid and 2) they have a less developed subsoil. The Mollisols and Vertisols that predominate on the Ewa plain are very different. They are much less weathered and characterized by high pH and a mineralogy dominated by smectite.

Table 1. Soil orders in the Pearl Harbor watershed. Data derived from spatial analysis conducted using ARCINFO.

Soil Order	Area (ha)	% of Total Area
Mollisols	3199.29	8.78
Inceptisols	3884.81	10.66
Oxisols	12716.25	34.90
Vertisols	1115.77	3.06
Entisols	24.50	0.07
Alfisols	112.53	0.31
Ultisols	1635.22	4.48
Land fill, Rock land, Rock outcrop and Stony land	13743.32	37.72

Charge Characteristics of Soils with Variable Charge Minerals

All soil particles have a charge. In general, soils can be conveniently classified into two groups based upon their electrochemical properties: soils composed of minerals with permanent charge and soils with minerals of variable charge. Soils in the temperate regions of the world are predominantly of the first category. They are characterized by a constant negative surface charge derived from an imbalance of charged ions in the crystal lattice. The negative surface charge arises when, for example, aluminum (Al^{+++}) is replaced by magnesium (Mg^{++}) in the tetrahedral sheet causing a surplus of negative charge. This process is called isomorphic substitution and is an irreversible process that takes place during the formation of the minerals. The clay fraction of these types of soils is composed primarily of smectite. Soils in the second category are most common in the humid tropics and their charge characteristics are determined by the electrostatic adsorption of the potential determining ions, H^+ and OH^-; the net charge is determined by the ion which is adsorbed in the largest quantity (Uehara and Gillman, 1981; Van Raij and Peech, 1972). Soil pH is a fundamental factor controlling the magnitude and sign of the soil surface charge.

The charge characteristics of soils with variable charge clays are best understood using Gouy-Chapman theory (Uehara and Gillman, 1981) which states that a charged colloid surface attracts ions of the opposite charge (counterion) in the liquid phase to form a diffuse layer dominated by the counterion at the interface between the solid and liquid phase. Thus cations are attracted to negatively charged surfaces and held by electrostatic forces. Similarly, surfaces with positive charge attract anions. The charged surface colloid and the distribution of counterions are called the double layer. The Gouy-Chapman model relates the surface charge density (σ) to the potential across the double layer using the equation

$$\sigma = (2n\epsilon kT/\pi)^{1/2} \sinh ze/2kT\Phi \tag{1}$$

where

σ = surface charge density
n = counterion concentration in the equilibrium solution
ϵ = dielectric constant
k = Boltzman constant
T = absolute temperature

z = counterion valence
e = charge of an electron
Φ = surface potential

We see that σ is dependent on the concentration of the counterion, the valence of the counterion and the potential difference across the double layer. In variable charge soil systems, the surface potential (Φ) is controlled by the relative activity of the potential determining ions, H^+ and OH^-, in solution. Φ can be expressed using the Nernst equation

$$\Phi = kT/e \ln H^+/H_0^+ \tag{2}$$

where

Φ = surface potential
H^+ = H^+ activity of the solution
H_0^+ = H^+ activity at which the surface potential is zero

and combined with equation 1 to obtain

$$\sigma = (2n\epsilon kT/\pi)^{1/2} \sinh z(1.15)(pH_0 - pH) \tag{3}$$

where pH_0 is the zero point of charge or the isoelectric point.

In soil systems dominated by variable charge clay minerals net surface charge is an important consideration for nutrient management. Net surface charge determines the movement of cations and anions in the soil environment important to plant growth. Where negative charge predominates, cations will be adsorbed on the soil surface while important anions like NO_3 will leach out of the system. Equation 3 illustrates the importance attributed to pH. The pH at which the net surface charge of the soil is reduced to zero is known as pH_0 or the isoelectric point. It is the most important parameter in these soils because it determines the sign of the net surface charge. For example, the iron oxide, hematite (Fe_2O_3), commonly found in Oahu soils has a pH_0 of 8.5 (Parks and deBruyn, 1962), but the pH_0 of the other oxides, goethite ($Fe_2O_3 \bullet H_2O$) and gibbsite ($Al_2O_3 \bullet 3H_2O$) may be lower. When soil pH is less than 8.5 ($pH < pH_0$), these minerals are net positively charged and under alkaline conditions ($pH > pH_0$) they carry a net negative charge.

Numerous laboratory studies have investigated charge characteristics and the isoelectric point of important agricultural soils in the tropics (Van Raij and Peech, 1972; Keng and Uehara, 1973; El-Swaify and Sayegh, 1975; Morais et al, 1976; Wann and Uehara, 1978ab; Gillman and Sumpter, 1986). These studies indicate that many soils common to the humid tropics contain substantial positive charge in their subsoil; El-Swaify and Sayegh (1975) reported that the pH_0 of a Hawaiian Oxisol (Gibbsihumox) occurred at pH 6.3, Morais and his co-workers (1976) found that the B horizon of three Brazilian Oxisols and one Ultisol (Gillman & Sumpter, 1986) had net positive charge at field pH, and the isoelectric point increased with increasing soil depth in a range of soils in tropical north Queensland. While the isoelectric point of oxidic subsoils tends to be high, the surface layer of the same soils has a much lower isoelectric point. In fact, the isoelectric point of surface soils is not controlled by oxide minerals, but by soil organic matter (Uehara and Gillman, 1981). The isoelectric point of organic matter is variable, but almost always below pH 3. The tendency of humus to coat oxide particles enables a small amount of organic matter to have an overriding effect on the isoelectric point of the oxide-organic matter mixture. This explains why surface soils, regardless of the pH, always have a highly negative surface charge.

A simple method for determining the algebraic sign of σ is to measure soil pH in a water suspension and again in a 1 *M* KCl suspension.

$$\Delta pH = pH_{KCl} - pH_{H2O} \quad (4)$$

The sign is net positive, net zero or net negative, respectively, if the difference in pH (ΔpH) between the pH in 1 *M* KCl and pH in water is positive, zero or negative (Mekaru and Uehara, 1972).

While ΔpH is a reliable indicator of the sign of σ in variable charge soils, its relationship to the magnitude of positive charge on the soil surfaces or the anion exchange capacity (AEC) is less dependable. If ΔpH were related to the magnitude of the charge, one would expect AEC to increase as values for ΔpH became less negative or more positive and AEC to decrease as ΔpH became more negative. Black and Waring (1979) reported a high correlation between ΔpH and nitrate adsorption in the subsoils of soils with uniform mineralogy. The correlation dropped significantly when soils with subsoil horizons of varying mineralogies were tested.

Nitrate Adsorption and Movement in Variable Charge Systems

Nitrate adsorption in soils is a phenomenon directly related to the charge properties of soils common to the tropics and subtropics. Laboratory studies have demonstrated that highly weathered acid soils common in the humid tropics adsorb substantial quantities of nitrate (Singh & Kanehiro, 1969; Kinjo and Pratt, 1971*a*; Black & Waring, 1979; Toner et al, 1989; Wong et al, 1990; Cahn et al, 1992). In a Hawaiian Oxisol, nitrate adsorption increased linearly with increasing concentration of electrolyte solution (Singh & Kanehiro, 1969). Furthermore, nitrate adsorption decreased as the pH of the system was increased. Black & Waring (1979) found that soils high in smectitic minerals adsorbed negligible amounts of nitrate while soils high in hydroxy aluminum and iron oxide surfaces adsorbed appreciable quantities of nitrate. They also reported that there was significant nitrate adsorption in the soils containing variable charge minerals despite negative ΔpH values. Furthermore, in agreement with Singh & Kanehiro (1969) they reported a significant negative correlation between pH and nitrate adsorption. In a study on representative soils of the coastal plains region of the Southeastern United States examining the potential threat of nitrate to the groundwater, an adsorption study was conducted on two Ultisols and an Entisol. Anion exchange capacity was found to increase with increasing depth and iron oxide content and nitrate adsorption was negatively correlated to soil pH (Toner et al, 1989). Wong and his group (1990) measured the retardation of nitrate movement through soil materials from the humid tropics repacked into columns. The leaching study was conducted on soils sampled throughout the humid tropics (Oxisols, Alfisols, Ultisols and Inceptisols) and known to carry positive charge. They reported that the positive surface charge in these soils had a significant retardation effect on the movement of nitrate through the soil columns in all the soils; the higher the AEC value, the greater the observed delaying effect. Significant levels of nitrate sorption in a Brazillian Oxisol were measured in a laboratory study designed to investigate nitrate adsorption under field conditions (Cahn et al, 1992). These researchers found that small amounts of nitrate were retained in the surface soil due to the predominantly negative surface charge from high organic matter content while adsorption increased with depth. The highest amount of adsorption occurred in the 90 to 120 cm layer and represented 25 to 50% of the nitrate in this layer normally found under field conditions.

In a two-part laboratory study Kinjo and Pratt (1971ab) compared nitrate adsorption in two Andisols and two Oxisols from Latin America. They showed that adsorption was pH dependent and concentration dependent and that soils high in amorphous oxides of aluminum and iron had high nitrate adsorption capacities. In the second part, they evaluated the competitive effect of chloride, sulfate and phosphate on nitrate adsorption. They concluded that Cl^- adsorption showed a slight preference over NO_3^- adsorption when both ions were held at the same concentration. Increasing Cl^- concentration resulted in a linear decrease in nitrate adsorption. On the other hand, sulfate and phosphate had a much more pronounced effect on nitrate adsorption. As sulfate concentration in solution increased, negative nitrate adsorption[1] was observed. In the case of phosphate this phenomenon occurred at a lower concentration of phosphate in solution. The authors concluded that chloride and nitrate adsorption was governed by a nonspecific adsorption mechanism while sulfate and phosphate adsorption was specific in nature. In a column study, Kinjo et al (1971) reported that adding sulfate or phosphate to the surface layer increased the mobility of nitrate through an 11 cm laboratory soil column.

Field studies conducted in the humid tropics have also measured nitrate

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[1] Negative adsorption is a term commonly used in soil chemistry to denote electrostatic repulsion between the soil colloid and the ionic species in the bulk solution.

adsorption in the subsoil. A lysimeter study in an Oxisol on the island of Mauritius reported that nitrate leaching from a sugarcane field was impeded due to electrostatic adsorption of nitrate ions on the positively charged iron and aluminum oxide surfaces (Ng Kee Kwong and Deville, 1984). Significant adsorption occurred within a 0 to 90 cm soil depth despite net negative charge determined by ΔpH. Nitrate movement and retention in an Entisol and Oxisol with contrasting charge characteristics was measured in a maize field study conducted in the central Amazon area of Brazil (Melgar et al, 1992). Negative surface charge was predominant and constant throughout the profile of the Entisol. In the Oxisol, the positive charge increased dramatically in the acid subsoil. Subsequently, nitrate retention in the subsoil of the Oxisol was significantly higher than in the Entisol. Arora and Juo (1982) monitored nitrate movement in an acid Ultisol under a variety of different conditions in a nutrient leaching study conducted at the International Institute of Tropical Agriculture in Nigeria. They measured nitrate movement to a depth of 120 cm in a plot that was kept fallow and another plot with a maize crop followed by an upland rice crop; two lime treatments were applied to both plots (0 and 2 T/ha $CaCO_3$). Liming increased the magnitude and vertical movement of nitrate in both the fallow and cropped plots. The authors attributed the increased movement to increased nitrification rate due to a rise in soil pH. The unlimed plots retained higher amounts of nitrate throughout the soil profile. The authors briefly mention a higher AEC in the subsoil as a possible mechanism responsible for the higher levels of nitrate in the unlimed plots. The fallow limed plot consistently contained lower nitrate levels throughout the profile than the unlimed plots. What mechanisms facilitated the movement of nitrate through the profiles? Arora and Juo did not address this issue. Perhaps nitrate movement through the profile was enhanced by the decrease in positive charges in the acid subsoil due to liming.

Diversified Agriculture on Oahu and Management Implications

In the recent past profitability in the sugarcane industry in Hawai'i has decreased dramatically. The market value of sugarcane dropped 12% in 1992 and the acreage harvested was the lowest since records were kept in 1909 (Statistics of Hawaiian Agriculture, 1992). Today, the Waialua Sugar Company, with operations outside of the Pearl Harbor watershed, is the only plantation in operation on the Island of Oahu, and it too, will end cane production following the harvest of the 1997 crop. Land formerly occupied by sugarcane is being converted to diversified agriculture. This land has been typically acidified with the prolonged and extensive use of nitrogen fertilizers. Many diversified crops, unlike sugarcane and pineapple, are not suited to acid environments and their survival will depend on an intensive liming program. Liming will have two important environmental consequences. First, lime applications will increase the nitrification rate in the surface layers of these soils leading to increases in available soil nitrate. Furthermore, raising the soil pH will alter the charge characteristics of these soils thereby increasing the likelihood of nitrate leaching. A combination of increased nitrification rates and reduction of positive charge in these soils poses a potential threat to the groundwater resources of the Pearl Harbor aquifer.

Objectives and Hypotheses

Due to the unique characteristics of the soils in the Pearl Harbor aquifer, groundwater contamination has not been an issue. However, the inevitable termination in sugarcane and pineapple production will lead to the conversion of these lands to alternative uses. In order to prevent possible contamination of a valuable and finite resource, the status of the pollutant in these soils needs to be measured, documented and accounted for. Research into the behavior of adsorbed nitrate as pH is altered must be conducted, and management practices that minimize hazards to groundwater resources need to be developed.

This research sought to investigate the consequence of high input diversified agriculture on the charge characteristics of variable charge soils and its impact on the fate of nitrate adsorbed on positively charged subsoil materials. There were two objectives and two hypotheses:

1. Assess the extent and distribution of nitrate accumulation in the subsoil of important agricultural soils in the Pearl Harbor watershed.

   Hypothesis: There is a large concentration of nitrate-N adsorbed in the acidified subsoil of former sugarcane and pineapple lands.

2. Assess the potential hazard of accumulated nitrate to the groundwater from liming these soils for improved productivity of acid intolerant diversified crops.

   Hypothesis: Nitrate ions will be desorbed when the soil is treated with lime ($CaCO_3$) or gypsum ($CaSO_4$).

CHAPTER TWO

MATERIALS AND METHODS

Experiment 1: Deep Soil Cores

Agricultural soils on the island of Oahu representing five soil orders were sampled. A Mollisol (*Mamala series*) and a Vertisol (*Honouliuli series*) were collected from abandoned sugar cane fields on the Ewa plain near Barber's Point. An Inceptisol (*Kunia* series) was collected from a corn field belonging to the ICI Seed Company in the Kunia area. The Oxisol (*Wahiawa* series) was collected from a Del Monte pineapple field in the Kunia area. The Ultisol (*Leilehua* series) was collected from a recently harvested Waialua Sugar cane field on Pupukea road. Soil samples were collected every 15 cm to a depth of 165 cm, except in the Mollisol where bedrock was encountered at a depth of 60 cm. The Inceptisol and Oxisol were collected by Dr. Aly-El Kadi as part of groundwater monitoring experiment in the Department of Geology and Geophysics at the University of Hawai'i. All soil samples were placed in plastic zip lock bags and promptly stored in the freezer room in Sherman lab until time of analysis.

Four deep soil cores drilled in 1985 were analyzed for nitrate concentration. The bore holes were located in four Dole pineapple fields in central Oahu (Fig.2)

(Table 2)[1]. Samples were collected every 1.5 m and placed in glass jars whose lids were sealed with caulk.

Both the soils collected from the field and the deep soil core samples were analyzed for nitrate-N and ammonium-N, and pH was determined in H_2O and 1*M* KCl. Soil samples were air-dried in the laboratory, ground, and sieved to <2mm. To extract nitrate and ammonium ions, five grams of the sieved samples were weighed into 100 ml plastic cups to which 50 ml of 2*M* KCl solution was added. The cups were covered securely and placed on an automated shaker. Following a 2-hour shaking period, the cups were removed and the suspension left to settle. The

Table 2. Description of soils from deep soil cores taken from Dole pineapple in central Oahu in 1986.

Hole #	Soil Classification	Location	Rainfall cm yr^{-1}	Sampling Depth m
4111	Tropeptic Eutrustox, *Lahaina Silty Clay*	South of Millilani Town	80	19.8
4101	Tropeptic Eutrustox, *Wahiawa Silty Clay*	East ridge of Kipapa Gulch	90	30.2
4213	Tropeptic Eutrustox, *Wahiawa Silty Clay*	North of Millilani Town	130	30.2
4201	Humoxic Tropohumult, *Leilehua Silty Clay*	NE of 4213	200	38.0

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[1] See Miller, 1987 M.S. in Geology and Geophysics for a detailed description of sample collection.

supernatant liquid was filtered through Whatman no. 42 filter paper. Aliquots from the extracts were analyzed for nitrate colorimetrically according to the cadmium reduction method (Maynard and Kalra, 1993) and for ammonia colorimetrically (Willis and Gentry, 1988) on a Technicon Autoanalyzer.

Experiment 2: Lime Incubation Study

The nitrate adsorption study was carried out in two parts. The first sought to characterize nitrate adsorption capacity of the soils taken from the deep soil cores at two depths, and the second investigated the effects of lime applications on nitrate adsorption capacity in agricultural soils collected on the island of Oahu. In both cases adsorption was determined by flow equilibration and subsequent displacement (Green & Corey, 1971).

Deep Soil Cores

Dry glass crucibles with a bottom section made of coarse fritted glass, a height of 3.0 cm and an inside diameter of 2.0 cm were weighed and the mass recorded. Four gram samples of air-dried sieved soil were placed in the crucibles and the weight recorded. A thin layer of glass wool was placed on top of the soil and the total weight recorded. Adsorption was determined using a three-step procedure (see figure 3 for a schematic representation of the apparatus). All samples were first leached with 50 ml of 2*M* KCl, the leachate was collected in 100 ml flasks, brought up to volume and analyzed for initial nitrate and ammonium.

Solutions with a known concentration of nitrate were then allowed to flow through the crucibles until equilibrium was achieved - until concentration of effluent solution was equal to the concentration of the input solution. A preliminary study indicated that input concentration was equal to effluent concentration after 40 ml of solution was passed through the soil over a 3-hour equilibration period. In order to insure that equilibrium was achieved 50 ml of the equilibrating solution was passed through the soil samples. Flow rate was regulated by screw clamps attached by rubber tubing to the bottom of each burette.

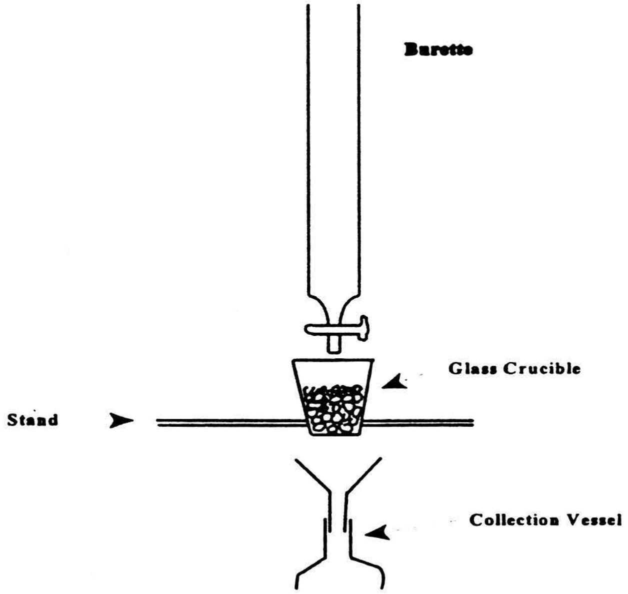

Figure 3. Schematic representation of apparatus used in the determination of nitrate adsorption by the flow equilibration method.

Once the equilibration step was complete, the crucibles were allowed to drain freely, carefully wiped dry on the outside and reweighed to determine the volume of retained solution. The entrapped solution and adsorbed nitrate were displaced by leaching the crucibles with 50 ml of a 2*M* KCl solution. The displacement procedure followed the same steps as the first step in the process. Nitrate concentration in the displaced solution was determined colorimetrically on the autoanalyzer. The equilibrium solution consisted of three known concentrations of nitrate, 0.42 mg NO_3-N L^{-1}, 4.20 mg NO_3-N L^{-1} and 42.0 mg NO_3-N L^{-1} in a background solution of 0.01 *M* $KClO_4$. These concentrations are within the range of nitrate concentrations commonly found in agricultural soils.

The quantity of nitrate adsorbed is calculated from the equation of Green and Cory (1971):

$$A = (D - R^*C)/W$$

where:

A = mg NO_3-N kg^{-1}
D = mg NO_3-N, mass of displaced NO_3-N, including both adsorbed nitrate and nitrate in the entrapped solution.
R = ml, volume of entrapped solution
C = mg NO_3-N ml^{-1}, concentration of entrapped solution
W = kg of soil, oven dry basis

Soil Incubation

Experiments to determine the effect of lime application on nitrate adsorption were performed on soils collected from the field using the surface sample (0 - 10 cm) and the deepest sample (ranging from 40 - 60 cm to 150 - 170 cm). Approximately 40 g of air-dried soil were sieved and placed in air tight plastic bags. A liming amendment was added to soils with variable charge clay minerals - the Oxisol, Ultisol and Inceptisol. Three liming rates based upon a series-liming curves for common Hawaiian soils (Hue & Ikawa, 1994) were applied to achieve a wide range of soil pH for the three soils. Lime was added as $Ca(OH)_2$, to ensure complete reaction in the short term (Table 3).

Table 3. Liming rates for the Ultisol, Oxisol, and Inceptisol collected from the field and used in the incubation study.

Soil	Depth (cm)	Lime Rate (T/ha)	
Ultisol (*Leilehua*)	0 - 10	2.96	5.92
	150 - 170	2.96	5.92
Oxisol (*Wahiawa*)	0 - 10	1.48	2.96
	150 - 170	2.22	4.44
Inceptisol (*Kunia*)	0 - 10	1.11	2.22
	150 - 170	0.74	1.48

In order to convert tonnes of $Ca(OH)_2$ per hectare to tonnes of $CaCO_3$ per hectare, a factor of 1.35 was used. For example, 2.96 T/ha of $Ca(OH)_2$ is equivalent to

(2.96)(1.35) = 4.00 T/ha of $CaCO_3$. $Ca(OH)_2$ was weighed out onto weighing paper and added to the air-dry soil. The bags were shaken thoroughly, and deionized water was added to the soil to achieve approximately 45 % moisture content (mass basis). Lime was not added to the Mollisol nor the Vertisol as their field pH values were 8.3 and 8.2, respectively. The moist soils were then incubated at 26°C for 30 days with three wetting and drying cycles to insure a more complete reaction in the soil. The bags were kept open to allow the soil to dry and at 7, 14 and 21 days after initiating the incubation period, the samples were thoroughly re-mixed, reweighed and water added to achieve original moisture content. Following the 30-day incubation all soils were analyzed for ammonium and nitrate by colorimetric methods on the autoanalyzer.

Adsorption Study

Many of the nitrate adsorption studies reported in the literature have used the batch method to quantify nitrate adsorption (Singh and Kanehiro, 1969; Kinjo and Pratt, 1971; Black and Waring, 1976*b*; Arora and Juo, 1982; Cahn et al. 1992). In two papers comparing the batch method and the flow equilibration method for measuring pesticide adsorption in soils (Green & Corey, 1971; Green et al 1980), the researchers discussed the high variance associated with the batch method and reported much higher precision using the flow equilibration method. In the present study, however, nitrate adsorption results for the first soil in the lime incubation experiment showed very low precision (Table 4). The low precision was most apparent in the treatments that received lime suggesting that the neutralization reaction was incomplete. Although differences in pH readings between the replicates were small, the variation in the nitrate-N adsorption within the limed treatments was high, especially at the higher equilibrating solution concentration.

Table 4. Nitrate adsorption by flow equilibration and subsequent displacement; preliminary results for the *Leilehua* soil at three different liming rates.

Liming Rate (tons CaCO$_3$/ha)	Concentration* (mg NO$_3$ l^{-1})	Nitrate Adsorption** (mg NO$_3$ kg^{-1})		Mean Adsorption (mg/kg)	Standard Error
0	1.86	1.90	1.42	1.66	0.17
0	18.6	7.41	16.27	11.84	3.13
0	186	163.37	149.13	156.25	5.04
4	1.86	0.947	0.93	0.94	0.01
4	18.6	13.487	13.89	13.69	0.14
4	186	80.61	130.05	105.33	17.48
8	1.86	0.52	0.81	0.67	0.10
8	18.6	227.50	14.55	121.02	75.29
8	186	-48.53	133.3	42.42	64.31

* Concentration of equilibrating solution

** Adsorption measurements were duplicated for each sample.

The high variance in the nitrate-N adsorption was attributed to the uneven mixing of lime with soil stemming from the presence of large aggregates in the sample. In order to rectify this problem, soils were removed from their respective bags air-dried, ground to pass a 20 mesh sieve, re-wet and allowed to equilibrate for

48 hours. The soils were air-dried once again and ground to pass a 20 mesh sieve to achieve a more even distribution of lime in a sample with more homogeneous aggregate sizes. The grinding and sieving process redistributed the lime and homogenized aggregate size. The revised procedure had the desired effect by diminishing the variation significantly. The adsorption study was performed using this modified procedure and the procedure as described in the section on the deep soil cores.

Chloride (Cl^-) is ubiquitous in agricultural soils originating from fertilizer applications, both organic and inorganic forms, and irrigation water. Chloride in the soil environment varies tremendously from as low as a few milligrams per liter to hundreds of milligrams per liter (Adriano & Doner, 1982). In an acid Ultisol from Hawai'i (*Paaloa* series) Cl^- concentration in the soil extract ranged from 30 mg/L in the native soil to as high as 524 mg/L in soil treated with 40 g/kg of a manure/sludge mixture (Hue, 1992). Chloride and nitrate have equal valencies and relatively similar ionic radii and have been shown to compete for exchange sites in soils containing positive charged surfaces (Black and Waring, 1979; Kinjo and Pratt, 1971*b*). Therefore, a preliminary experiment was conducted to characterize the competition between Cl^- and NO_3^- for adsorption sites in an acid subsoil. The adsorption study followed the same procedures as those outlined earlier. Three solutions with increasing Cl^- concentration (18.6, 186 and 1860 mg Cl^- L^{-1}) were prepared in which the nitrate concentration was held constant at 4.2 mg NO_3^--N L^{-1}

(4.2 mg NO_3^--N L^{-1} is equivalent to 18.6 mg NO_3^- L^{-1}). Increasing levels of Cl^- significantly reduced NO_3 adsorption (Fig. 4). When NO_3^- and Cl^- concentration were equal, NO_3^- adsorption decreased by only 3%. When Cl^- concentration was 10 times higher than NO_3^- concentration, NO_3^- adsorption was decreased by 22%. Increasing Cl^- concentration to 100 times greater than NO_3^- concentration caused a 73% reduction in NO_3^- adsorption.

Experiment 3: Column Study

A soil column study was conducted to measure the effect of surface applied lime (as $Ca(OH)_2$) and gypsum ($CaSO_4$) on NO_3^- mobility in the subsoil. An Oxisol (*Wahiawa* series) and an Ultisol (*Leilehua* series) were collected from two different recently harvested sugarcane fields along Pupukea road in the Waialua area of Oahu. Soil from each location was collected at two depths: the surface layer (0 - 15 cm) and the subsoil (80 - 100 cm). The soils were air-dried, sieved to < 2 mm and stored in zip lock bags. The soils were analyzed for pH and initial NO_3^- (Table 4).

Table 5. Initial soil pH and NO_3 for soils collected from the field.

Soil		pH (H_2O)	pH (1*M* KCl)	Initial NO_3-N (mg kg^{-1})
Leilehua	0 - 15 cm	4.53	3.95	2.27
	80 - 100 cm	4.06	3.82	1.33
Wahiawa	0 - 15 cm	4.92	4.34	1.94
	80 -100 cm	5.52	5.82	0.75

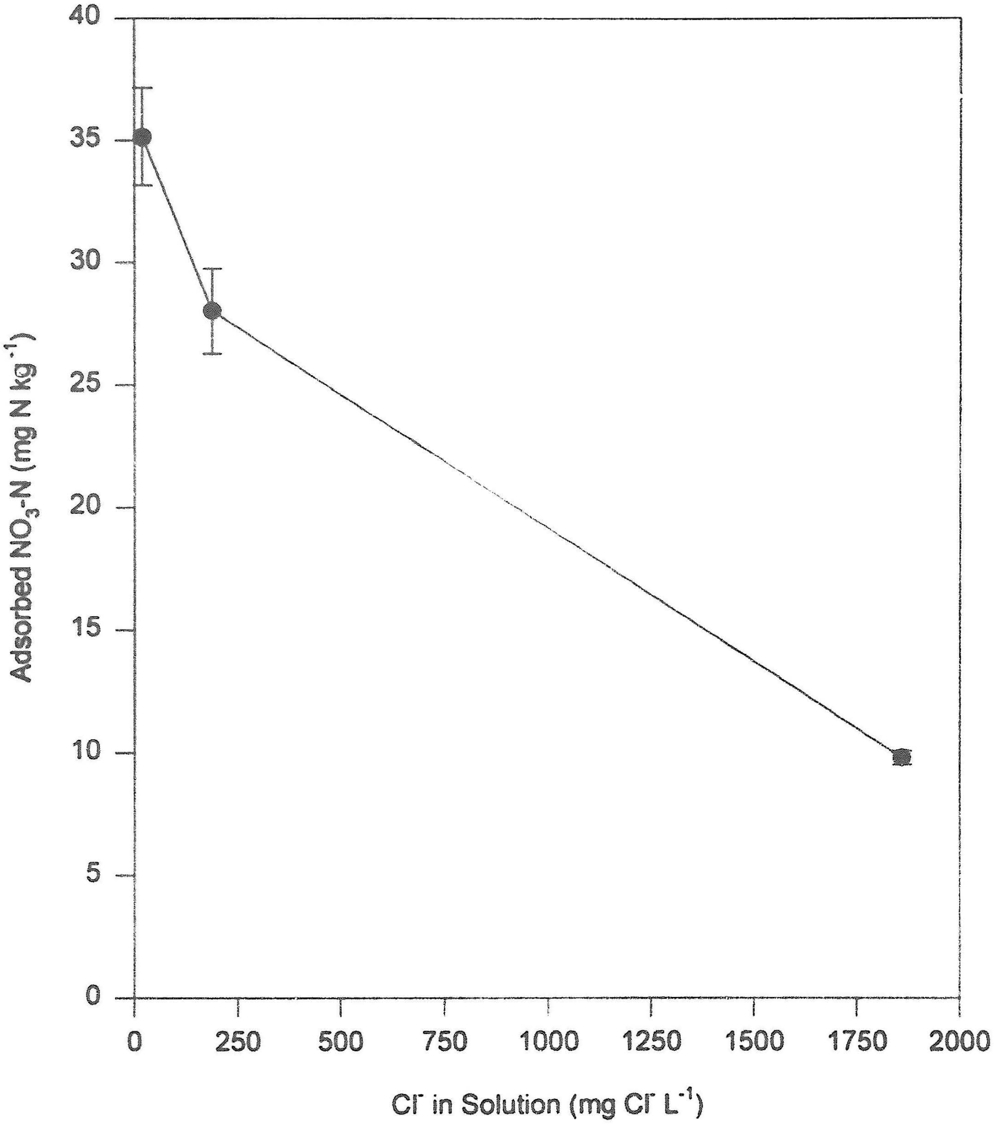

Figure 4. Cl^- interference on NO_3 adsorption in the subsoil of the Leilehua soil was tested by equilibrating soil in a 18.6 mg NO_3 L^{-1} solution in 3 concentrations of Cl^- (18.6, 186 and 1860 mg Cl^- L^{-1}). As Cl^- concentration in the equilibrating solution increased, NO_3 adsorption decreased.

A PVC pipe with an inside diameter of 5.6 cm was cut into 60 cm sections and the bottom wrapped with a nylon meshing secured by two heavy duty rubber bands. A total of eighteen columns were prepared. A Whatman # 5 filter paper was placed in the bottom of each PVC column. The columns were lined with a sheet of clear plastic and a thin layer of clean quartz sand (1-2 cm thick) was then poured into each column. Sieved subsoil (862 g oven dry basis) of both the Ultisol and Oxisol was packed into the columns to achieve a bulk density of 1.0 g cm^{-3}.

The surface layers of both the Oxisol and the Ultisol were prepared in the following way. A mass of 369 g (oven dry basis) of each soil was weighed into plastic ziplock bags. To each bag 0.355 g KNO_3 was added to correspond to a fertilization rate of 200 kg N ha^{-1}. Both soils received one lime treatment with a rate of 4 metric tons $CaCO_3$ equivalent per hectare and a gypsum treatment consisting of 6.88 metric tons of gypsum ($CaSO_4$) per hectare. The lime treatment consisted of adding 0.728 g of $Ca(OH)_2$ to the air-dry surface soil. The treated soils were mixed thoroughly in airtight plastic bags, moistened thoroughly and allowed to equilibrate for 14 days to insure that the lime had sufficient time to react with the soil. Gypsum was added to achieve the same mass of Ca^{2+} found in the lime treatment; 1.692 g of $CaSO_4$ was added to the surface soil. The treated soils were mixed thoroughly in airtight plastic bags. The gypsum treatment did not require an equilibration period.

Following the preparation of the surface soils with their respective treatments, the surface soils were added to the columns containing the subsoils to achieve a bulk density of 1.0 g cm^{-3} (Fig. 5). The height of the soil in all the columns was approximately 50 cm. The height and weight of each column were recorded (Appendix 1). The columns were then placed into a large plastic bucket and wet by capillarity by gradually adding distilled water until the soils were completely saturated. The columns were kept saturated for 24 hours and then allowed to drain freely for an additional 48 hours. They were reweighed and then randomly attached to a metal stand. Plastic collection bottles with funnels, numbered according to treatment, were placed beneath each column.

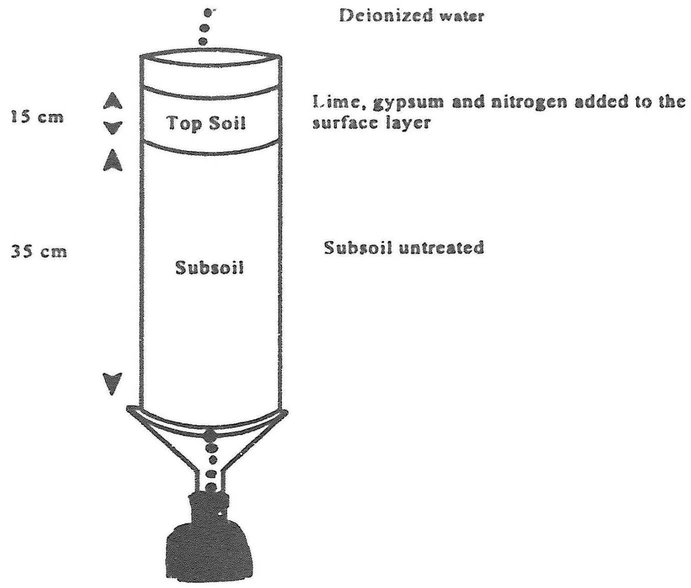

Figure 5. Schematic representation of column construction.

In order to simulate an annual rainfall of 1000 mm over a 30 day leaching period, 40 ml of deionized water was added to the columns in 10 ml increments at a set time once daily. Leachate was collected every two days, the volume recorded (determined by weighing each plastic bottle) and analyzed for NO_3^- following the procedure outlined above. In addition, pH and electrical conductivity were measured on the leachate (Appendix 2 and 3). At the conclusion of the leaching period, the soil columns were removed from the PVC pipe by pulling on the plastic sheeting surrounding the soil. The top 15 cm, representing the surface soils, were cut and placed in bags. The subsoils were divided into three layers, the upper two layers 10 cm in length and the bottom increment 15 cm long, cut and placed in airtight plastic bags. Nitrate content was determined for each depth (Appendix 4). Subsamples for each depth were prepared and sent to the Agricultural Diagnosis Service Center in Sherman Lab where calcium, sulfate and pH in H_2O and 1 *M* KCl were determined on all samples (Appendix 5). The Ultisol columns (9 in total) and the gypsum treatment of the Oxisol (3 columns) were dismantled after 6 weeks while the control and lime columns (6 columns) ran an additional 2 weeks because nitrate movement was delayed in these columns.

Statistical Analysis

In order to quantify the treatment effect on the mobility of nitrate in the column experiment, the data were first plotted as a nitrate breakthrough curve (BTC). Nitrate in the effluent volume was plotted on the y-axis as N/N_0 where N was the cumulative mass of N in the effluent and N_0 was the total mass of N present in the column at the outset of the experiment. Cumulative effluent volume in terms of pore volumes was plotted on the x-axis. One pore volume was equivalent to the total porosity of the subsoil section of each column minus the volumetric water content after the columns had drained for 48 hours (Kinjo and Pratt, 1971c). The surface layer was not included in the calculation of pore volume because nitrate (as KNO_3) was added to the surface layer and thus it was considered the source of the nitrate.

Since theory predicts that the BTC intersects at $N/N_0 = 0.5$ at one pore volume for a non-reacting tracer, this point was chosen as the most meaningful to perform a statistical analysis. The pore volume intersecting $N/N_0 = 0.5$ was determined by fitting a straight line through the three points on the BTC closest to $N/N_0 = 0.5$ and interpolating the pore volume associated with $N/N_0 = 0.5$. Each soil had 9 coordinate pairs upon which a one-way ANOVA was performed for each of the two soils. Pore volume was designated as the dependent variable. Analysis was performed on a personal computer using statistical tools in the QuattroPro package. Changes in pH and ΔpH with depth in the columns were evaluated by performing a one-way ANOVA on each depth increment separately using Statistix Analytical Software (version 4.0).

CHAPTER THREE

RESULTS AND DISCUSSION

Deep Soil Cores

Nitrate data from the deep soil cores are discussed in terms of distribution, mineralogy of the profile, and adsorption capacity related to ΔpH distribution.

Nitrate Distribution

Nitrate-nitrogen (NO_3-N) distribution in the soil cores taken from pineapple fields in central Oahu indicates that large quantities of NO_3-N have accumulated in the subsoil and weathered saprolite region. Bore hole sites 4111 and 4101, located at the lower elevations, contain approximately 3.5 and 11.2 tonnes of nitrate-nitrogen per hectare respectively (Figs. 6 and 7)[1]. Data from the cores exhibit pronounced nitrate bulges between five and ten meters below the surface with nitrate concentrations decreasing rapidly to near zero levels below fifteen meters. At the higher elevation, approximately four tonnes of nitrate-nitrogen were measured in bore holes 4213 and 4201 (Figs. 8 and 9). The nitrate was more evenly distributed down the soil profile and persists at mean concentrations of 15 to 20 mg kg^{-1} to a depth of about 25 meters; below 25 meters the concentration decreases to near zero. The high

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[1] See Appendix 6 for replicated data used to calculate means.

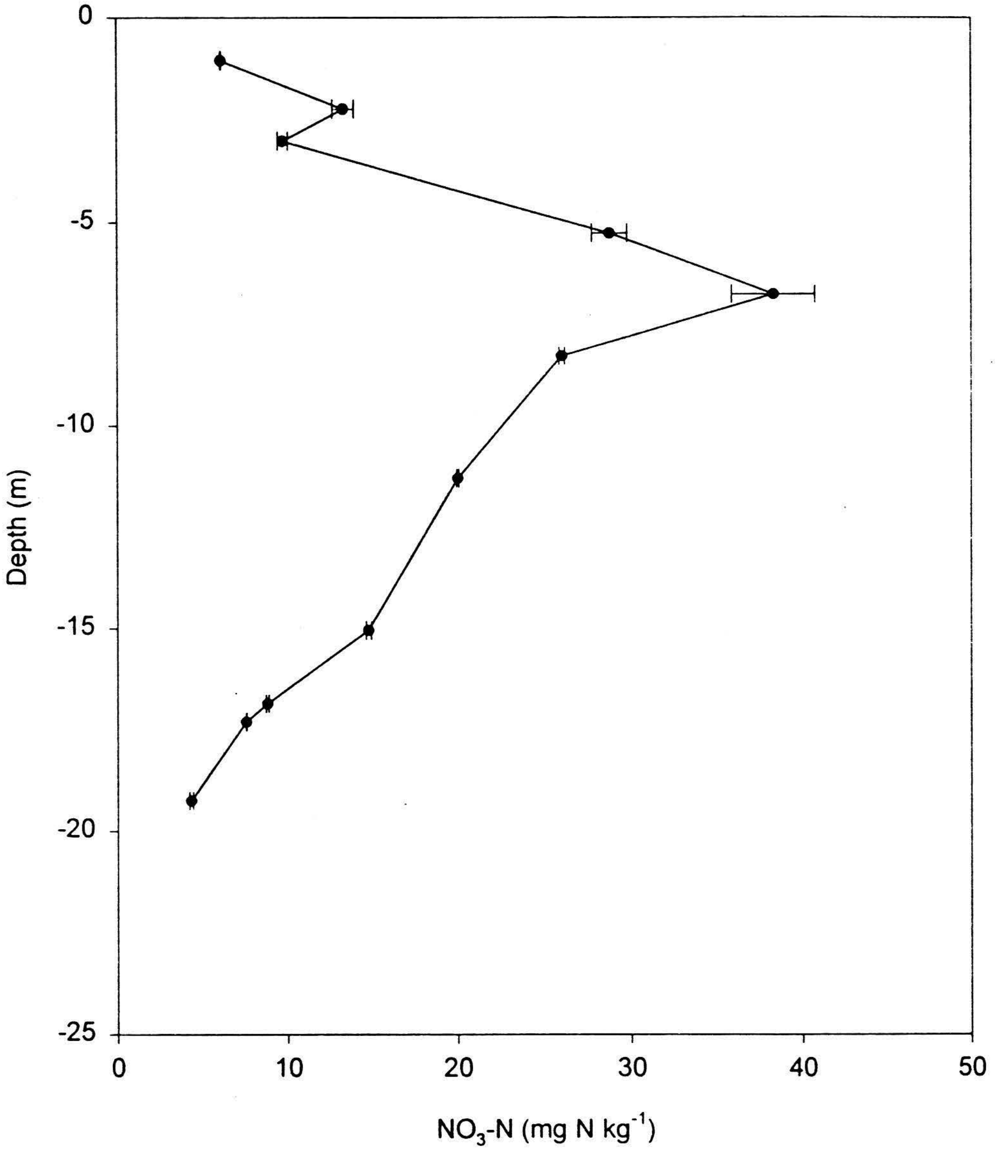

Figure 6. Nitrate -N in borehole # 4111 (Typic Torrox *Lahaina* series). Each point represents a mean of three replicates and bars are the standard error.

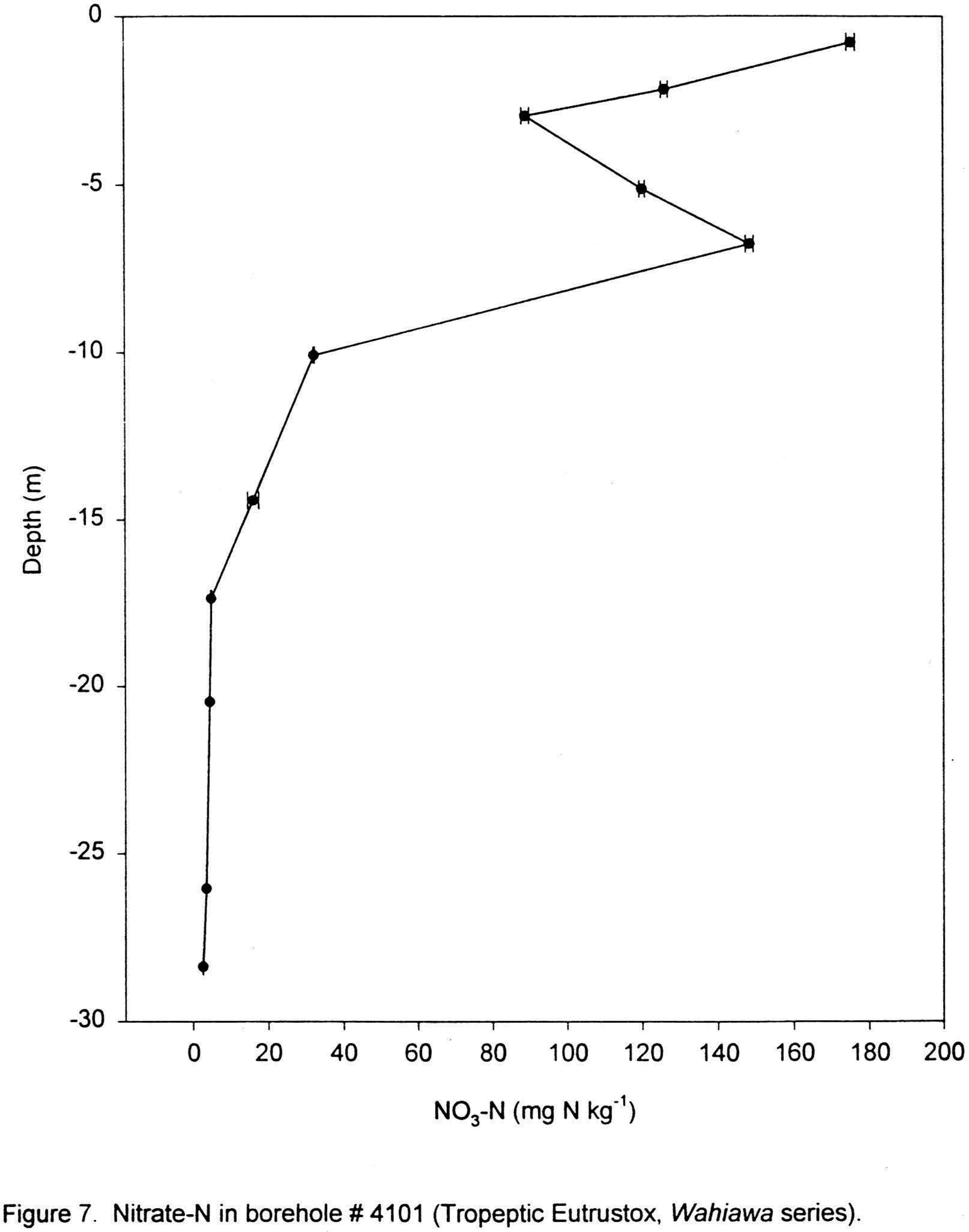

Figure 7. Nitrate-N in borehole # 4101 (Tropeptic Eutrustox, *Wahiawa* series).

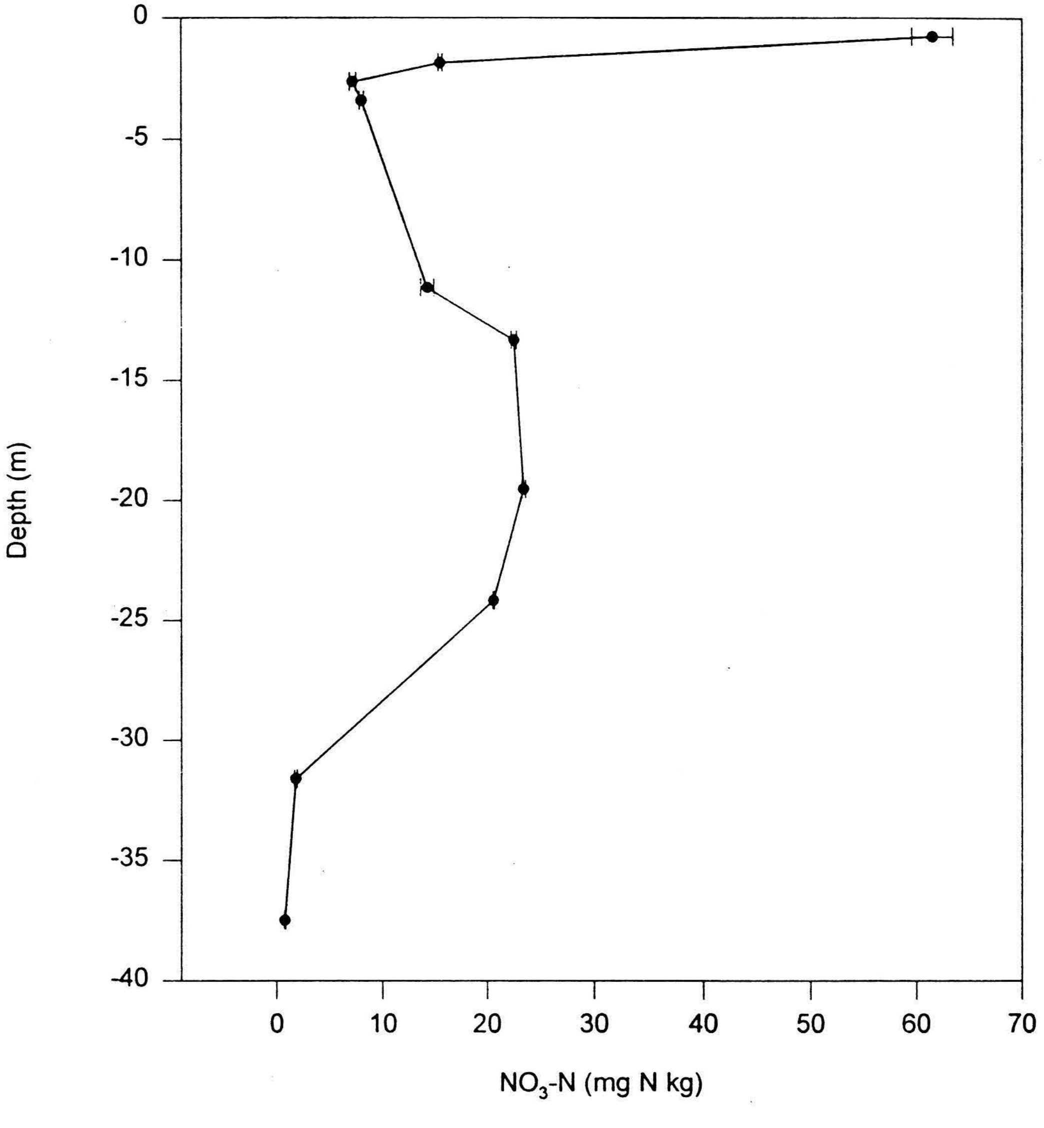

Figure 8. Nitrate-N distribution in borehole # 4213 (Tropeptic Eutrustox, *Wahiawa* series)

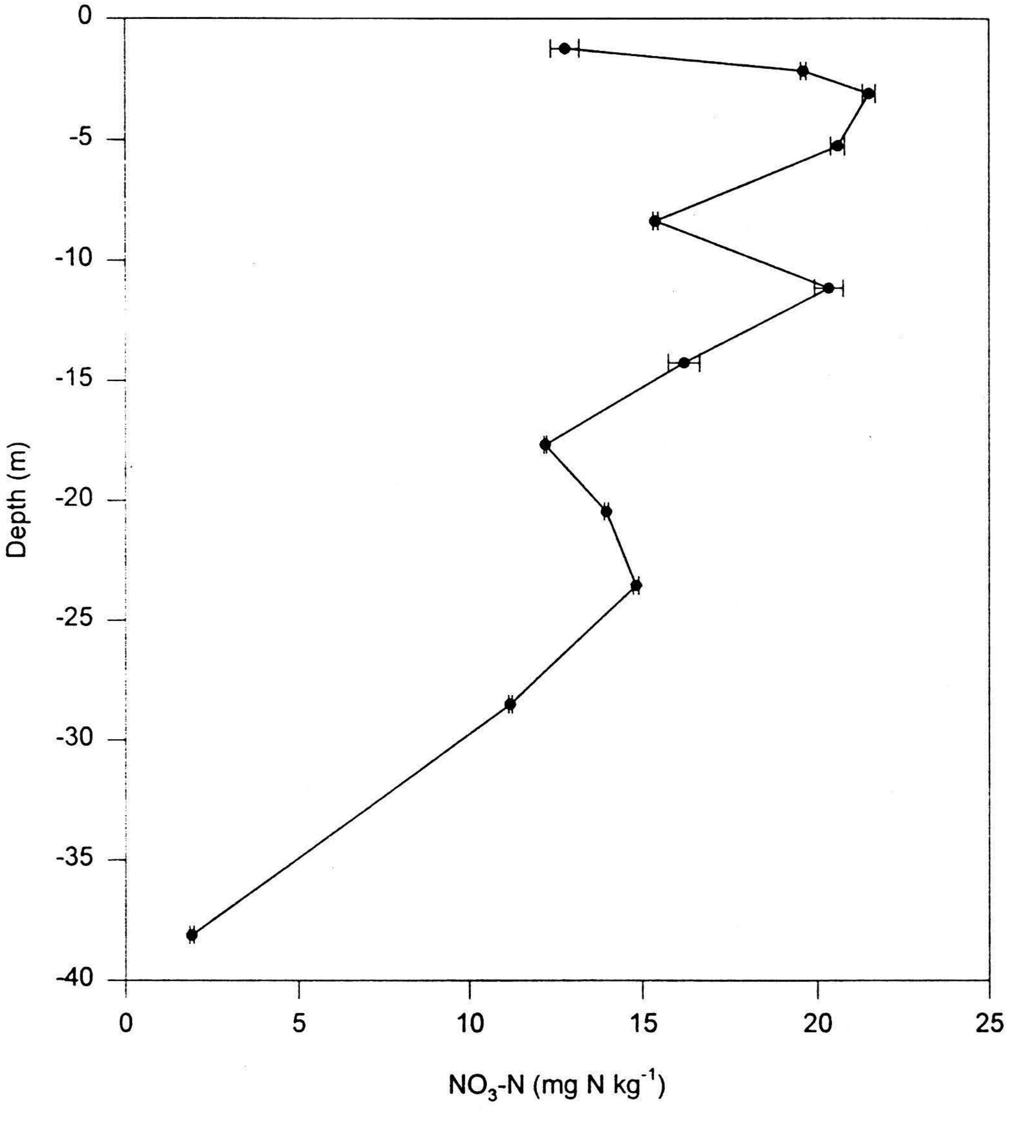

Figure 9. Nitrate-N in borehole # 4201 (Humoxic Tropohumult *Leilehua* series).

nitrate concentrations measured near the surface of bore holes 4101 and 4213 reflect probable fertilizer applications immediately prior to the sampling date.

Mineralogy

The shapes of the nitrate profiles are related to the rainfall regimes and hydraulic properties associated with each site, and the mineralogy of the individual soils. A distinctive nitrate bulge occurs in boreholes 4111 and 4101 between two and seven meters below the surface. These two sites received the lowest amount of annual rainfall and have low hydraulic conductivities relative to the other sites (Miller, 1987). Furthermore, kaolinite and hematite are the dominant minerals detected at the depths coinciding with the nitrate bulge (Table 6). These minerals have pH dependent charge and the presence of positive charges in the subsoil will retard the movement of nitrate. Delta pH measurements[2] in samples above five meters indicate that positively charged sites are present (Fig. 10). In bore hole 4101, the nitrate distribution is highly correlated to delta pH while the relationship in bore hole 4111 is less apparent (Fig. 11). Nitrate concentrations measured at depths below seven meters decrease rapidly in both cores. In borehole 4111, the decline occurs at the same depths where large quantities of nontronite were detected. Nontronite, a form of smectite, is known to be a common weathering product of basaltic rocks high in iron. It is a 2:1 clay mineral that carries a permanent negative charge, and thus nitrate ions will not be adsorbed on its surface. In bore hole 4101, the relationship

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[2] Delta pH data for all four bore holes can be found in Appendix 7.

Table 6. Mineral composition of bore hole samples from sites 4111 and 4101 taken from central Oahu (*Source, Miller, 1987*).

Bore Hole	Depth (m)	Mineral Detected (%)				
4111		Kaolinite	Gibbsite	Hematite	Goethite	Nontronite
	0.3	18	10	45	3	0
	1.5	29	0	38	7	0
	2.4	32	0	37	8	0
	4.6	39	0	33	7	0
	6.1	22	0	7	2	30
	7.6	24	0	16	1	31
	9.2	21	0	9	1	29
	10.7	22	0	3	0	51
	12.2	16	0	3	0	42
4101	0.3	32	0	31	0	0
	1.5	31	0	37	4	0
	2.4	32	2	24	6	0
	4.6	31	0	24	8	0
	6.1	29	0	27	12	0
	7.6	22	3	15	21	0
	9.2	32	0	17	10	0
	10.7	45	0	9	9	0
	12.2	36	0	40	5	0
	13.7	43	0	2	7	0
	15.2	39	0	8	14	0
	16.8	37	0	4	6	0
	18.3	43	0	0	0	39

Table 7. Mineral composition of samples from bore holes 4213 and 4201 taken from central Oahu (*Source, Miller, 1987*).

Bore Hole	Depth (m)	Mineral Detected (%)				
		Kaolinite	Gibbsite	Hematite	Goethite	Nontronite
4213	0.3	21	8	32	5	0
	2.1	24	16	21	6	0
	4.6	18	18	8	12	0
	7.6	50	0	20	5	0
	13.7	55	2	11	15	0
	18.3	42	1	12	16	0
	21.4	38	0	27	7	0
	24.4	37	2	5	9	0
	29.0	42	1	30	10	0
4201	0.6	11	20	39	7	0
	2.4	18	5	49	9	0
	6.1	9	36	29	1	0
	9.2	36	4	34	1	0
	14.0	11	22	21	9	0
	24.4	38	1	30	8	0
	27.4	42	1	14	17	0
	29	39	1	33	6	0
	30.5	44	3	27	1	0

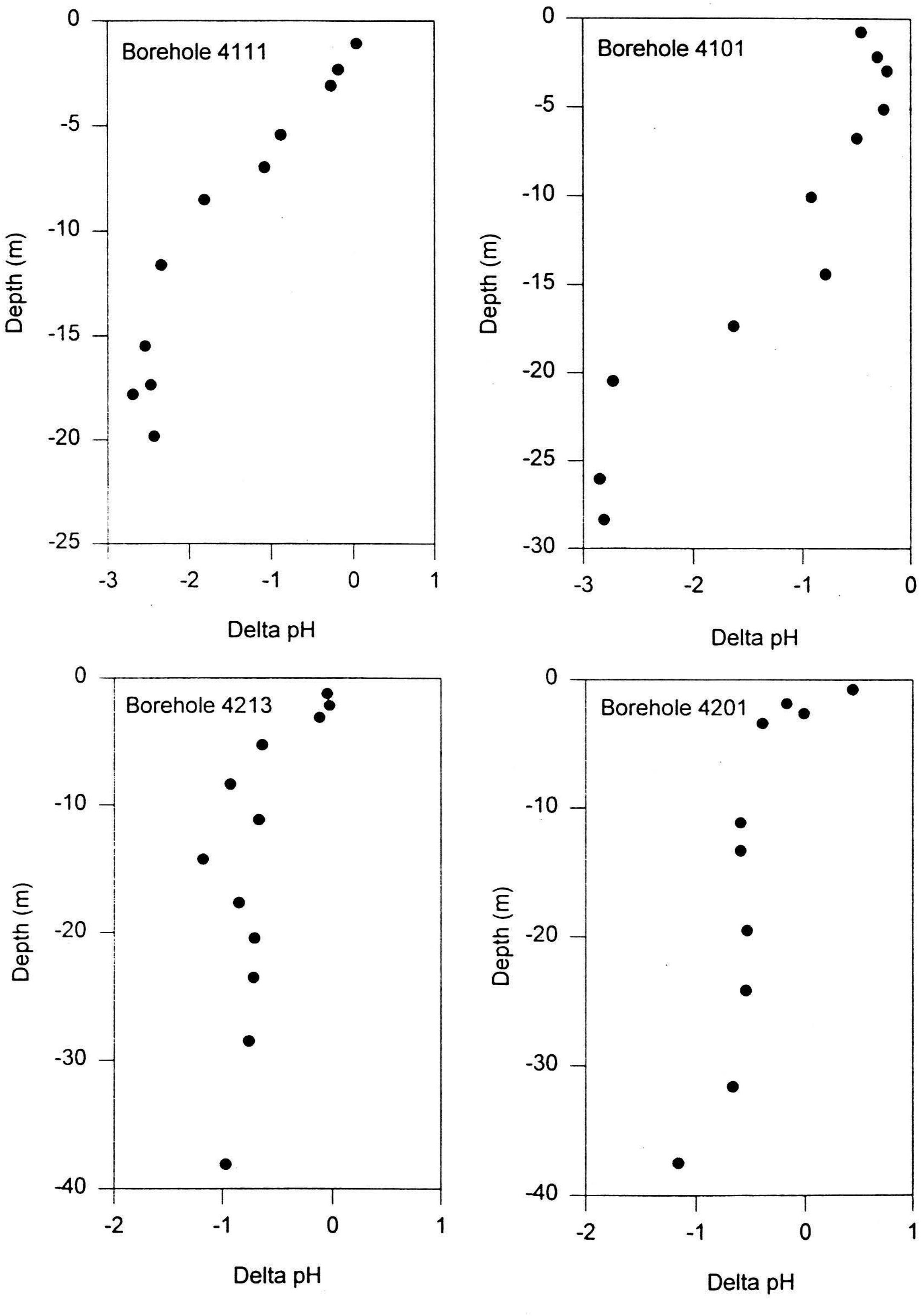

Figure 10. Delta pH measured in deep soil cores. Delta pH = $pH_{1M\ KCl}$ - pH_{H2O}.

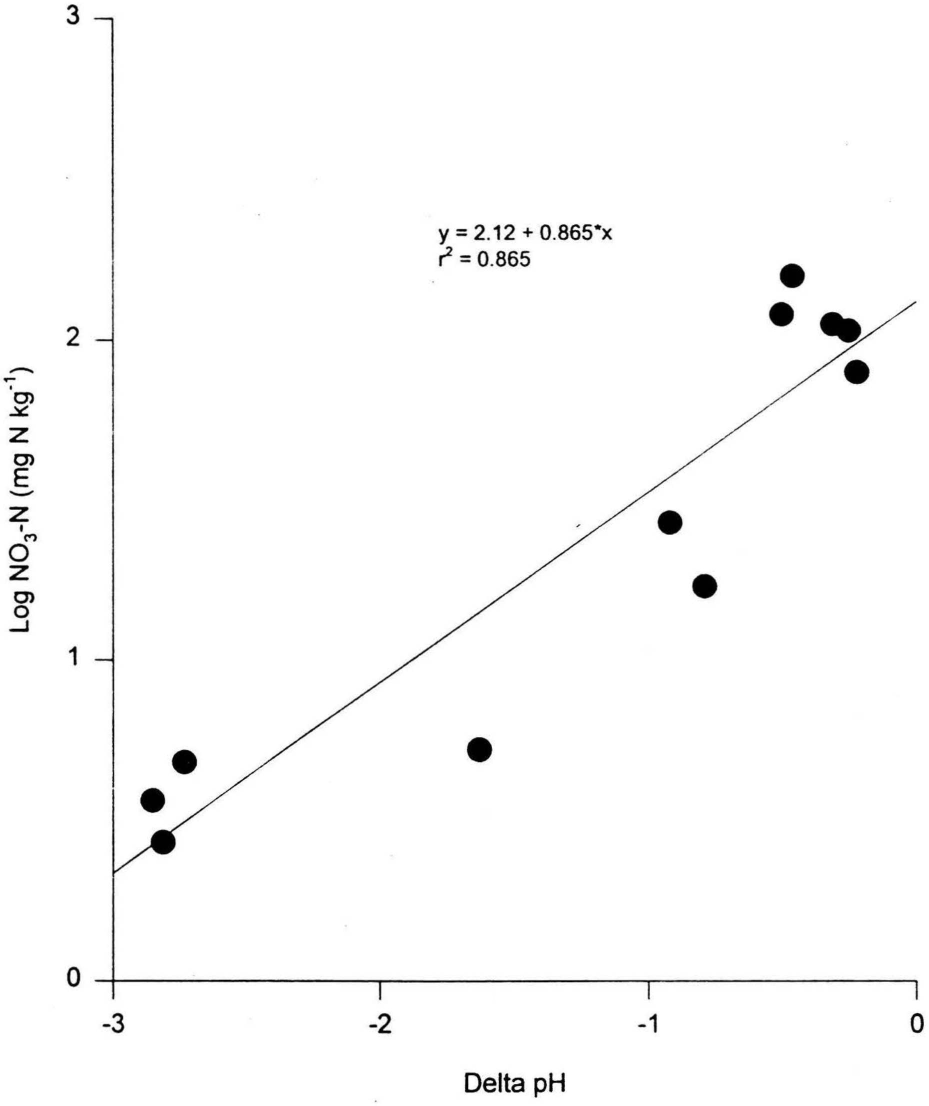

Figure 11. Delta pH versus the log of N concentration in bore hole 4101.

between nitrate concentration and mineralogy below 10 meters is less clear. Nontronite is present in bore hole 4101, but not until the 18 meter depth. Significant increases in net negative charge occur at the same depths where nontronite was detected (Fig. 10). Decreasing nitrate levels below 10 meters may be due to the decline in hematite.

At the higher elevations, higher precipitation and hydraulic conductivity rates have worked to transport nitrate to greater depths. In boreholes 4201 and 4213 nitrate concentrations do not approach zero until below 25 meters. Mineralogical analysis of the core samples provides evidence of weathering throughout the profile (Table 7). The predominance of iron oxide minerals (gibbsite, hematite and goethite) with their pH dependent charges to 30 meters depth suggest that nitrate may be adsorbed in the saprolite zone. Delta pH values were not greater than -1 with depth indicating that positive charges exist throughout the profiles (Fig. 10).

Nitrate Adsorption

An adsorption study was conducted to test the hypothesis that high nitrate levels measured in the subsoil were related to the capacity of these soils to adsorb nitrate ions. The results confirm that nitrate adsorption in the subsoil is substantial. Adsorption magnitude varies with location, depth and mineralogy (Figs. 12-15). Nitrate adsorption was highest in the subsoil of borehole 4101 and explains why this site had the largest amount of nitrate retained among the sites tested (Fig. 12 and 7).

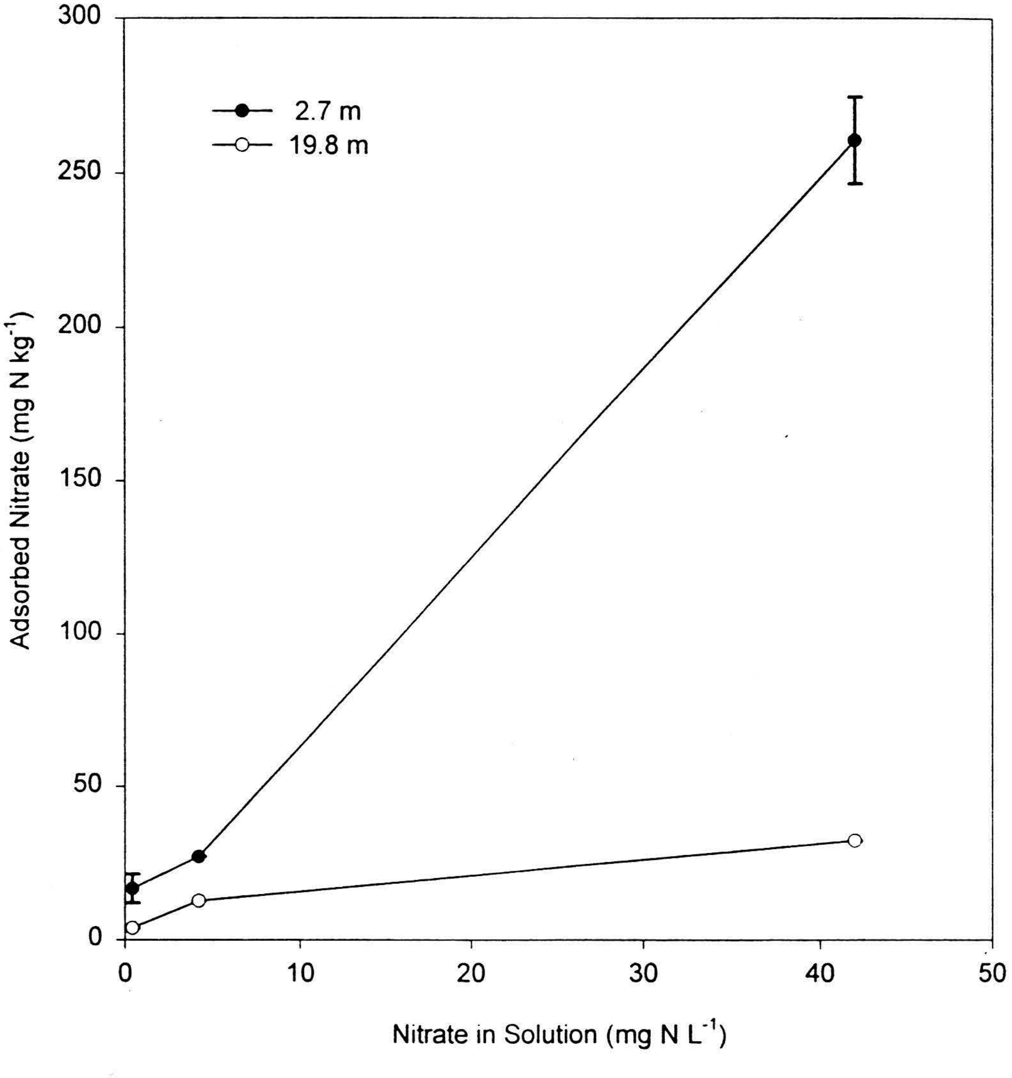

Figure 12. Nitrate-N adsorption isotherms in surface and saprolite samples in bore hole 4101. Points represent a mean of 2 replicates and bars are the standard error.

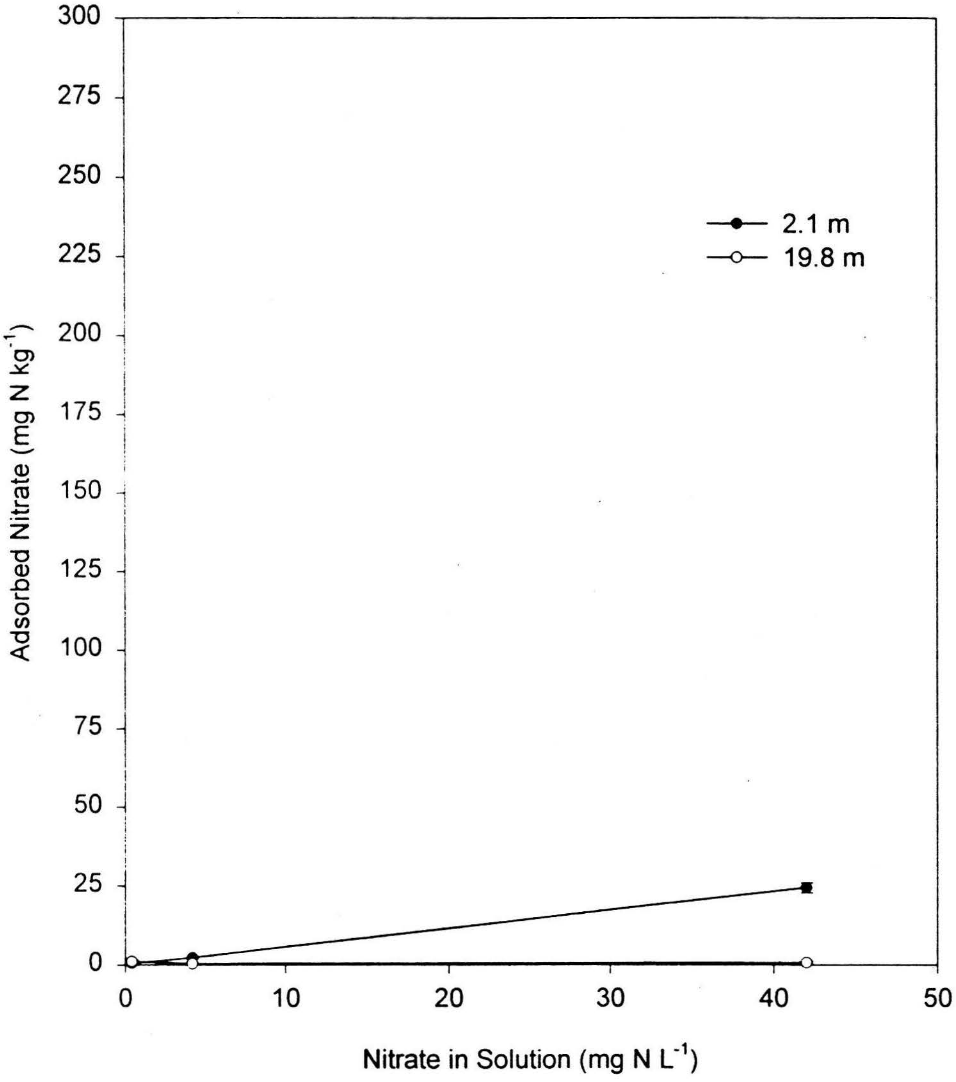

Figure 13. Nitrate-N adsorption isotherms in subsoil and saprolite samples from bore hole 4111.

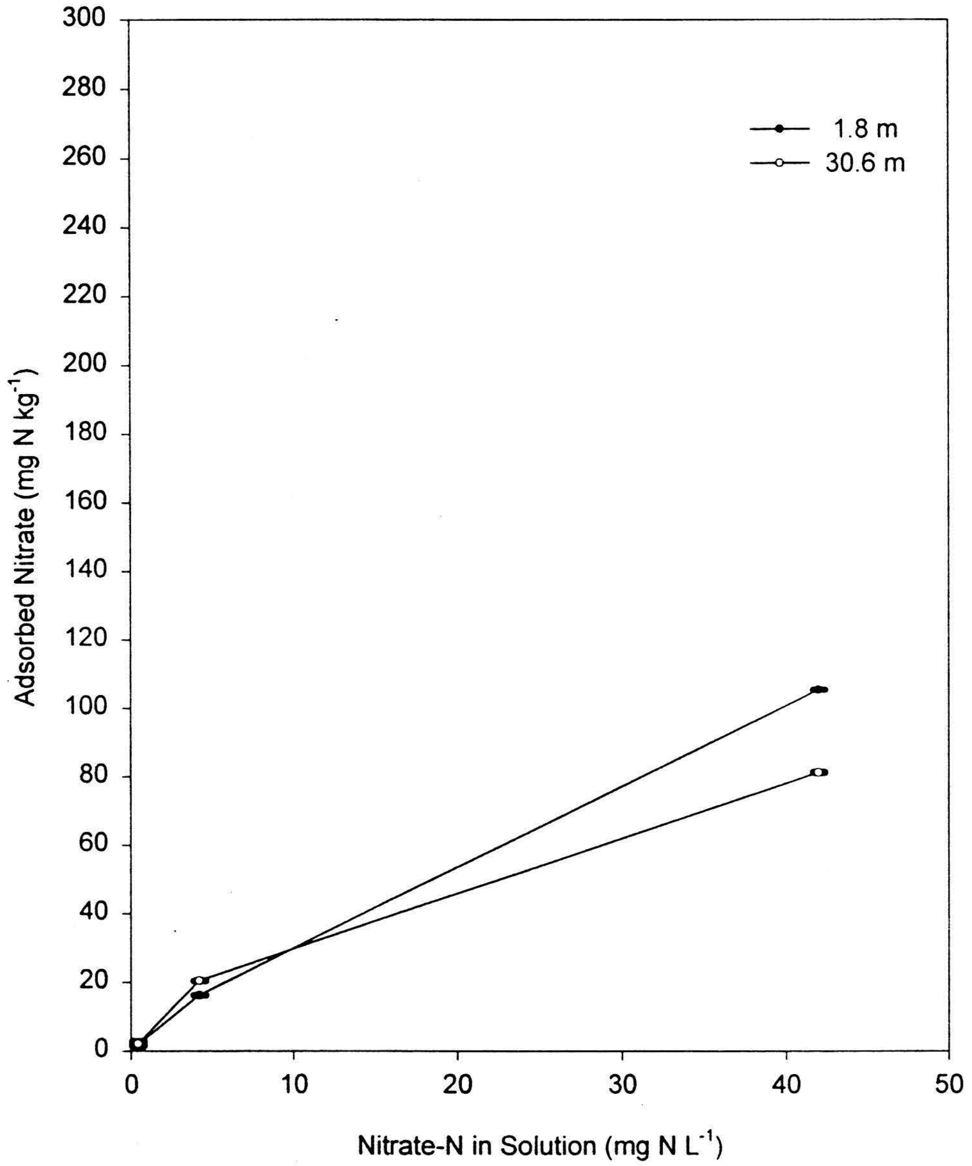

Figure 14. Nitrate-N adsorption isotherms in subsoil and saprolite samples from bore hole 4213.

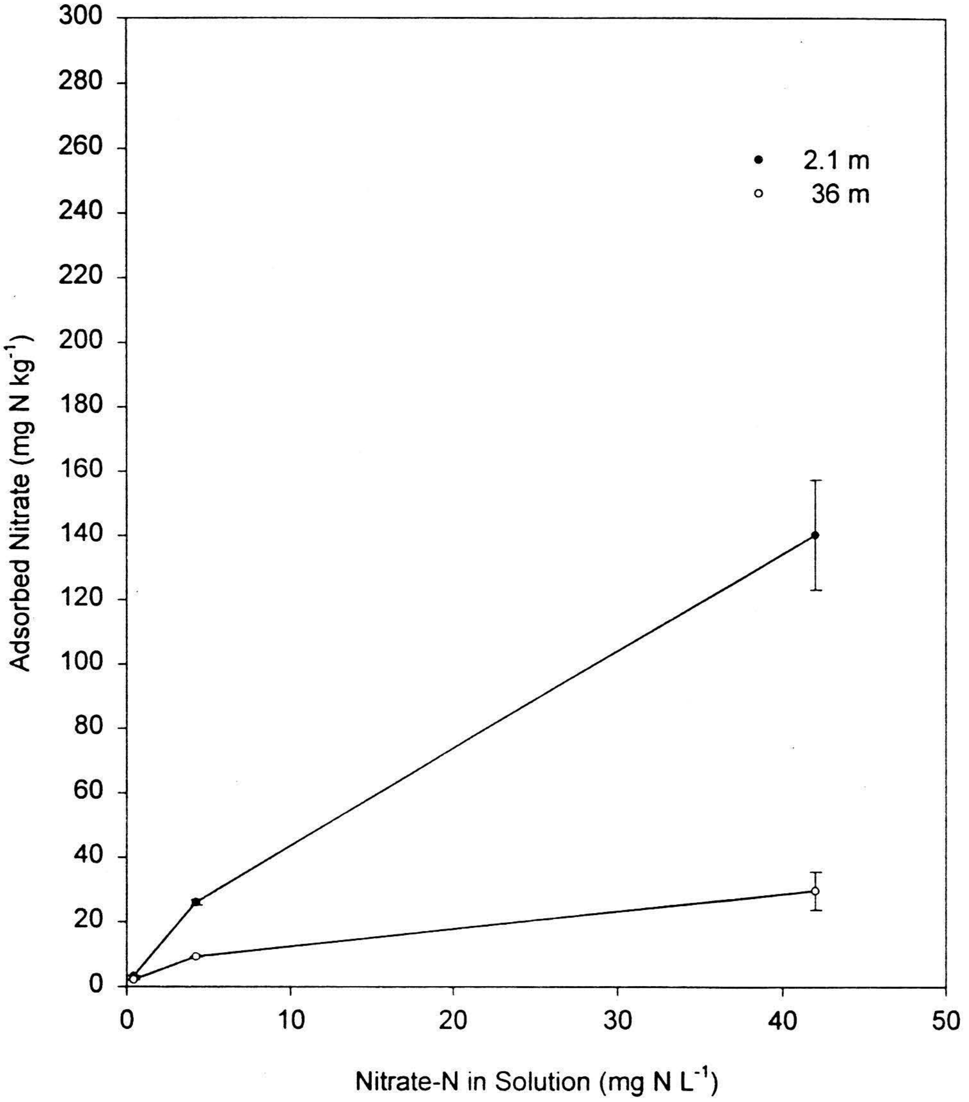

Figure 15. Nitrate-N adsorption isotherms in subsoil and saprolite samples from bore hole 4201.

In the saprolite zone, adsorption decreased significantly with the increased presence of nontronite. The lowest adsorption was measured at the lowest elevation at site 4111 (Fig. 13). In the subsoil, the adsorption rate was low because the Lahaina series is less weathered, less acidic and has more net negative charge than the soils at the other three sites. Adsorption was essentially zero at 20 meters due to the effect of nontronite. High adsorption was measured at the 2 meter depth in boreholes 4213 and 4201 (Figs. 14 and 15). However, adsorption at 30 meters in bore hole 4213 was surprisingly high in comparison with adsorption at the lowest depth in the other cores. Low adsorption in the saprolite region would be expected because weathering is less severe and minerals tend to carry more negative charges, a trend that is present in the other three cores. The high adsorption obtained in 4213 may be due to the presence of larger amounts of goethite (10%) at 30 meters than in the other cores. Goethite is an iron oxide mineral with a large surface area and a high nitrate adsorption capacity (Black & Waring, 1979). This mineral is absent at the lowest depths in cores 4111 and 4101, and present only in small proportions in core 4201.

In order to make meaningful comparisons it is useful to express nitrate adsorption in terms of an adsorption coefficient (K_d), where K_d = N adsorbed (mg N kg^{-1})/N in solution (mg N L^{-1}). K_d values ranging from 0.58 to 6.2 were obtained in the subsoils of the deep soil cores (Table 8). Significantly lower values were reported for the deeper saprolyte zone. Adsorption coefficients for nitrate are not common in the literature, but those that do exist are significantly lower than the values measured in this study (Table 9). In a number of the cases, the low values for K_d can be attributed to sampling depth. Shallow samples often contain large amounts of organic matter that impart a negative charge to the particle surface and contribute to low K_d values (Singh & Kanehiro, 1969). Soil texture also influences the adsorption capacity and may explain low K_d values in a Nigerian Ultisol containing 66% sand (Arora and Juo, 1982). A later study (Wong et al, 1990) using the same Ultisol also reported similar K_d values.

Table 8. Adsorption coefficient (K_d) values for deep soil cores.

Bore Hole #	Depth (m)	K_d*
4111	2.1	0.58
	19.8	0.02
4101	2.7	6.2
	36	0.77
4213	1.8	2.51
	30.6	1.93
4201	2.1	3.34
	36	0.71

* K_d = mg N kg^{-1} (adsorbed N) / mg N L^{-1} where mg N L^{-1} = 42 at all depths. This concentration was chosen because it was the closest to those found in the literature.

Table 9. Some published values for k_d at varying concentrations of N in solution.

mg N L^{-1}	Soil	Depth (m)	K_d	Source
140	Oxisol	Surface	0.35	Singh & Kanehiro, 1969
140	Ultisol	1.2	0.29	Arora & Juo, 1982
280	Ultisol	1.35	0.28	Wong et al, 1990
70	Krasnozem	1.5-2.0	0.58	Black & Waring, 1979
"	"	2.7-3.0	0.62	"

Estimating Nitrate Mobility

In the state of Hawai‘i, scientists have accumulated data on nitrate in the surface soils as it relates to plant nutrition and have also monitored nitrate in the groundwater. No data exist, however, on nitrate in the subsoil and vadose zone. The nitrate data obtained from the deep soil cores provide evidence that a considerable quantity of nitrate remains in the vadose zone once it is leached past the root zone. These data raise interesting questions: can knowledge and understanding of the mechanisms of solute transport in porous media be used to simulate nitrate transport in the deep soil cores and how might the results compare with the field data? Modeling solute transport in soils is complex and has been the subject of intense experimental and theoretical research for a number of years (van Genuchten and Jury, 1987). The detailed modeling of nitrate mobility in soils is beyond the scope of the present study, but the application of a set of simple conceptual models may help discern the relative importance of the different processes at work. The following section will use two principal transport mechanisms, (1) mass flow and (2) mass flow combined with diffusion, to simulate nitrate mobility compared with field data. The effect of adsorption will also be assessed in both cases. It must be emphasized that these models are simple and the results can only be treated as first approximations, and not as accurate descriptions of the complex phenomena involved.

Mass flow or convection states that the solute moves with the wetting front uniformly through the soil media maintaining a constant concentration as it moves (assuming no sources or sinks). This type of flow can move solutes large distances in short periods. The solute moves as a single pulse through the media as shown in Fig.

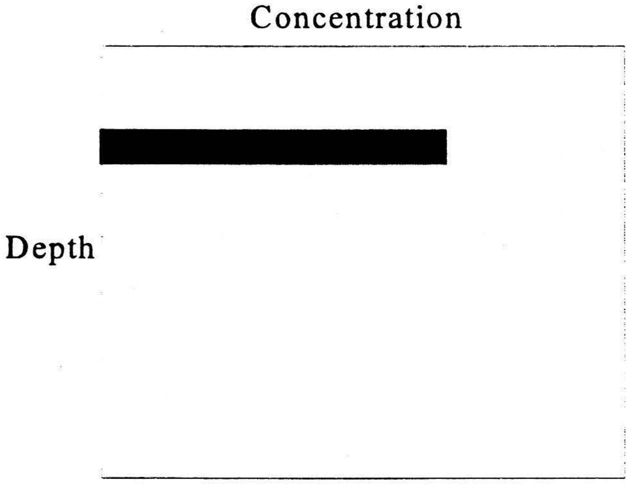

Figure 16. Idealized solute concentration distribution in the soil when only mass flow is operative.

shown in Fig. 16. Although mass flow is an oversimplification of the complexity of solute transport in soils, it illustrates that solutes can be transported with water as it moves rapidly through the larger pore spaces. Mass flow in soils can be calculated using the following equation:

$$X_N = W_L/\theta_{eff} \tag{1}$$

where X_N is the depth to which the nitrate front has moved along with the water, W_L is the quantity of water leached (in meters), and θ_{eff} is the volumetric water content associated with macro pores. X_N represents the depth to which the water and the solute have traveled following the application of a certain amount of water.

It is clear that solutes are transported with water flow. At the same time, however, solute molecules or ions move with reference to each other as water flows. This movement is slow and is known as diffusion. While water moving by mass flow can move several meters in a few hours, the solute will only move a few millimeters in the solution in the same time period. As water and solutes move through soils with disparate pore sizes the effects of mass flow and diffusion working in concert result in a solute distribution similar to that in Fig. 17. The effect of diffusion causes solutes to be distributed in a bell-like fashion, with tails both above and below the peak. As the peak moves vertically through the soil it begins to lose the peak as the tails spread further above and below the peak. In the second scenario where nitrate transport is assumed to be controlled by both mass flow and diffusion, the peak movement was

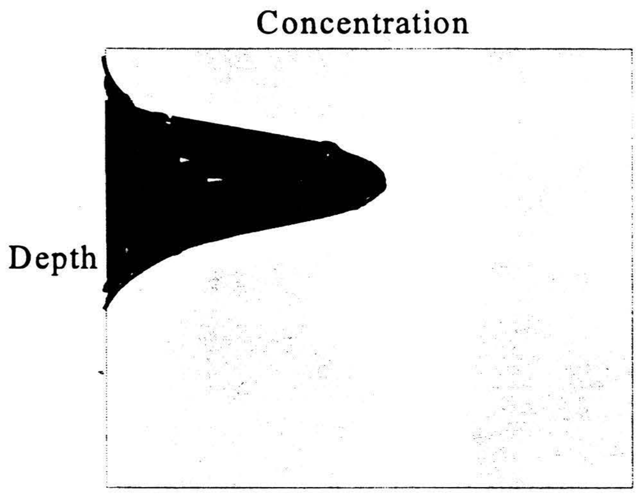

Figure 17. Idealized solute concentration profile where both mass flow and diffusion are operative.

calculated based upon findings by Balasubramanian and co-workers (1973). They observed that when surface applied nitrate was allowed to equilibrate for one week prior to a leaching event, nitrate diffusion into the aggregate micro pores caused the nitrate peak to disperse and move more slowly behind the bulk wetting front with distribution similar to the shape depicted in Fig. 17. Relative nitrate movement was expressed as the ratio of nitrate peak movement to pore water movement, and a value of 0.28 was obtained from experimental data. Therefore, when diffusion is considered in the transport of nitrate, the position of the front was estimated by

$$X_N = (W_L/\theta_{eff})*0.28 \tag{2}$$

The maximum concentration of the peak is given as a function of depth by

$$C_{max} = C_0X_0\,(2\pi\beta X_N)^{-1/2} \tag{3}$$

where C_0 is the initial concentration of nitrate, X_0 is the depth of incorporation (0.2

cm), β (0.24 cm) is a dispersion coefficient estimated by fitting the equation to experimental data[3] and X_N is the depth at which maximum concentration occurs. Balasubramanian et al (1973) were able to use equations 2 and 3 to predict the movement of the nitrate through an Oxisol (*Molokai series*) to a depth of 120 cm.

The adsorption study conducted on the samples from the deep soil cores illustrated that the subsoils found under pineapple can adsorb large quantities of nitrate. The effect of adsorption on the retardation of nitrate movement through soils can be quantified by the following equation:

$$R = 1 + \rho_b K_d / \theta_{\text{eff}} \qquad (4)$$

where R is the retardation factor, ρ_b is the bulk density and K_d is the adsorption coefficient. The third and fourth scenarios look at the effect of adsorption on mass flow and mass flow and diffusion respectively by dividing X_N in both cases by R. In all coring sites two R values corresponding to the two values for K_d per deep core were employed - one for the depth increment above 3 m and the other for depths below 20 m.

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[3] A good fit was achieved with experimental data, but β cannot be applied to a different set of conditions with confidence. Developing characteristic constants or coefficients that describe the movement of nitrate in soils is complicated by the complex nature of pore size distribution, the resultant variability in pore-water velocity, and the tendency of nitrate to undergo biological transformations in the soil. The same β was used in this study merely to make a first approximation.

The modeling effort presented in the following pages consists of four simple scenarios: 1) mass flow, calculated by equation 1, 2) mass flow and diffusion, calculated by equations 2 and 3, 3) mass flow with adsorption, and 4) mass flow and diffusion with adsorption.

Assumptions

In all cases a number of assumptions were made regarding annual rainfall, evapotranspiration, soil physical properties, fertilization, and N transformations. The total amount of water leaving the root zone was approximated by multiplying pan evaporation values for each site (gleaned from Ekern and Chang, 1985) by a pan coefficient (a factor used to estimate evapotranspiration from a planted pineapple field, Ekern, 1965) with a numerical value of 0.3 and subtracting the result from total rainfall for each site. Water movement was assumed to occur in the macro pores and volumetric water content was calculated based upon the fraction of macro pores. Macro pore water content (θ_{eff}) was estimated by subtracting residual water content from saturated water content (these data are available in Miller, 1987). In calculating R bulk density values for the four sites were also taken from Miller, 1987.

Typical nitrogen applications for pineapple production in Australia are reported to be between 200 and 400 kg N ha^{-1} per crop (personal communication Bartholomew, 1997). Assuming 300 kg N is applied to the first crop which takes two years to mature and an additional 300 kg N for a single ratoon crop, the full cycle involves three years and a total of 600 kg N ha^{-1} of applied N fertilizer. Under the assumption that pineapple utilizes 40% of the applied N (Ling, 1996 and personal communication M. Li, 1997), a total of 360 kg N ha^{-1} remains in the soil. If denitrification does not exceed 10% (Balasubramanian, 1974) and ammonia volatilization is neglected, then approximately 324 kg N ha^{-1} is subject to leaching beyond the root zone and represents the total amount of nitrate-N that can move toward the groundwater in a three year period.

While the results of the four scenarios outlined above are only first approximations and cannot adequately describe the complex phenomena involved, they simply provide an opportunity to compare the results of a set of idealized transport models with nitrate distributions observed in the field.[4] The results are presented graphically in Figures 18-25. The bar plots on each individual graph depict the movement of a single peak of nitrogen applied 30 years ago as it moves vertically through the vadose zone under the conditions specified above. For example the first bar on each plot represents the distance the nitrate peak would have traveled under the specified conditions following one three-year pineapple cycle. Similarly, the last bar indicates the position of the peak after ten cycles or thirty years.

As expected, when mass flow was assumed as the sole mechanism of transport, vertical transport of the nitrate peak was far in excess of the measured nitrate at all four coring sites. At site 4201, the combination of mass flow and

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[4] In order for a realistic comparison, nitrate measured in the deep soil cores, expressed as mg N kg^{-1}, were converted to mg N L^{-1} using volumetric water content from Miller (1987) and dividing mg N kg^{-1} by water content.

adsorption (Fig. 18b) estimated that the nitrate peak would reach a depth of just over 40 meters in 30 years. At 40 meters nitrate in the field was very low indicating that either the peak had not reached that depth or that it does not accumulate below 30 meters. Low adsorption measured at this depth provides evidence for the latter explanation. The mass flow and diffusion model estimated that after thirty years the nitrate peak would have reached a depth of about 50 meters - still in excess of the measured nitrate, but suggesting that other forces in addition to diffusion may be delaying the movement of the nitrate peak (Fig. 19a). Beyond 30 meters the model overestimated the nitrate concentration. The mass flow and diffusion with adsorption (Fig. 19b) predicted that the vertical transport of nitrate would be significantly retarded. After the thirty-year period, the nitrate peak would have migrated to a depth of just over 10 meters. The concentration of the peak as it migrates vertically indicates a match with measured nitrate concentrations up to ten meters. If three cycles are calculated (Fig. 19c), equivalent to 90 years of production, the predicted movement of the peak with measurements in the field are strikingly similar.

In borehole 4213, combining mass flow with adsorption (Fig. 20b) appears to exaggerate the effect of adsorption on nitrate mobility as the model predicts that nitrate would not move past just a few meters. The mass flow and diffusion model (Fig. 21a) predicted the nitrate peak would have traveled to a depth of about 32 meters. Nitrate distribution from the measured data indicate that a significant peak exists above 30 meters suggesting that some sort of delaying process is active. At the lower elevations, the results were less informative (Figs. 22-25) However, the mass flow with adsorption model correctly predicted that large quantities of nitrate should be detained above ten meters in borehole 4101 (Fig. 22b)

Up until recently in Hawaii, research has focussed primarily on nitrate dynamics in the root zone. The recent detection of elevated nitrate concentrations in drinking water wells in the Millilani area of central Oahu has shifted focus to nitrate leaching and its potential to contaminate the groundwater (El-Kadi, 1994). Incipient modeling efforts based upon nitrate leaving the root zone under fields planted to corn and pineapple indicate that increased nitrate levels in wells located in agricultural areas can be attributed to agricultural practices (El-Kadi, 1995). El-Kadi's modeling efforts begin with a known concentration of nitrate in the groundwater and work backward to find how much nitrate must leave the root zone to support the groundwater levels of nitrate. Setting a time frame that began in 1950, he found that the amount of nitrate leaving the root zone must increase over to time to explain the steady rise in nitrate concentration measured in the groundwater. Additionally, based upon data gathered from a pineapple plot, El-Kadi found that only a small fraction of nitrate leaving the root zone actually reaches the groundwater.

Data gathered from the analysis of the four deep soil cores provide substantial evidence that nitrate movement through the vadose zone has been delayed significantly where mineralogy is dominated by minerals carrying variable charges. In the deep saprolite zone, where 2:1 clay minerals such as nontronite are present, nitrate moves with the bulk solution and may even undergo repulsion from the negatively charged materials. The delayed movement of nitrate can be attributed to a number of factors: 1) nitrate adsorption in the subsoil; 2) large degree of micro porosity in the saprolite region resulting in low conductivities which delay the movement of nitrate through the profile; and 3) the great distance between the surface and the aquifer. Modeling the transport on nitrate through the vadose zone is the next challenge scientists face. Such an endeavor is essential to improving our understanding of solute transport and assessing the vulnerability of drinking water on Oahu.

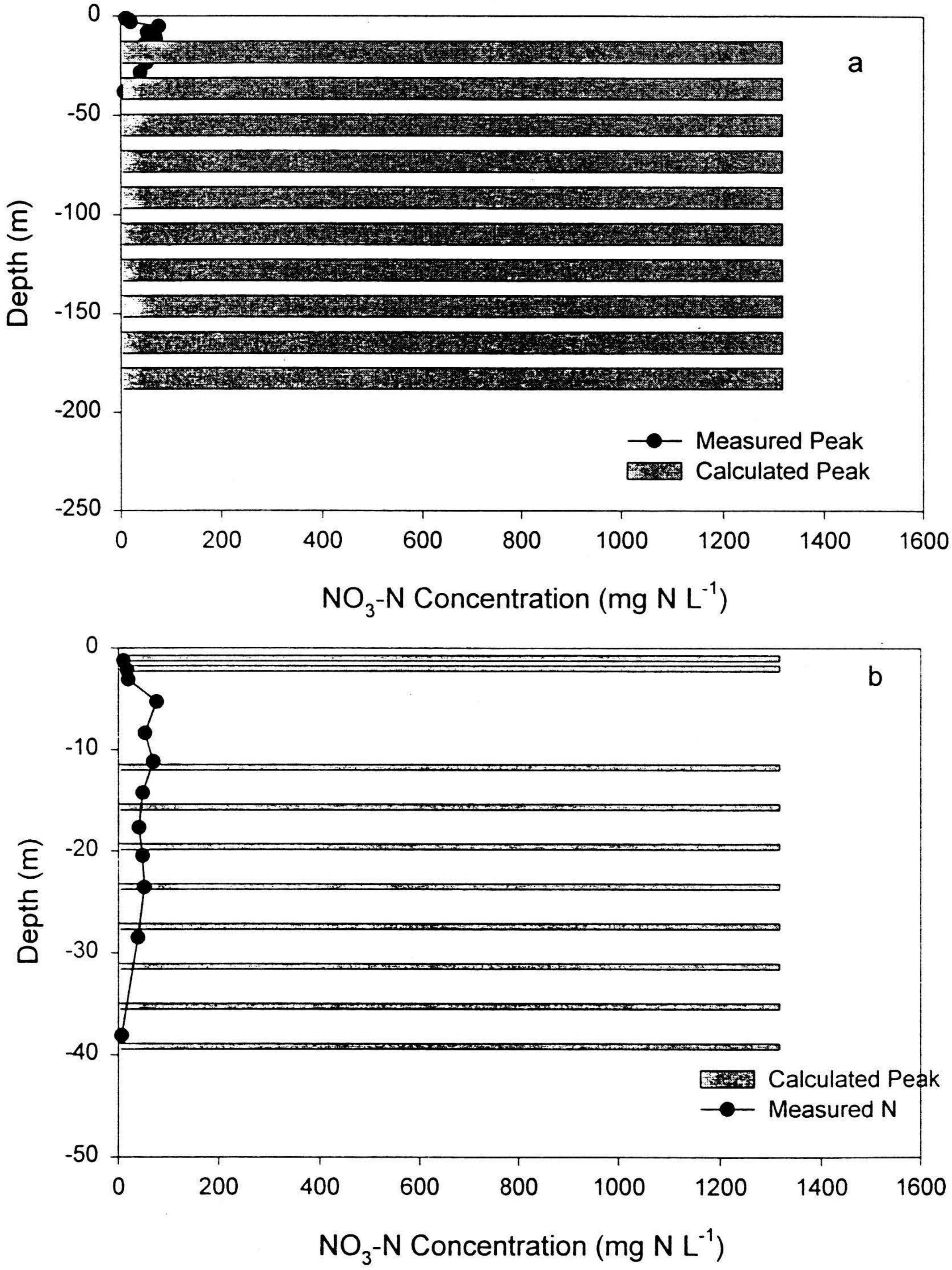


Figure 18. Calculated nitrate movement assuming mass flow (a) and mass flow with diffusion (b) in bore hole 4201. Calculated peaks from top to bottom represent successive 3-year cropping cycles; the top peak represents nitrate distribution after 3 years and the bottom peak corresponds to 30 years.

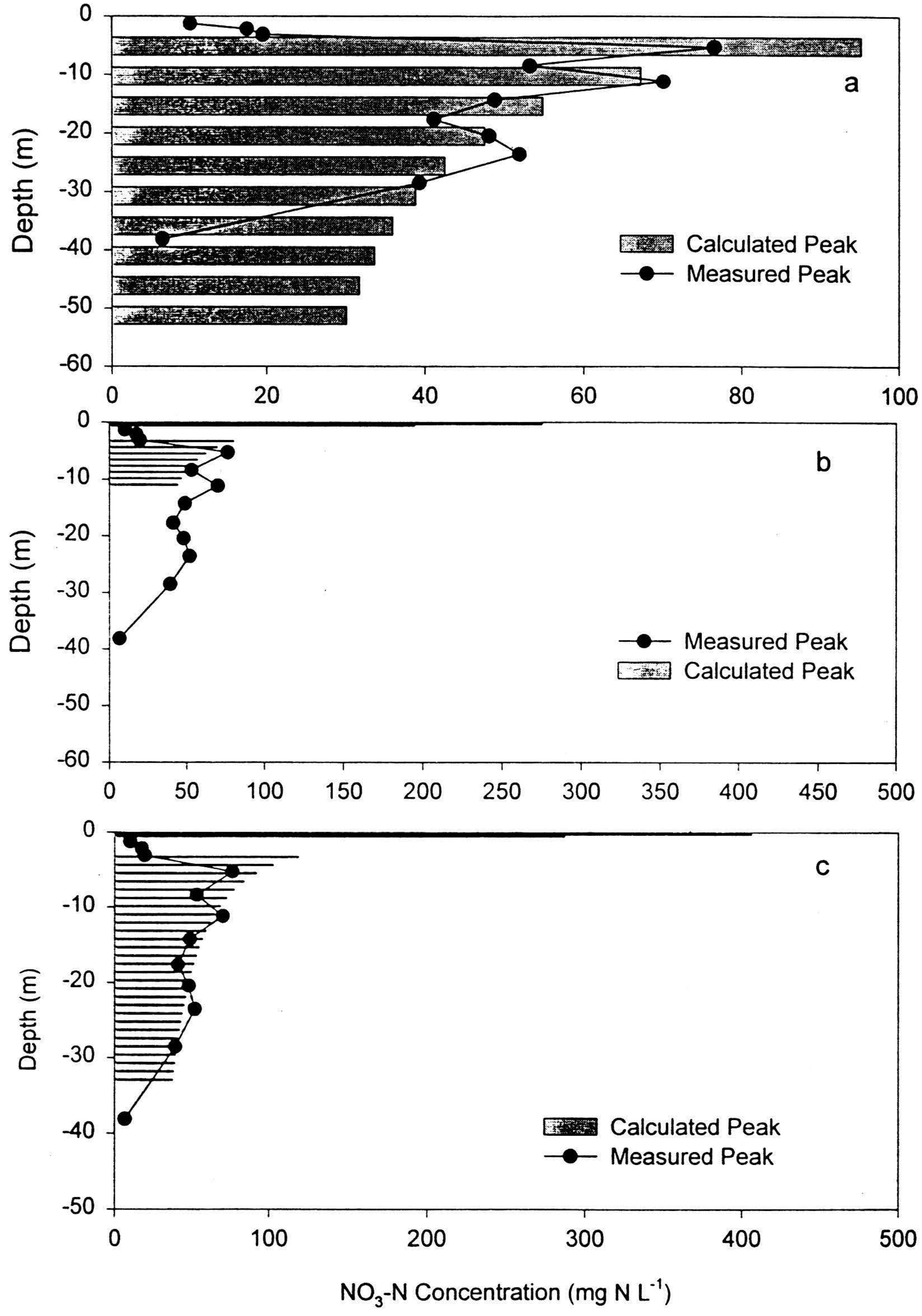


Figure 19. Calculated nitrate movement assuming mass flow and diffusion (a) and mass flow and diffusion with adsorption (b) in bore hole 4201. In (c) 30 cycles, or a 90 year period, was used.

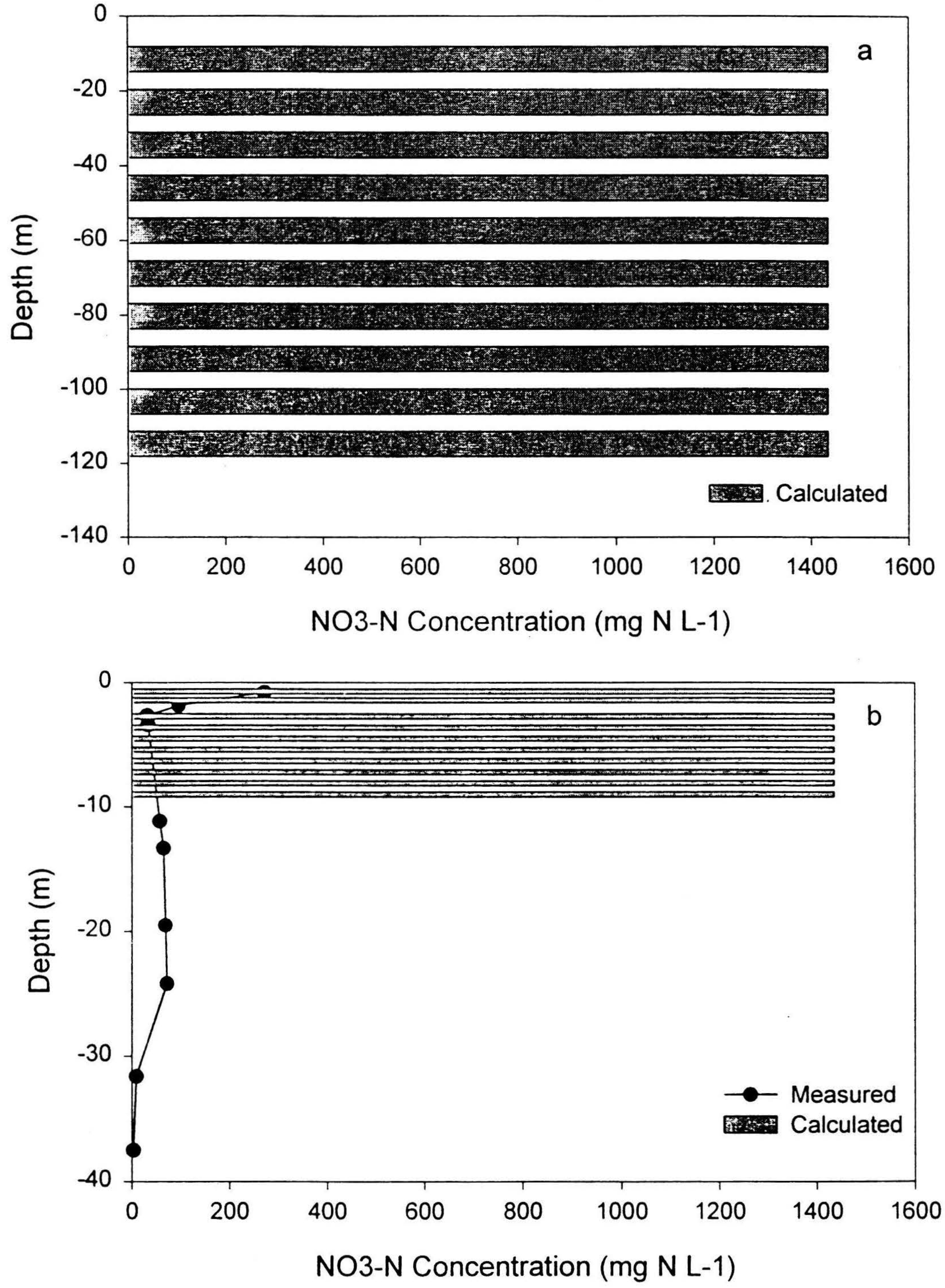


Figure 20. Calculated nitrate movement assuming mass flow (a) and mass flow with adsorption (b) in bore hole 4213.

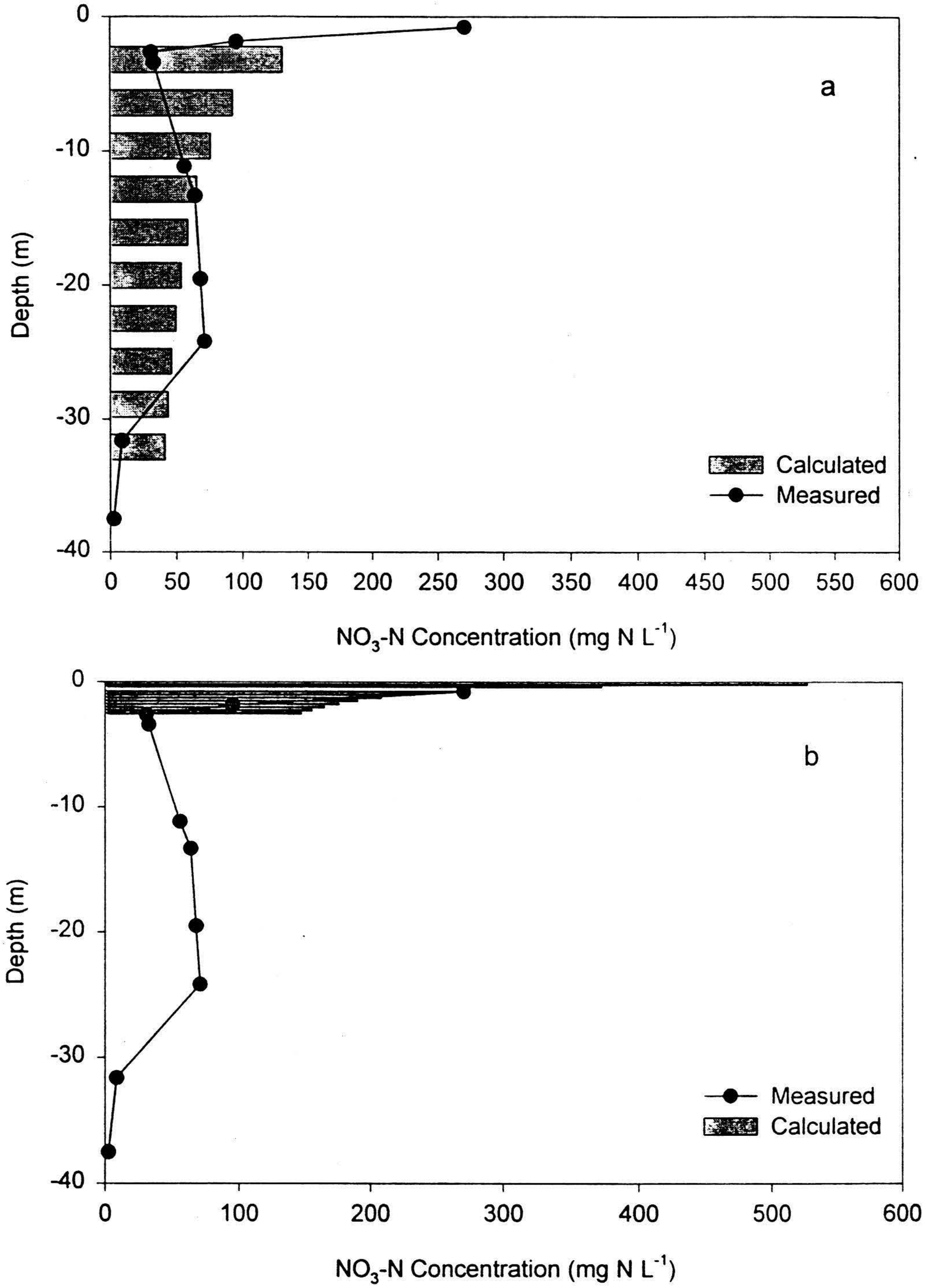


Figure 21. Calculated nitrate movement assuming mass flow and diffusion (a) and mass flow and diffusion with adsorption (b) in bore hole 4213.

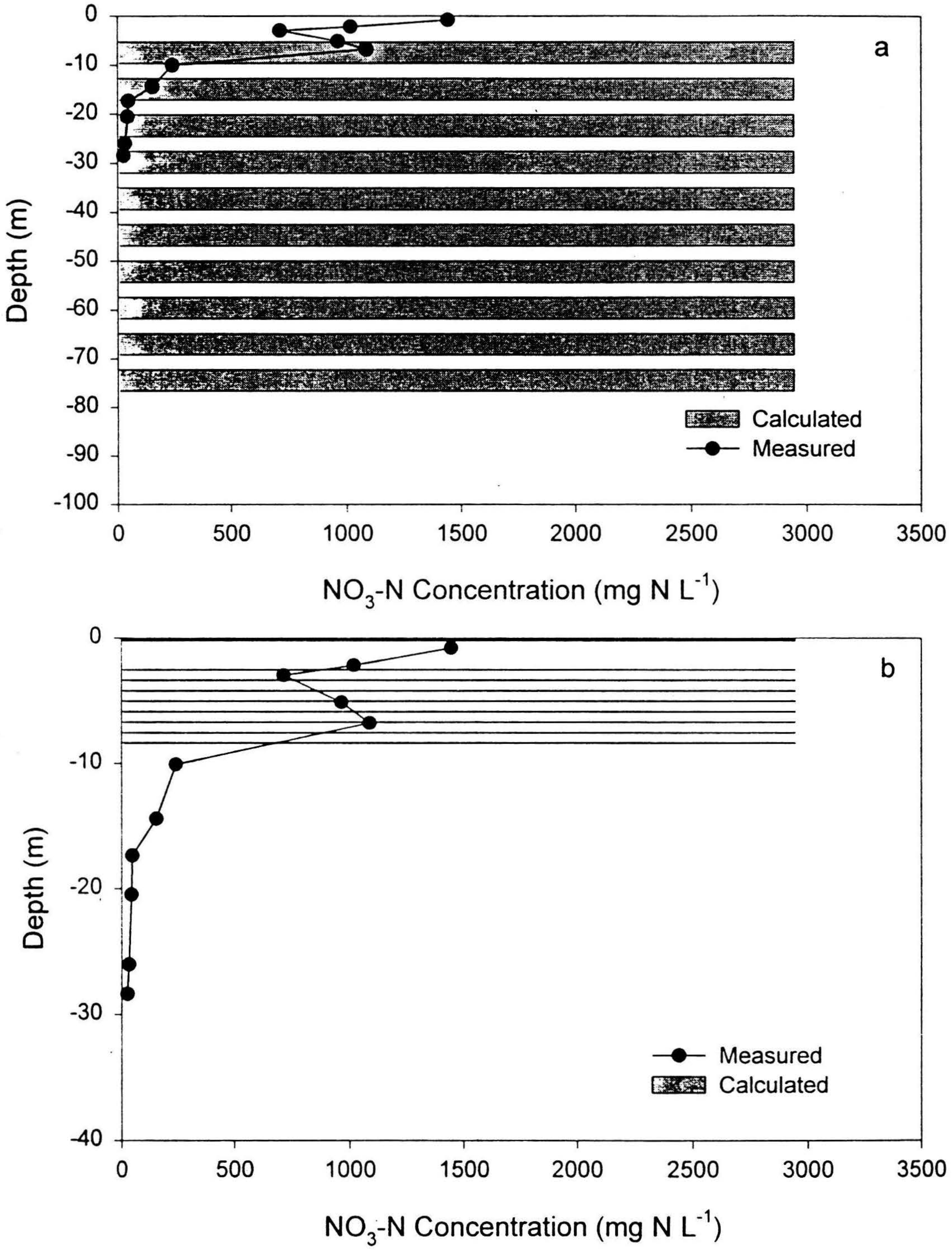


Figure 22. Calculated nitrate movement assuming mass flow (a) and mass flow with adsorption (b) in bore hole 4101.

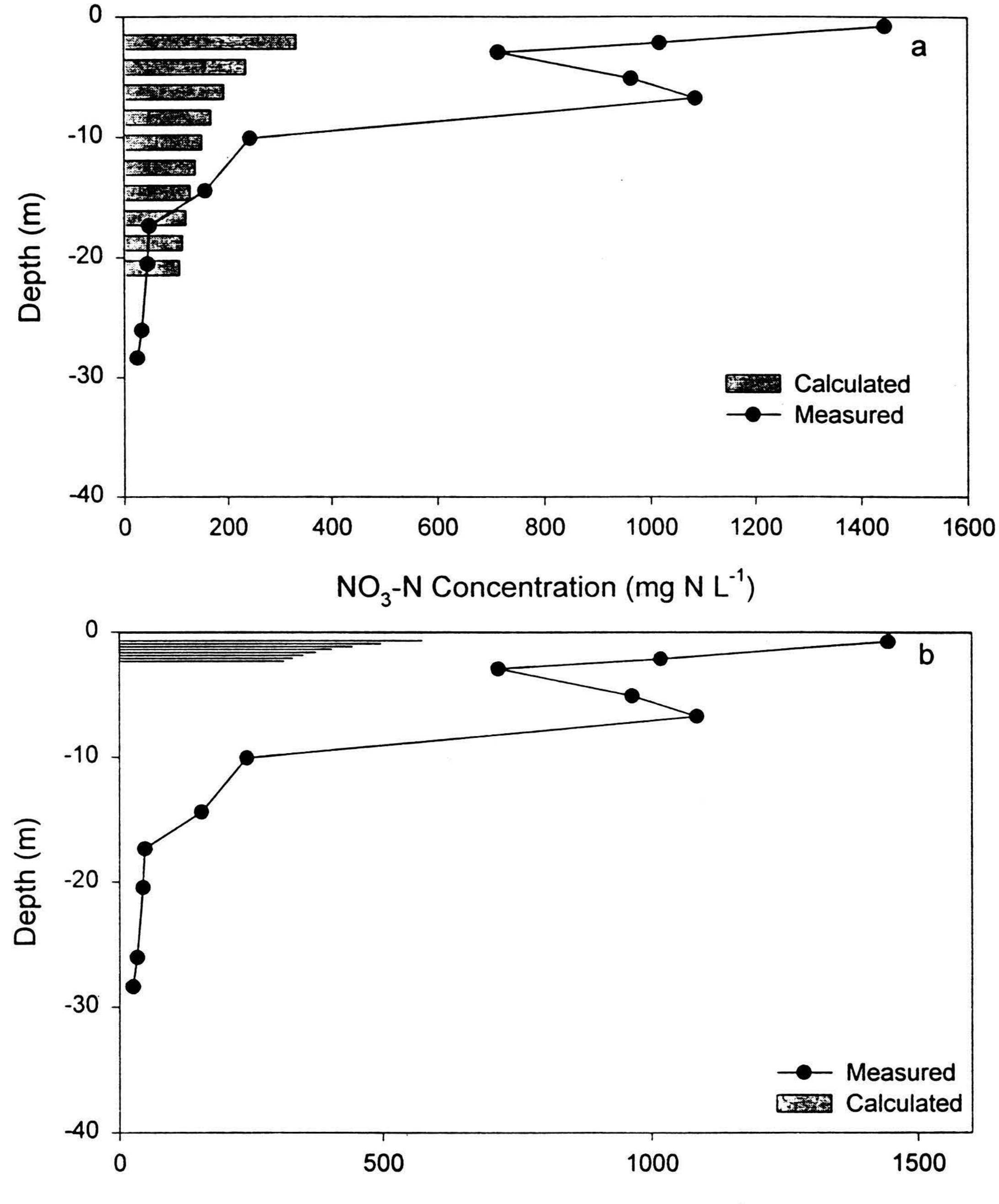
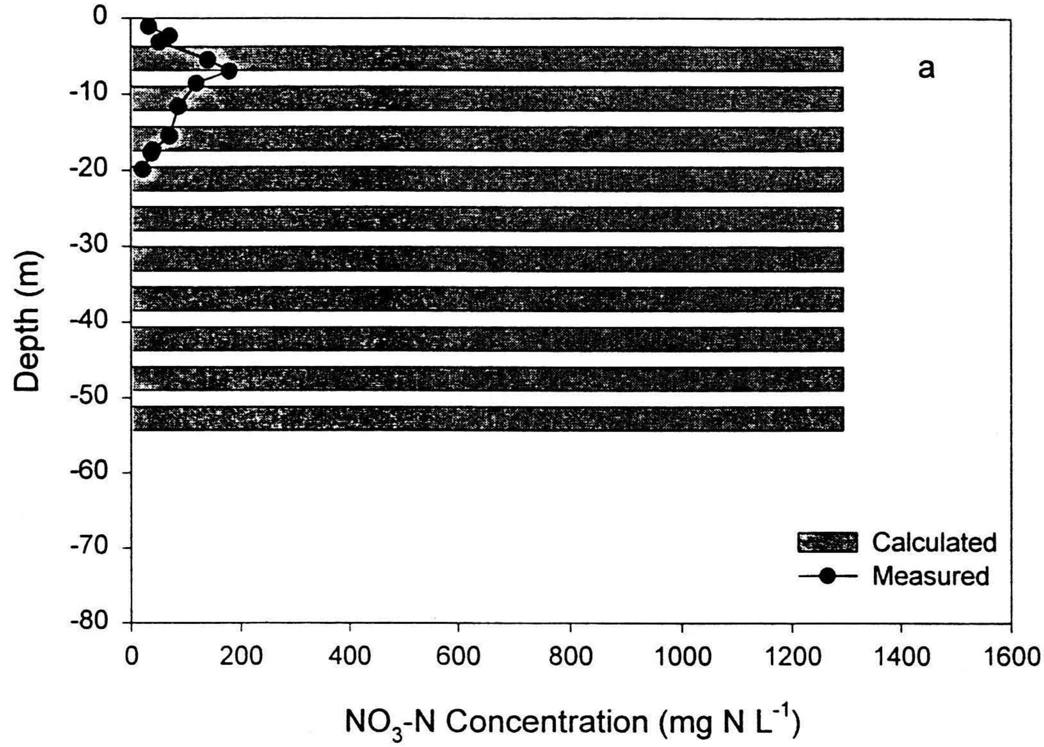


Figure 23. Calculated nitrate movement assuming mass flow and diffusion (a) and mass flow and diffusion with adsorption (b) in bore hole 4101.



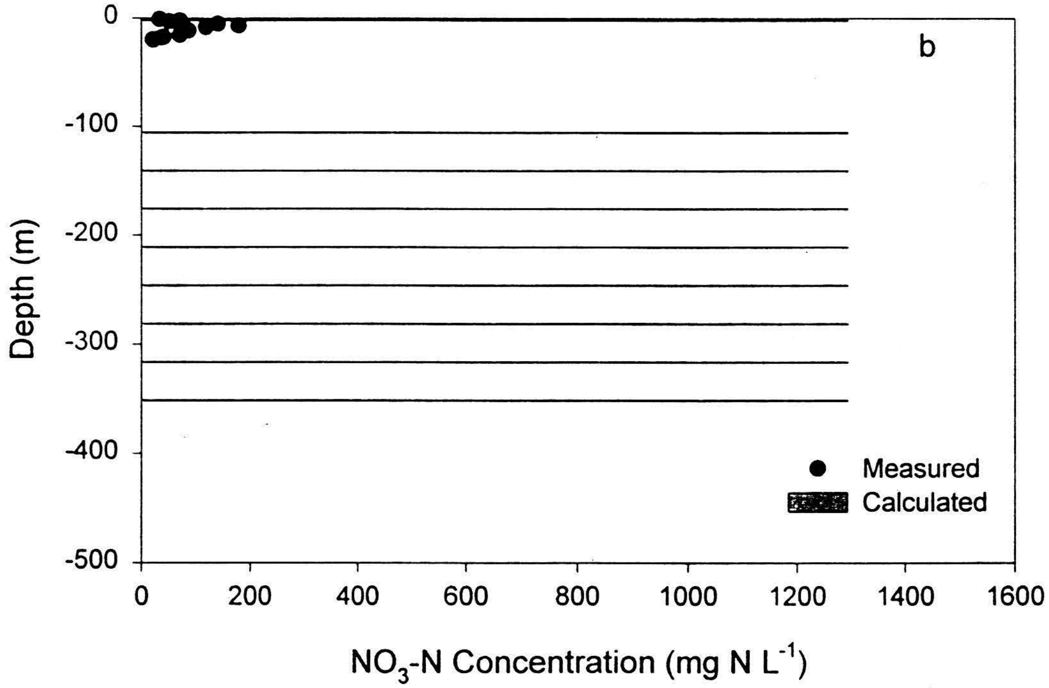
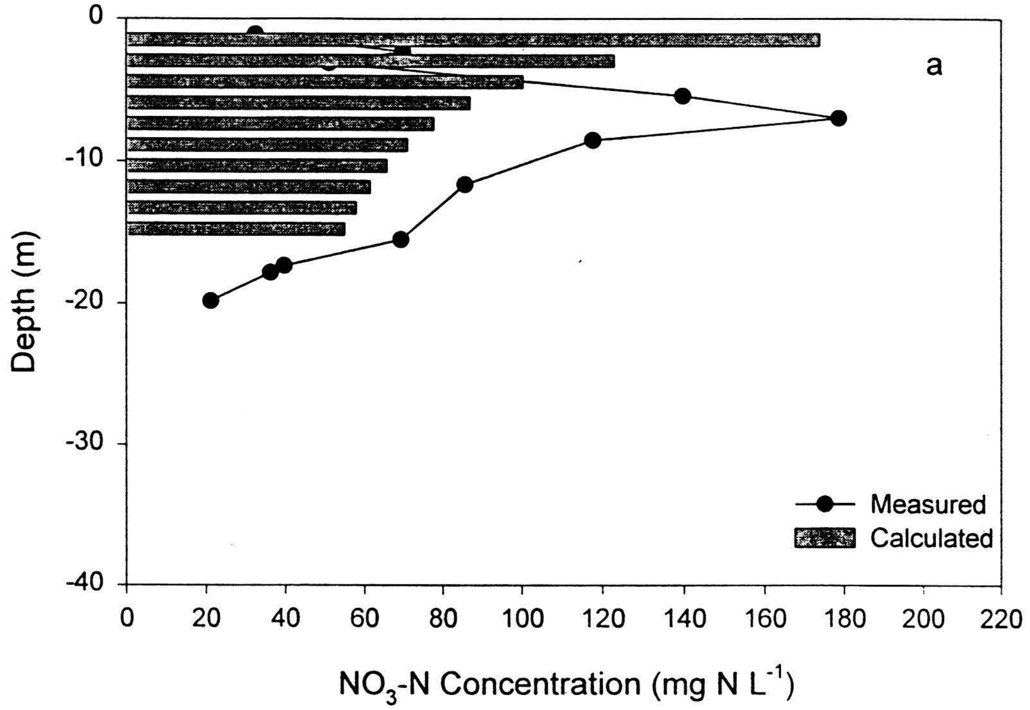


Figure 24. Calculated nitrate movement assuming mass flow (a) and mass flow with adsorption (b) in bore hole 4111.



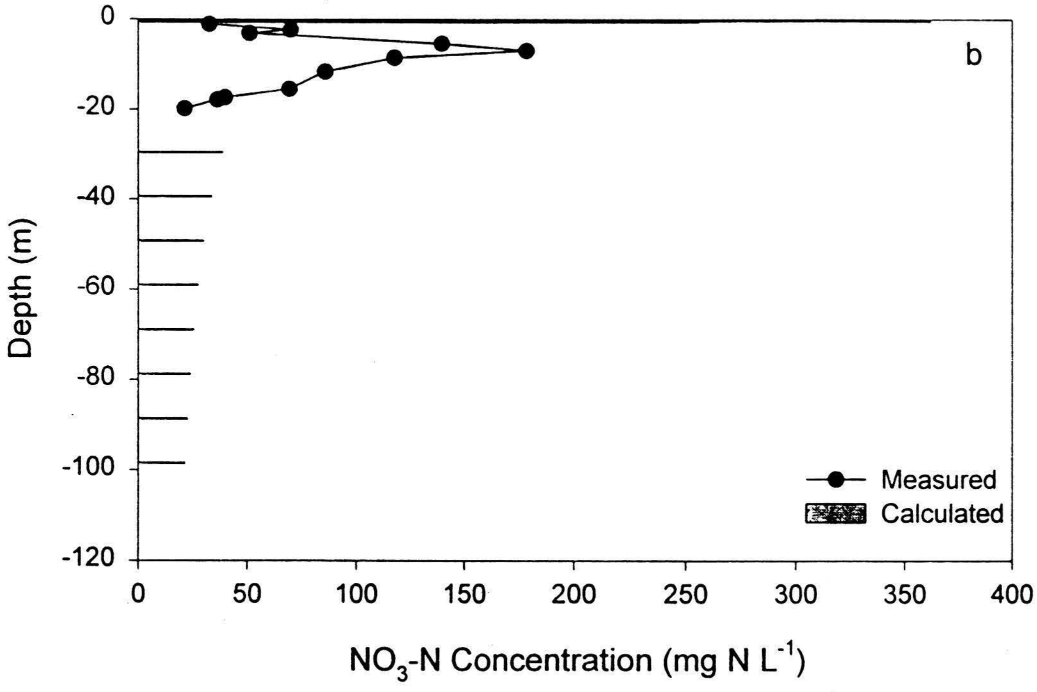


Figure 25. Calculated nitrate movement assuming mass flow and diffusion (a) and mass flow and diffusion with adsorption (b) in bore hole 4111.

Incubation Study

Nitrogen Transformations

Incubating an Ultisol, Oxisol and Inceptisol for 30 days at 26°C at three liming rates increased the nitrogen mineralization and nitrification rates in the surface layer (Figs. 26-28). No nitrogen source was added to samples prior to incubation. In the subsoil treatments, liming did not affect nitrification rates appreciably. Mineralization and nitrification increased significantly in the surface layer of a Vertisol (Fig. 29) that received no lime, while in the subsoil only mineralization of nitrogen increased. In all samples, with the exception of the surface layer treatments for the Inceptisol, a significant increase in NH_4^+ production was observed following the 30 day incubation period in the unlimed treatments. The NH_4^+ concentration increased more than fivefold in the *Leilehua* subsoil treatment that received no lime. The unusually high numbers obtained for NH_4^+ are an artifact of how the soils were prepared for the nitrate adsorption study prior to the measurement of NO_3^- and NH_4^+. The soils were incubated with different liming rates to test the effect of lime on the adsorption of nitrate at increasing pH levels. The first adsorption run used the soil directly from the incubation bags with highly variable results for adsorption. In order to reduce the variation, the soils were dried, crushed, sieved to pass a 20 mesh sieve, wet to field capacity, re-dried, crushed and finally sieved through a 20 mesh sieve. This procedure resulted in a dramatic increase in the mineralization of native organic N and explained the high levels of NH_4^+ found in the incubated samples. When NH_4^+ and NO_3^- were measured in

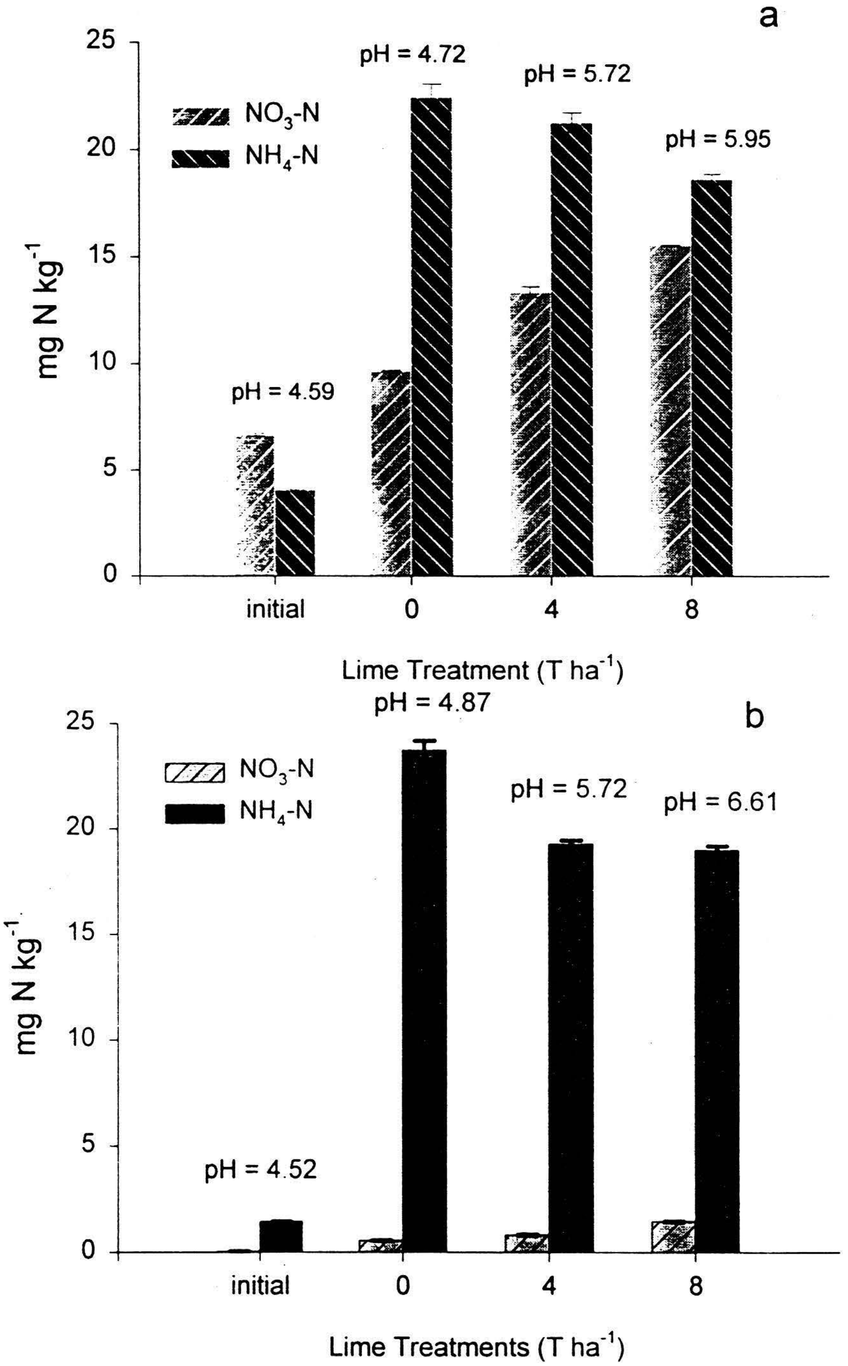


Figure 26. Initial N (first set of bars on each graph) and N mineralization and nitrification in an Ultisol (Leilehua series) after thirty day incubation; (a) represents the surface (0-10 cm) and (b) the subsoil (200-220 cm). Each bar is a mean of 3 replicates and error bars are the standard error.

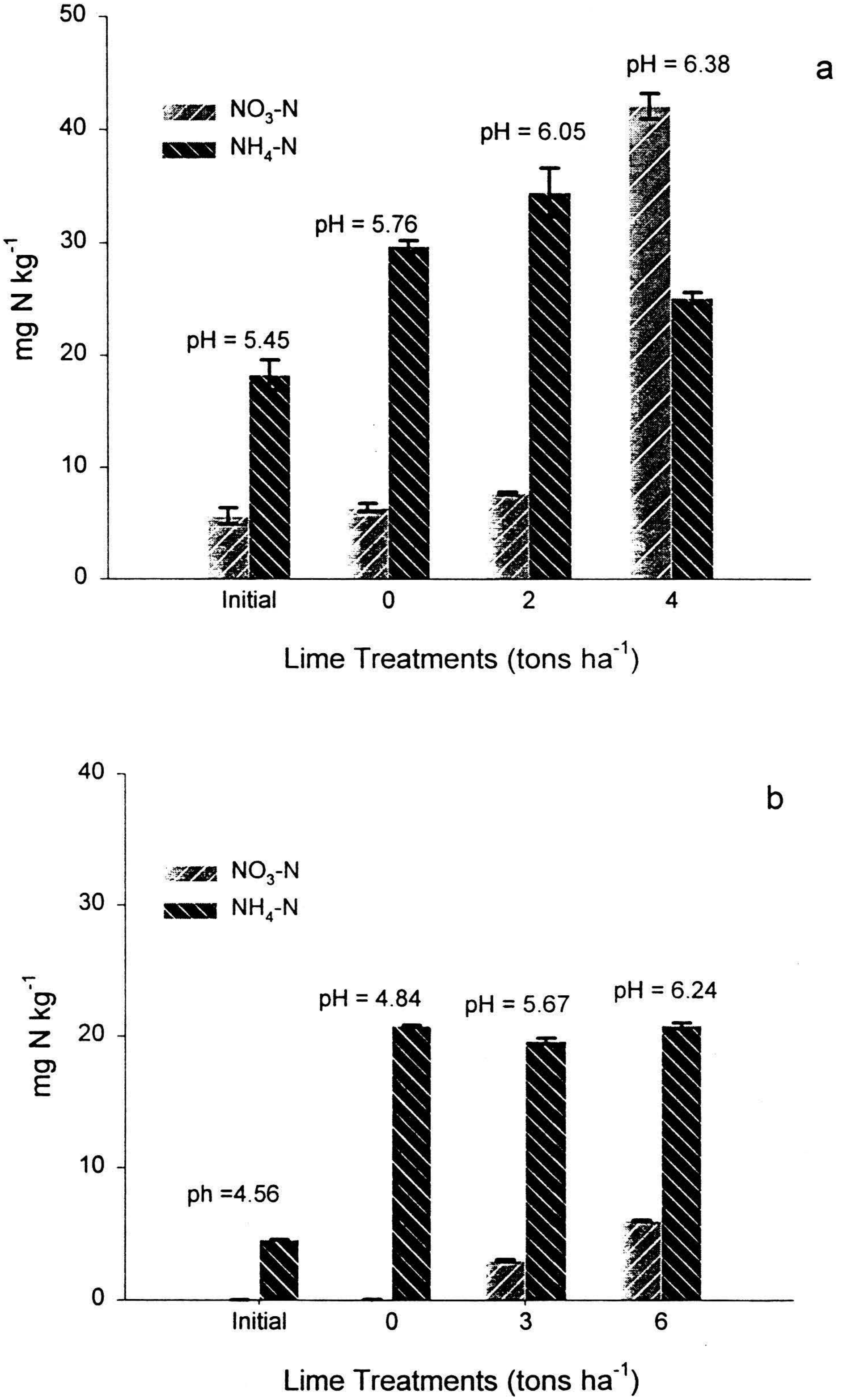


Figure 27. Initial N and N mineralization and nitrification after 30 day incubation in an Oxisol (Wahiawa series); (a) is the surface soil (0-10 cm) and (b) is the subsoil (180-200 cm).

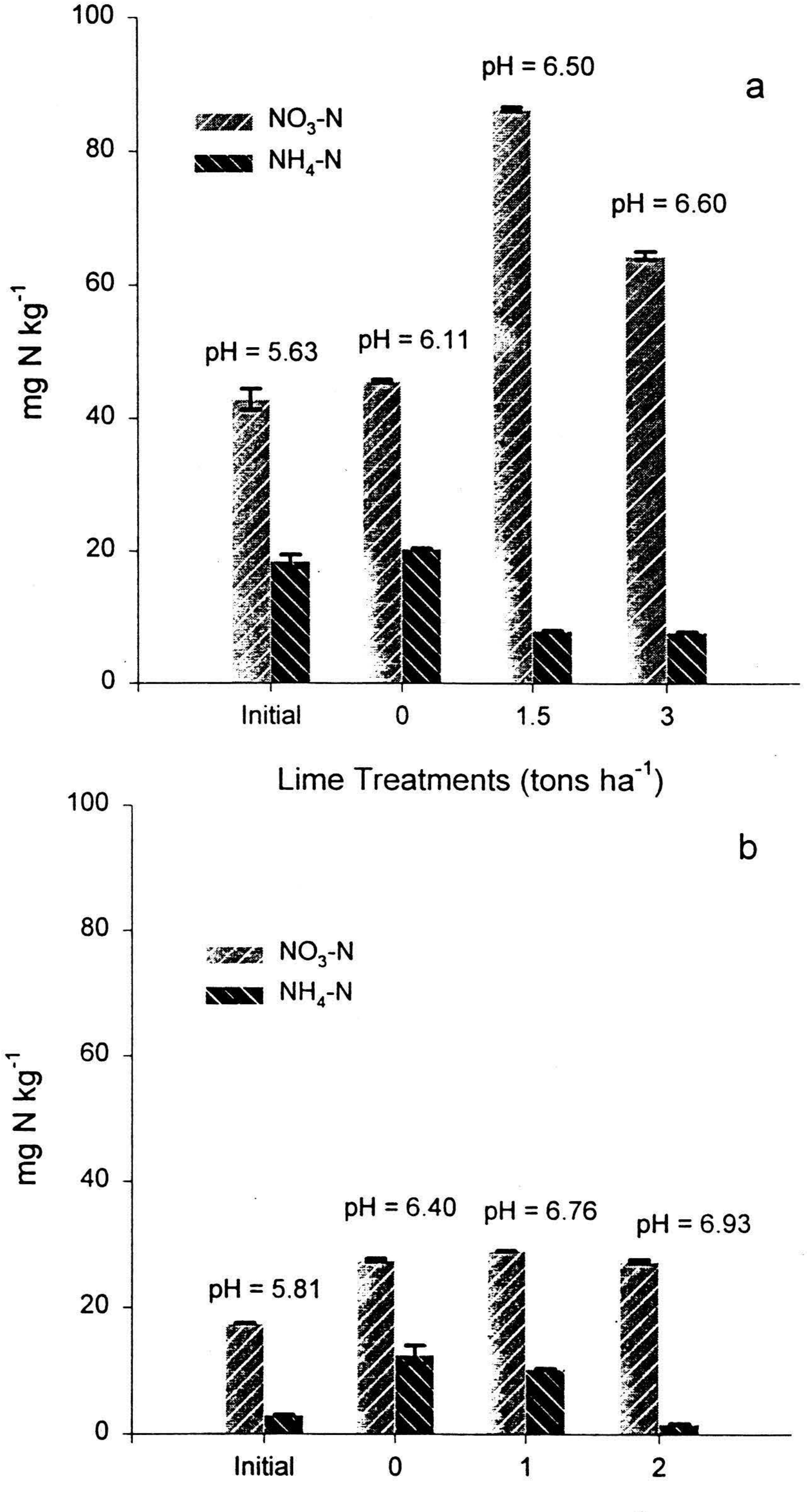


Figure 28. Initial N and N mineralization and nitrification after 30 day incubation in an Inceptisol(Kunia series) after 30 day incubation; (a) represents the surface (0-10 cm) and (b) the subsoil (150-165 cm).

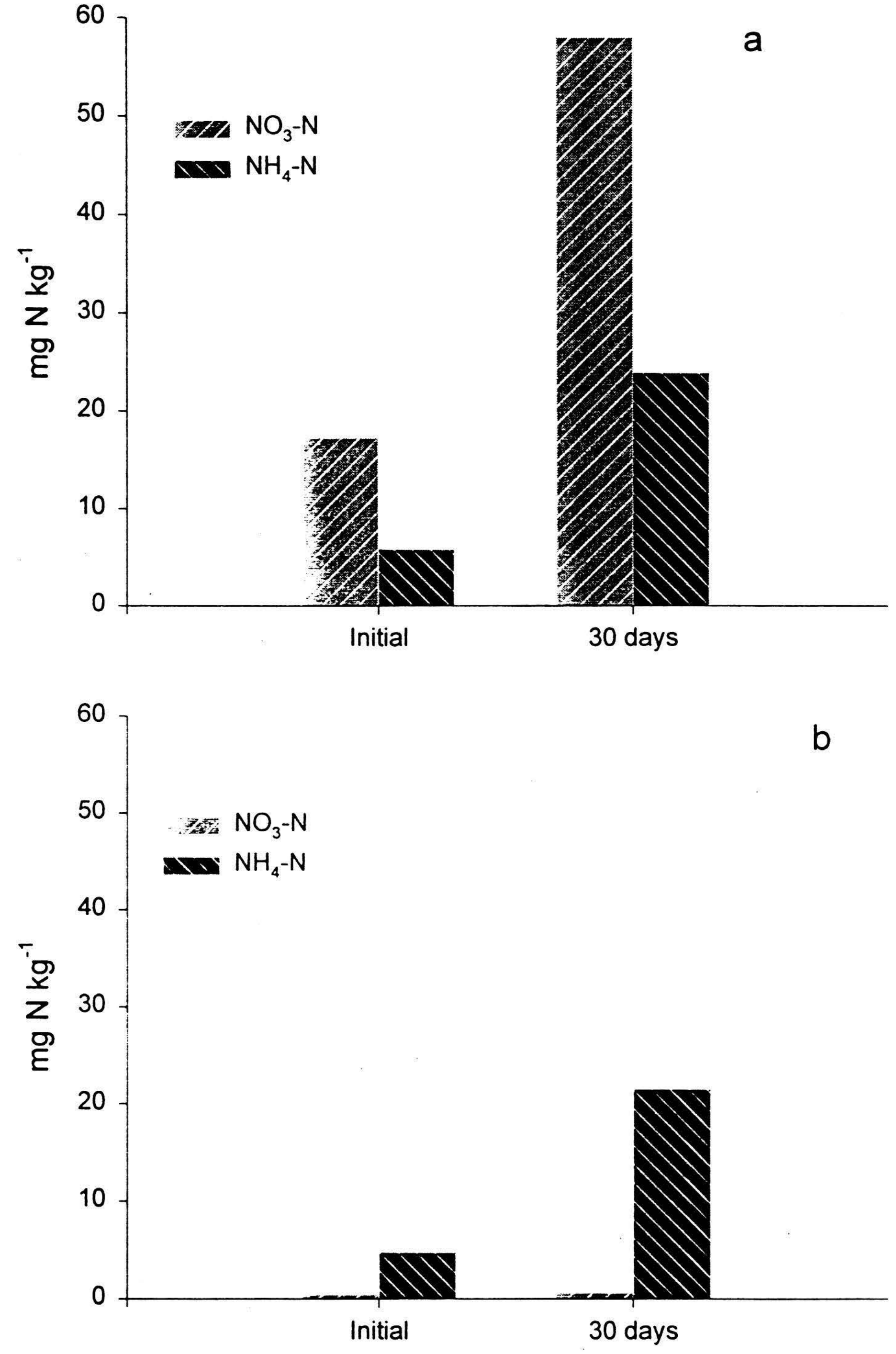


Figure 29. N mineralization and nitrification in a Vertisol (Honouliuli series) in the surface layer (0-10 cm) (a) and the subsoil (200-220 cm) (b) after thirty days incubation.

surface layer of the *Leilehua* soil that did not undergo the sieving process following the incubation period, the changes in NH_4^+ and NO_3^- from the unsieved and sieved samples were considerably smaller (Table 10). The sieving process resulted in a tremendous flush of NH_4^+ in the system - an increase from 1.92 mg NH_4^+-N kg^{-1} in the unsieved sample to 20.91 mg NH_4^+-N kg^{-1} in the sieved sample. When soils are put through a series of wetting and drying cylces in concert with physical disturbances, they often exhibit dramatic increases in mineralized N. This flush in mineral N has been termed the Birch effect.

Table 10. Effect of sieving and drying the *Leilehua* surface sample in preparation for the adsorption study. The unsieved sample had much lower mineralization and nitrification rates.

	Unsieved			Crushed and Sieved		
	NO_3-N	NH_4-N	Sum	NO_3-N	NH_4-N	Sum
			mg N kg^{-1}			
0 Lime	6.01	1.92	7.93	8.99	20.91	29.90
4 tons ha^{-1}	6.27	1.31	7.58	12.55	19.97	32.52
8 tons ha^{-1}	8.23	2.05	10.28	14.68	17.60	32.28

Adding lime to raise the pH of the surface soils increased the nitrification rate in the three soils. Liming the subsoil did not change NO_3^- levels in the subsoil despite significant increases in soil pH. The conversion of NH_4^+ to NO_3^- is a microbial two step process mediated by two forms of autotrophic bacteria. The first step requires the presence of the *Nitrosomonas* species to transform NH_4^+ to NO_2^- and in the second step

Nitrobacter mediates the oxidation of NO_2^- to NO_3^-. The nitrification process is highly dependent upon soil pH. Optimum pH for *Nitrosomonas* and *Nitrobacter* lies between 6.0 and 9.0 and 6.3 and 9.4, respectively (Fenchel and Blackburn, 1979). In acid soils nitrification rates are severely limited. Raising soil pH from 4.7 to 5.9 increased nitrate production by approximately 65% in the surface layer of an Ultisol (Fig. 26). In the surface horizon of an Oxisol, increasing soil pH from 5.8 to 6.4 resulted in a fivefold rise in NO_3^- levels (Fig. 27). Liming nearly doubled the NO_3^- concentrations in an Inceptisol (Fig. 28).

Liming had no significant effect on nitrification rates in the subsoils of all three samples. Since the process is microbially mediated and microbial activity in the subsoil is known to be less vigorous these findings were not surprising.

Adsorption Study

Nitrate adsorption was measured in all five of the soils and their respective treatments following a 30-day amended soil incubation period. The Oxisol, Ultisol and Inceptisol received three lime treatments while the Vertisol and Mollisol were incubated without lime due to high initial soil pH, 8.3 in both cases. Nitrate adsorption was negligible in both the Vertisol and Mollisol samples in both the surface and subsoil (Figs. 30 and 31). In fact, negative adsorption was observed in the Mollisol. These results were expected as the clay fraction of both soils is dominated by smectite which carries a permanent and negative surface charge arising from ion substitution

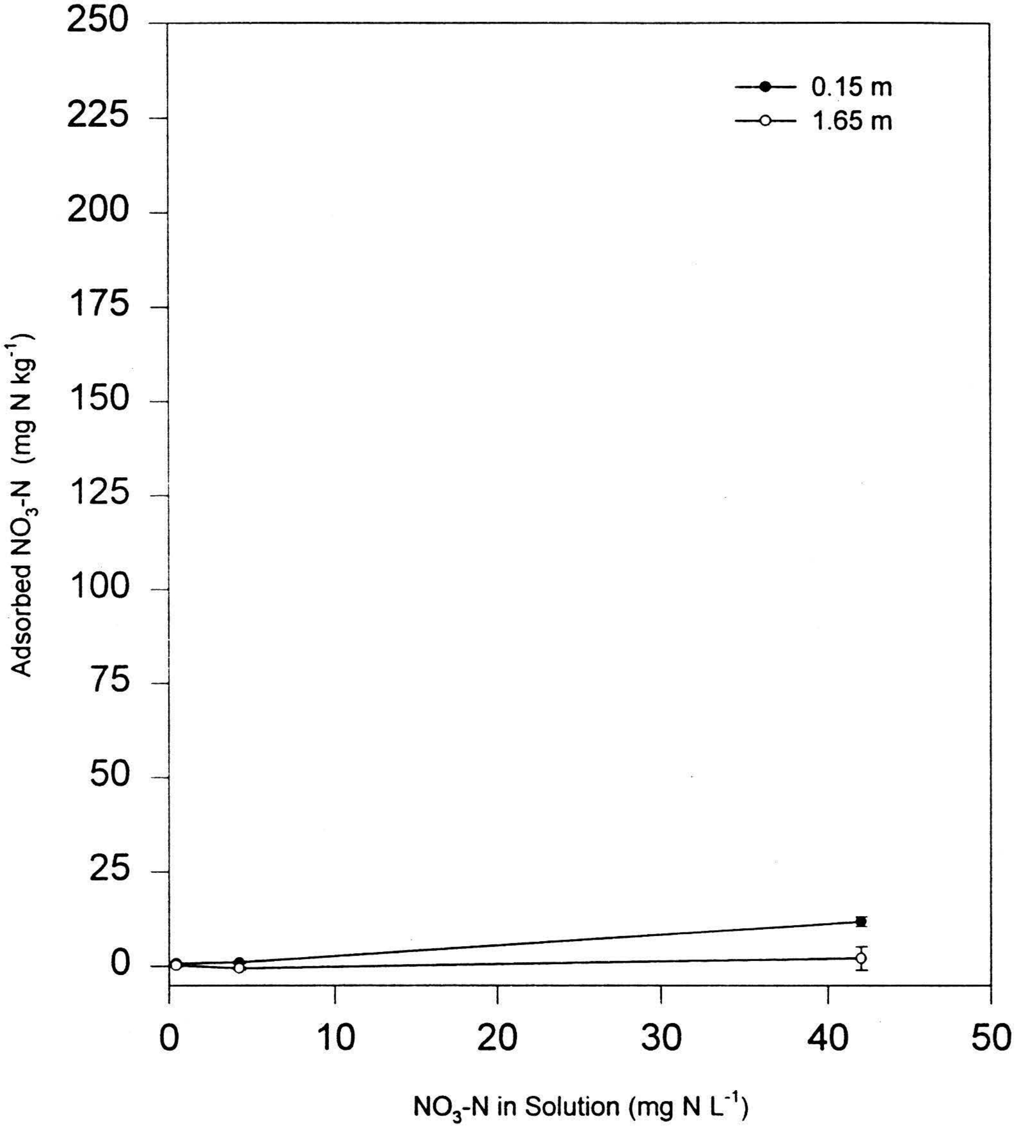


Figure 30. Nitrate adsorption isotherms of surface and subsoil samples from a Vertisol (Honouliuli series).

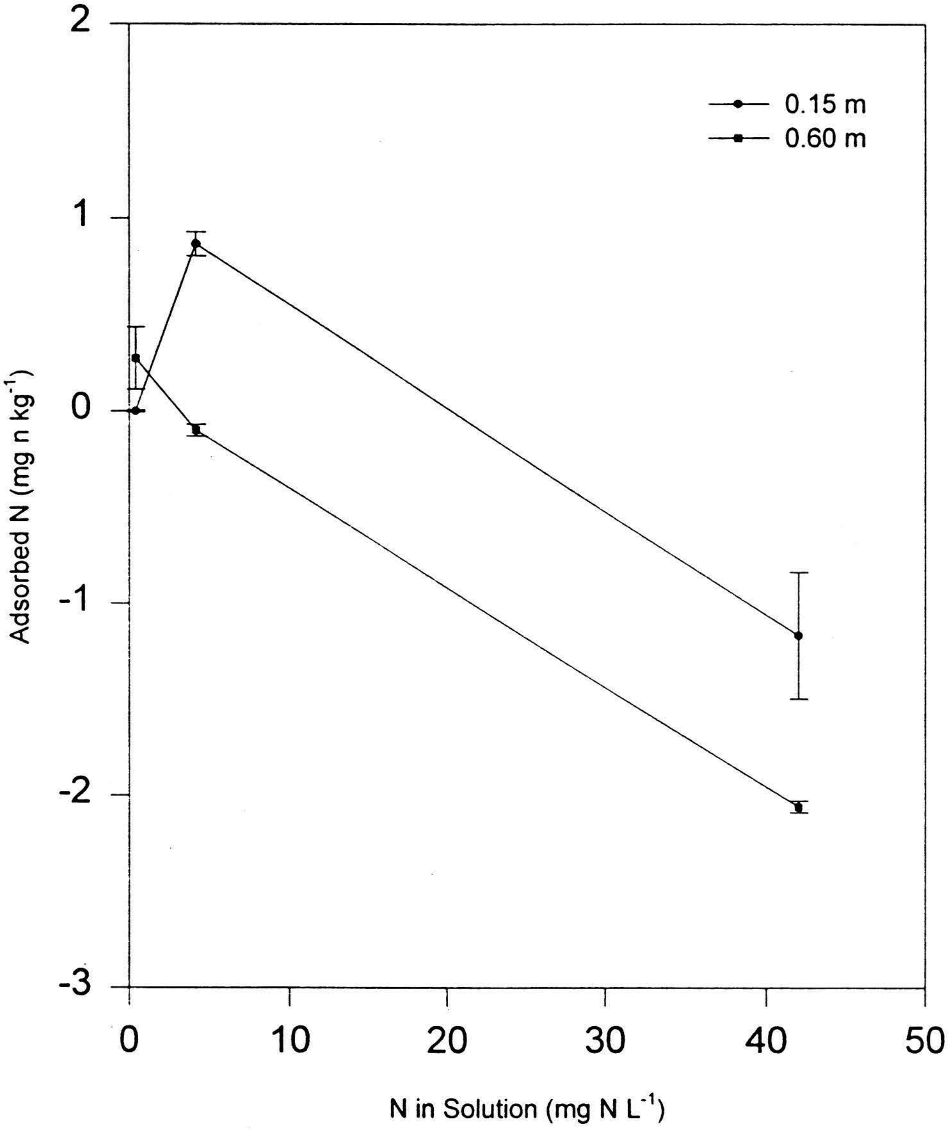


Figure 31. Negative nitrate adsorption isotherms of surface and subsoil samples from a Mollisol (Mamala series).

within the crystal lattice structure. The constant and negative charge associated with the clay particles results in electrostatic repulsion between the nitrate anion moving in the soil solution and the clay surfaces. The charge characteristics of soils of this type are permanent and cannot be altered by management practices.

Nitrate adsorption in the surface layer (0-0.15m) was negligible in the Ultisol and Inceptisol at all three liming levels (Figs. 32 and 33). The surface horizon of most soils often contains significant quantities of organic matter that carries a net negative charge. The tendency of organic matter to coat oxide particles enables even a small quantity of organic matter to have an overriding effect on the surface charge characteristics and therefore the soil acquires a net negative charge regardless its oxide content (Uehara & Gillman, 1981). Organic carbon in the surface layer of the *Leilehua* series is typically higher than in the Oxisol and Inceptisol. Wang (1997) reported 5% organic carbon in the surface layer of a *Leilehua* soil and 2% in a *Wahiawa*. Higher levels of nitrate adsorption were observed in the surface layer of the *Wahiawa* soil (Fig. 32) than in the other four soils and appear to be related to the lower organic carbon content typically associated with this soil series (< 2%) (SCS, 1976). Nevertheless, nitrate adsorption in the *Wahiawa* surface soil is negligible when it is compared with adsorption measured in the subsoil; the adsorption in the surface was approximately eightfold smaller than adsorption in the subsoil.

Nitrate adsorption isotherms for the unlimed subsoil treatments of the Ultisol, Oxisol and Inceptisol (Fig. 35) confirm the hypothesis that the subsoil of weathered

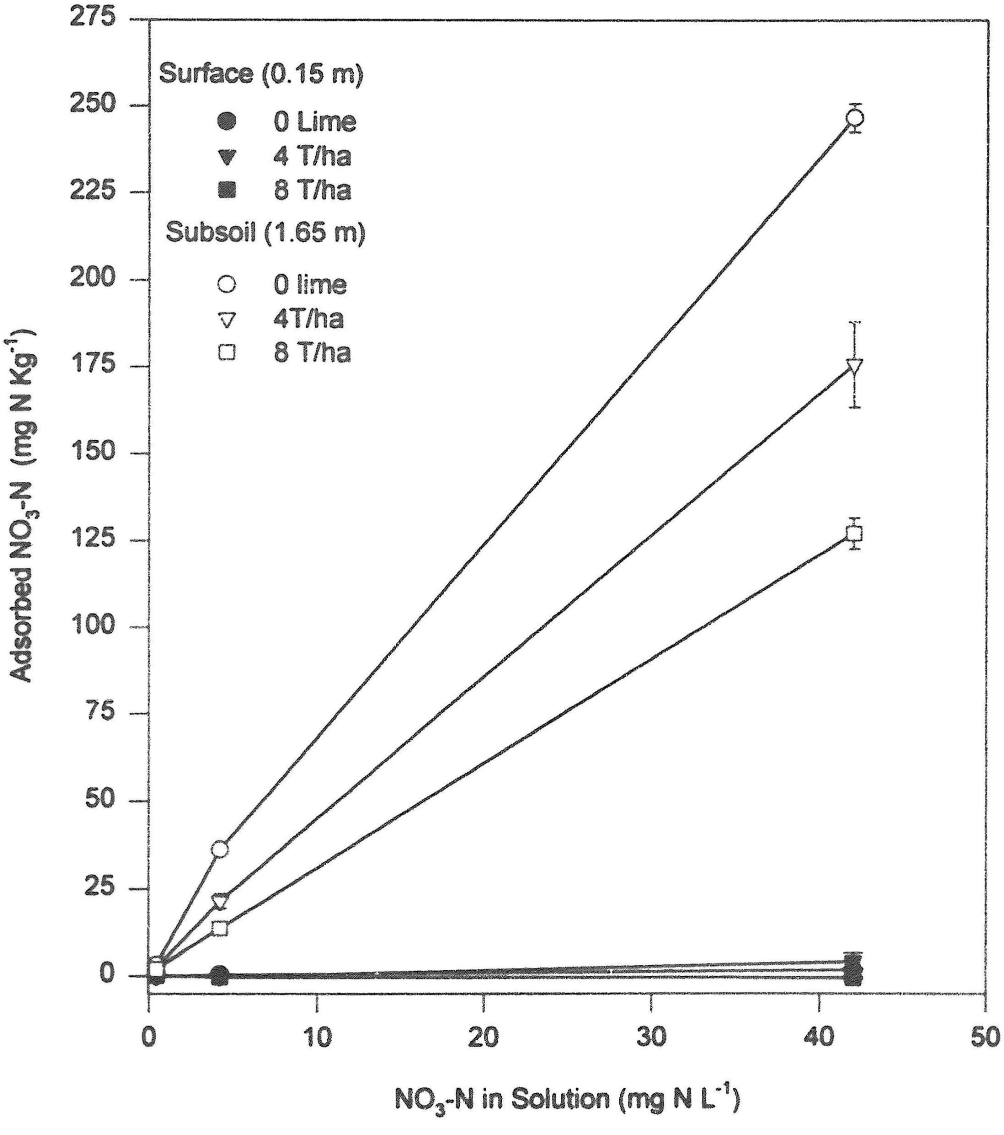


Figure 32. Nitrate adsorption isotherms of surface and subsoil samples from an Ultisol (*Leilehua* series) at three liming rates.

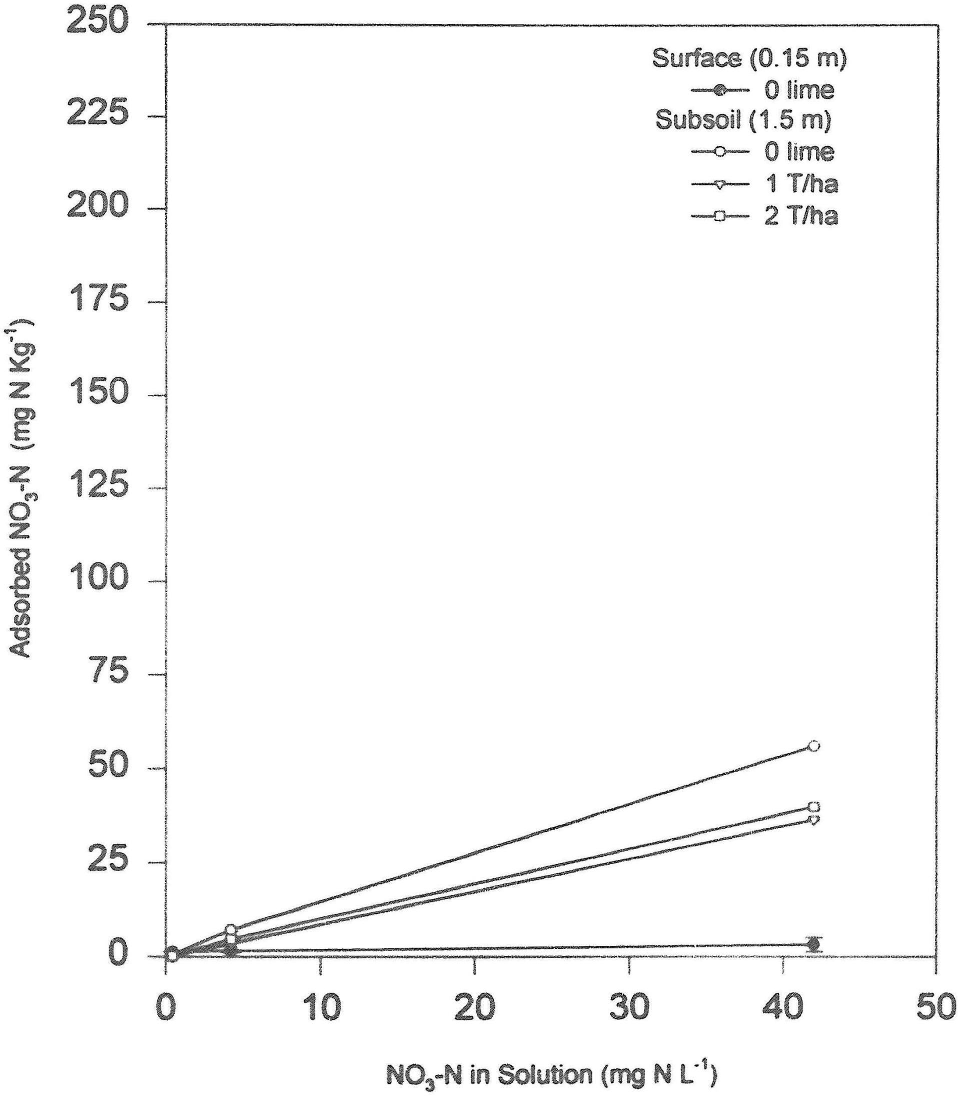


Figure 33. Nitrate adsorption isotherms of surface and subsoil samples from an Inceptisol (*Kunia* series) at three liming rates in the subsoil. Adsorption was not conducted for the limed treatments in the surface layer.

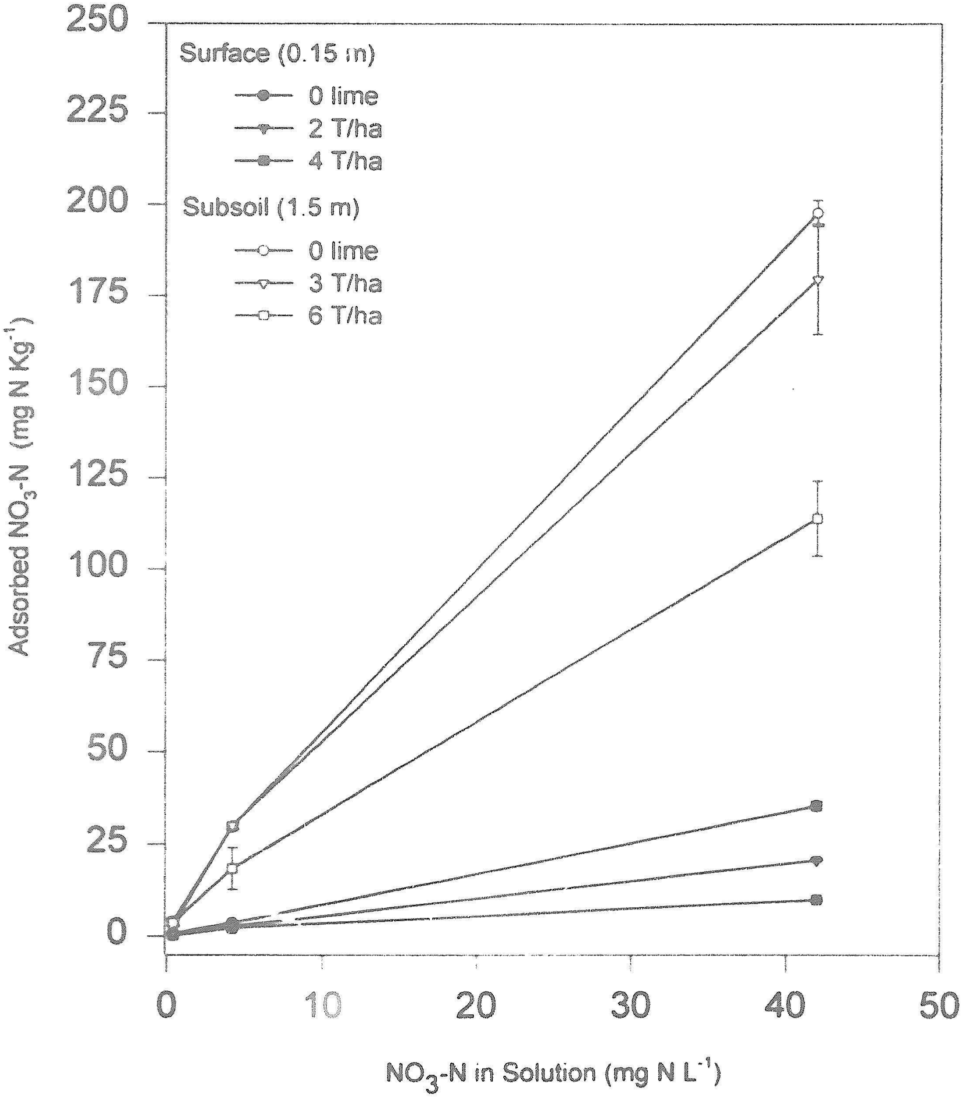


Figure 34. Nitrate adsorption isotherms of surface and subsoil samples from an Oxisol (*Wahiawa* series) at three liming rates.

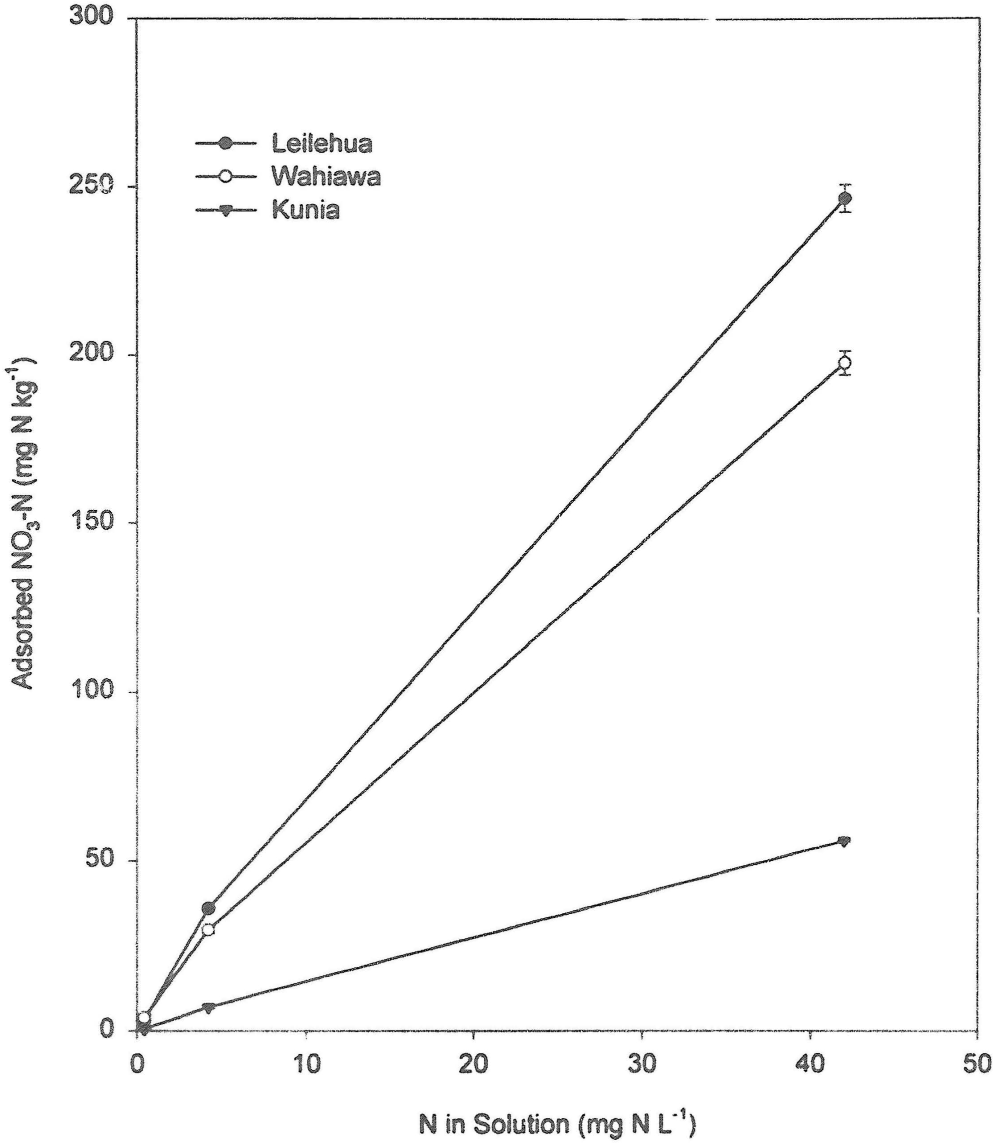


Figure 35. Nitrate adsorption isotherms for the control treatments of three subsoil samples from central Oahu.

oxidic soils commonly found under sugarcane and pineapple cultivation in Hawai'i have a tremendous capacity to adsorb nitrate. In figure 35 one observes the large difference between the *Leilehua* and the *Wahiawa*, both adsorbing large quantities of nitrate, and the *Kunia* soil that exhibits a relatively low adsorption capacity. A comparison of ΔpH measurements for the three soils did not correlate well with the adsorption data (Table 11). Contrary to expected results, the *Kunia* soil had the least negative ΔpH value. These data indicate that ΔpH is not a reliable predictor of AEC and nitrate adsorption. The pH values in water or in KCl, however, correlate well with the adsorption data. The highest adsorption occurred in the *Leilehua* soil which was the most acidic.

Table 11. ΔpH in soils collected from the field at a depth of 1.65 m. $\Delta pH = pH_{KCl} - pH_{H2O}$

Soil	pH (H_2O, 1:5)	pH (1 *M* KCl, 1:5)	ΔpH
Oxisol, *Wahiawa*	4.84	4.31	-0.53
Ultisol, *Leilehua*	4.87	4.24	-0.63
Inceptisol, *Kunia*	6.40	6.11	-0.29

Nitrate adsorption in the unlimed subsoils of the *Leilehua* and *Wahiawa* in the present study are very high. In both subsoils the clay content is high and the mineralogy is dominated by oxides of aluminum and iron for which surface charge is pH dependent. Mineralogical analysis of the crystalline portion of the clay fraction of the *Leilehua* soil found 46% kaolinite, 15% hematite, 2% magnetite and 2% gibbsite. The surface charge characteristics of these minerals are dependent upon the soil pH and where it falls in relation to their isoelectric point (pH_0), or the point at which the surface charge is net zero. While the isoelectric point of kaolin-oxide mixtures is usually less than 5, the relatively large fraction of hematite with pH_0 between 7 and 9 would carry a significant amount of positive charge at the ambient pH of 4.9. In both subsoils pH was well below 7 and the high nitrate adsorption correlates well with the presence of increasing positive charge as pH decreases.

Anion exchange has also been associated with amorphous materials. In a series of experiments, Mattson (1927, 1928) demonstrated that synthetic gels with a low silica-sesquioxide ratio had high anion exchange capacities when the ambient pH was below the isoelectric point. The Oxisols and Ultisols in Hawai‘i have undergone a great deal of weathering resulting in low silica-sesquioxide ratios. Nitrate adsorption studies in Latin America (Kinjo and Pratt, 1971; Reynolds-Vargas et al, 1994) and Hawai‘i (Singh and Kanehiro, 1969) reported a high correlation between nitrate adsorption and the amorphous fraction of the soil. Kinjo and Pratt (1971) reported much higher adsorption capacity in two volcanic ash soils in a comparative nitrate adsorption study between volcanic ash soils high in amorphous material (20-50%) and an Oxisol containing 10 to 20% amorphous material. The *Leilehua* soil in the present study contained 35% amorphous material and the large amorphous fraction may partly explain the high adsorption values. Electron micrographs of soils from Hawai‘i high in amorphous material of low silica-sesquioxide ratios reveal that these materials coat the crystalline particles and increase the specific surface significantly (Jones and Uehara, 1973). Anion exchange capacity (AEC) is a function of both specific surface and surface charge density. Therefore, one should expect high AEC in acidic soils with a substantial amorphous fraction and variable charge minerals.

Increasing lime levels in the subsoil of the Ultisol, Oxisol, and Inceptisol reduced the nitrate adsorption capacity of these soils (Figs. 32-34). In all three cases, nitrate adsorption at the highest nitrate equilibration concentration was reduced by approximately one half at the highest liming level. Increasing soil pH from 4.5 to 6.6 in the Ultisol lowered adsorption from approximately 250 mg NO_3-N kg^{-1} to 125 mg NO_3-N kg^{-1}. Similarly, adsorption in the Oxisol dropped from around 200 mg NO_3-N kg^{-1} at a pH of 4.6 to just over 100 mg NO_3-N kg^{-1} when the pH increased to 6.2. The lime effect was less dramatic in the Inceptisol presumably due to its lower initial adsorption capacity. Adsorption decreased from about 55 mg NO_3-N kg^{-1} to 38 mg NO_3-N kg^{-1} when pH was raised from 5.8 to 6.9. Nitrate adsorption exhibited a strong inverse relationship with soil pH (Fig. 36). The correlation was stronger when the nitrate equilibrating solution was of higher concentration. The correlation decreased at the lowest concentration due to lower precision in the method at the low nitrate concentration. Kinjo and Pratt (1971) showed how nitrate adsorption increases when the soil pH is lowered. These data look at the other end of the spectrum and illustrate how raising soil pH decreases the soil's capacity to adsorb nitrate.

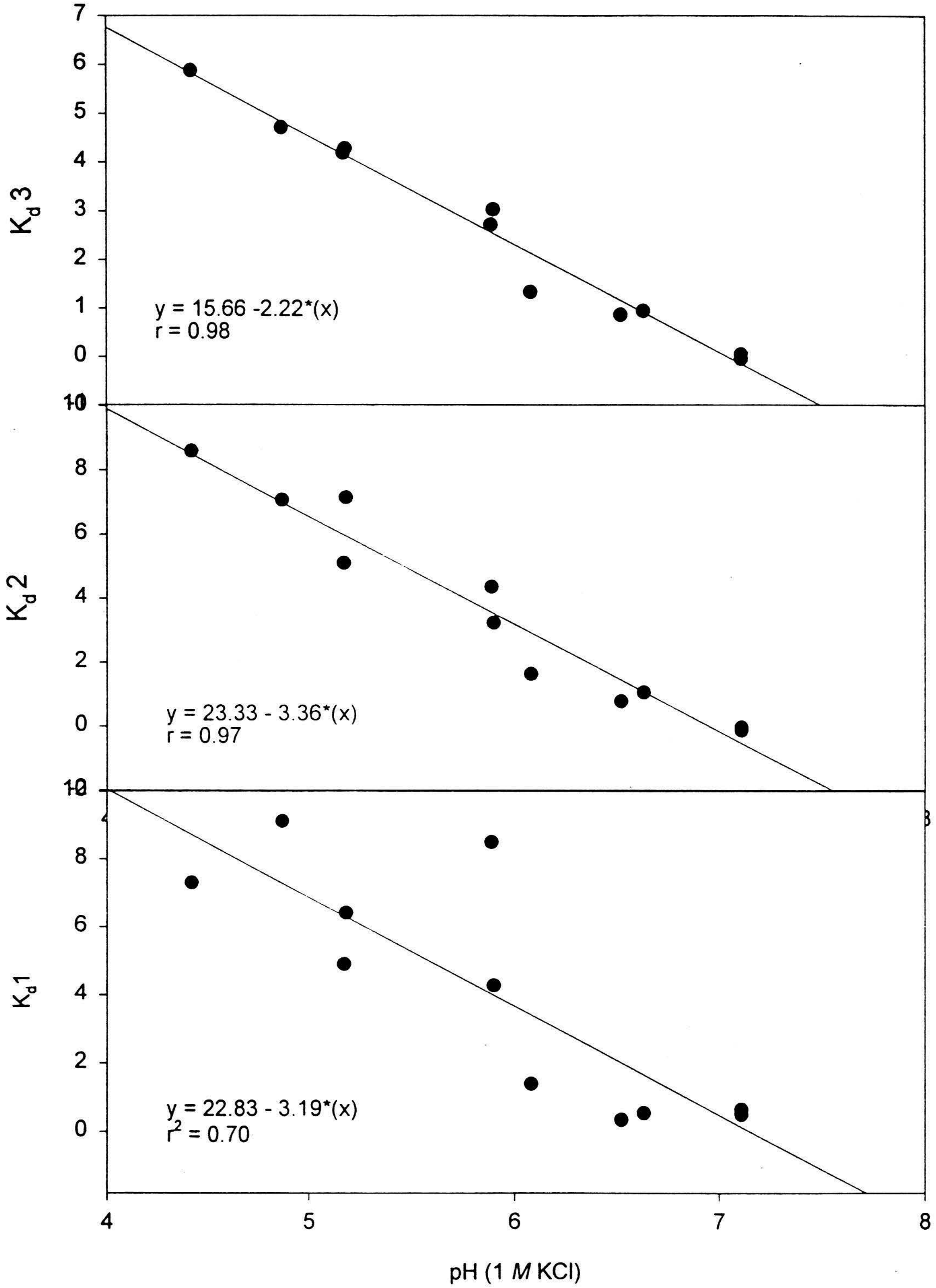


Figure 36. The relationship between nitrate adsorption (expressed as K_d = mg N kg^{-1}/mg N L^{-1}) and increasing pH; where equilibrating solution for K_d 3 is 42 mg N L^{-1}, 4.2 mg N L^{-1} for K_d 2 and 0.42 mg N L^{-1} for K_d1.

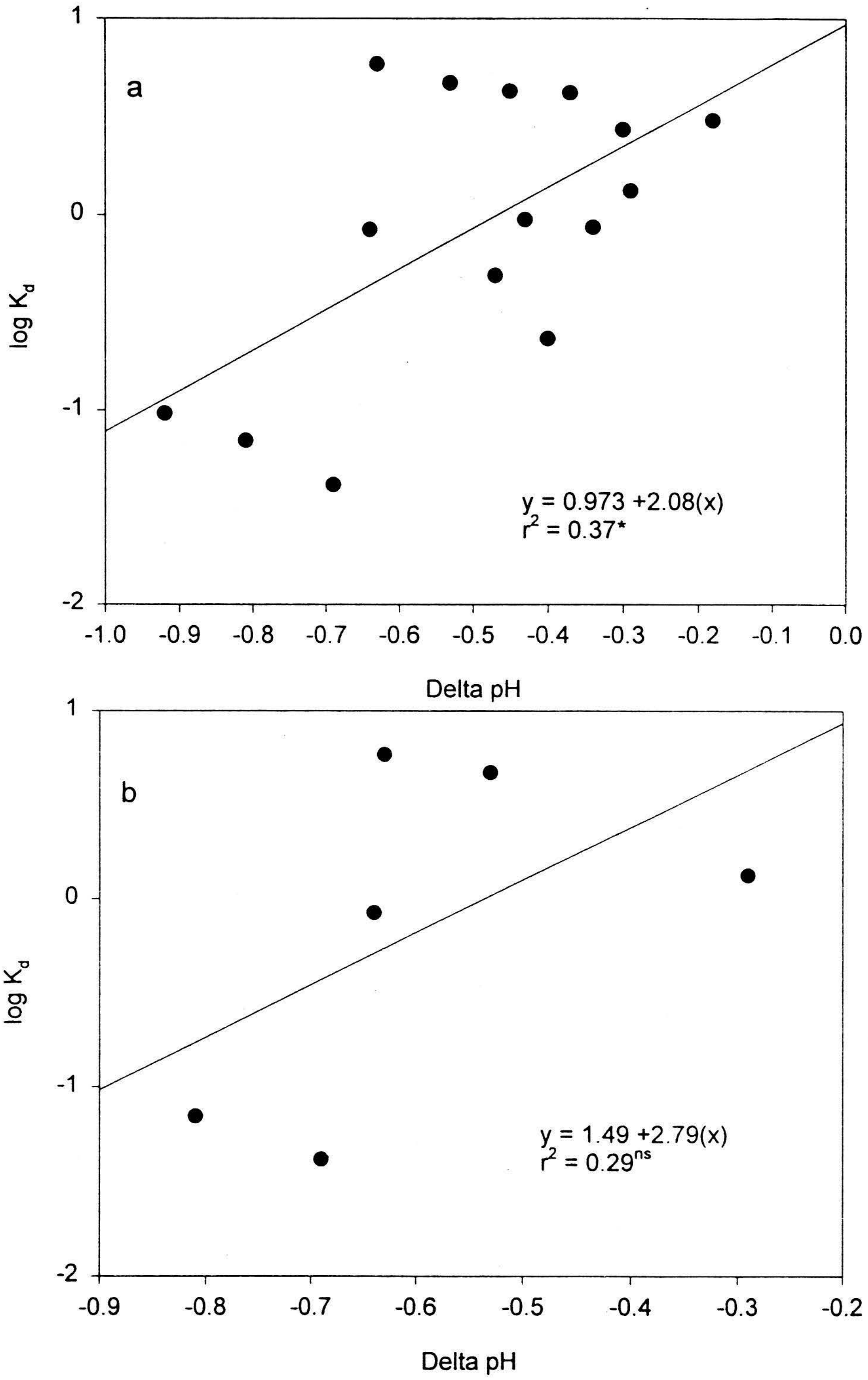


Figure 37. Nitrate adsorption expressed as log K_d (where K_d = sorbed N/N in solution) in relation to delta pH for all treatments (a)(* denotes significance at $P < 0.05$) and for the unlimed treatments (b). ns following r^2 term in b not significant at $P < 0.05$.

ΔpH has been proposed as a simple and quick method to determine the sign of the surface charge in soils containing variable charge minerals (Mekaru and Uehara, 1972). Correlating ΔpH with nitrate adsorption in variable charge soils is an attractive alternative since it could be used to predict adsorption capacity in lieu of running a more expensive and time consuming adsorption study. Nitrate adsorption studies conducted on some highly weathered soils from Southeast Queensland, Australia found that ΔpH was highly correlated with nitrate adsorption in soils with uniform mineralogical properties, but when used for a wider range of soils the relationship became weaker (Black and Waring, 1976b; Black and Waring, 1979). The relationship between ΔpH and nitrate adsorption capacity for all the treatments and the unlimed soils used in this study is shown in Fig. 37. When the entire data set is used there is a significant positive relationship between ΔpH and the log of K_d (K_d is adsorbed nitrate/nitrate in solution at the highest concentration). While the relationship is statistically significant at the 95% level, the distribution of points indicates that the relationship is weak. Based upon these findings, the use of ΔpH as a reliable indicator for nitrate adsorption capacity is unadvisable.

Mathematical Models

A variety of mathematical models have been developed to describe the shape of nitrate isotherms. The Freundlich isotherm is commonly used in the literature to describe the relationship between nitrate adsorbed on the soil surface and nitrate in the soil solution (Singh and Kanehiro, 1969; Cahn et al, 1992; Kinjo and Pratt, 1972a), and has the form

$$X = aS^{b} \qquad (1)$$

where X is amount of nitrate adsorbed per unit weight of soil (mg N kg^{-1}) and S is the concentration of nitrate in solution (mg N L^{-1}). In the linear form, equation 2 becomes

$$\log X = \log a + b \log S \qquad (2)$$

where a and b are parameters developed to fit the experimental data. This equation permits the prediction of sorbed nitrate given the concentration of the equilibrating solution.

Nitrate adsorption is also a function of the surface charge density (σ) associated with clay minerals. This relationship can be described by the Gouy-Chapman equation discussed earlier. This equation shows that the surface charge density on the particle surface is proportional to the square root of the concentration of the equilibrating solution. Assuming the expression to the right of the square root sign is constant and $\sigma = Y/A$ where Y is adsorbed nitrate in mg kg^{-1} and A is the specific surface in $cm^2\ kg^{-1}$, then the Gouy-Chapman equation can be rewritten as

$$Y = A(2\epsilon kT/\pi)^{1/2}(n)^{1/2} \qquad (3)$$

Taking the log of both sides results in

$$\log Y = \log A + 1/2 \log(2\epsilon kT/\pi) + ½ \log n \qquad (4)$$

Equation 4 is a linear expression where $\log A + 1/2\log(2\epsilon kT/\pi)$ is the y-intercept and ½ is the slope. Since the $\epsilon kT/\pi$ term is composed of constants that can be looked up in textbooks, the specific surface of the soil can be determined from the Y-intercept by difference.

Nitrate adsorption in soils can also be described by a linear function with the form,

$$X = K_d S \tag{5}$$

where X is the amount of nitrate adsorbed (mg N kg^{-1}), S is the concentration of the equilibrating solution (mg N L^{-1}) and K_d, the slope of the isotherm, is called the distribution coefficient. If the assumption that adsorption in soils is linear at all times, the K_d is an extremely important parameter that can be used to describe the mobility of the adsorbate (Jury et al, 1991). As values for K_d increase, the mobility of the solute decreases proportionately.

The data from the present adsorption study were plotted according to the three models. Regression analysis was performed on each model in order to determine the "goodness" of the fit. In all three of the soils the three models fit the data well with r^2 values either 1.00 or very close to 1.00 (Figs. 38-40). High r^2 values for the linear model in all three soils permits the use of K_d (the slope of the line) as a valid parameter for comparing adsorption between soils and also as a measure of nitrate mobility in the soil. The use of K_d will be employed to predict nitrate mobility in the column experiment of this study.

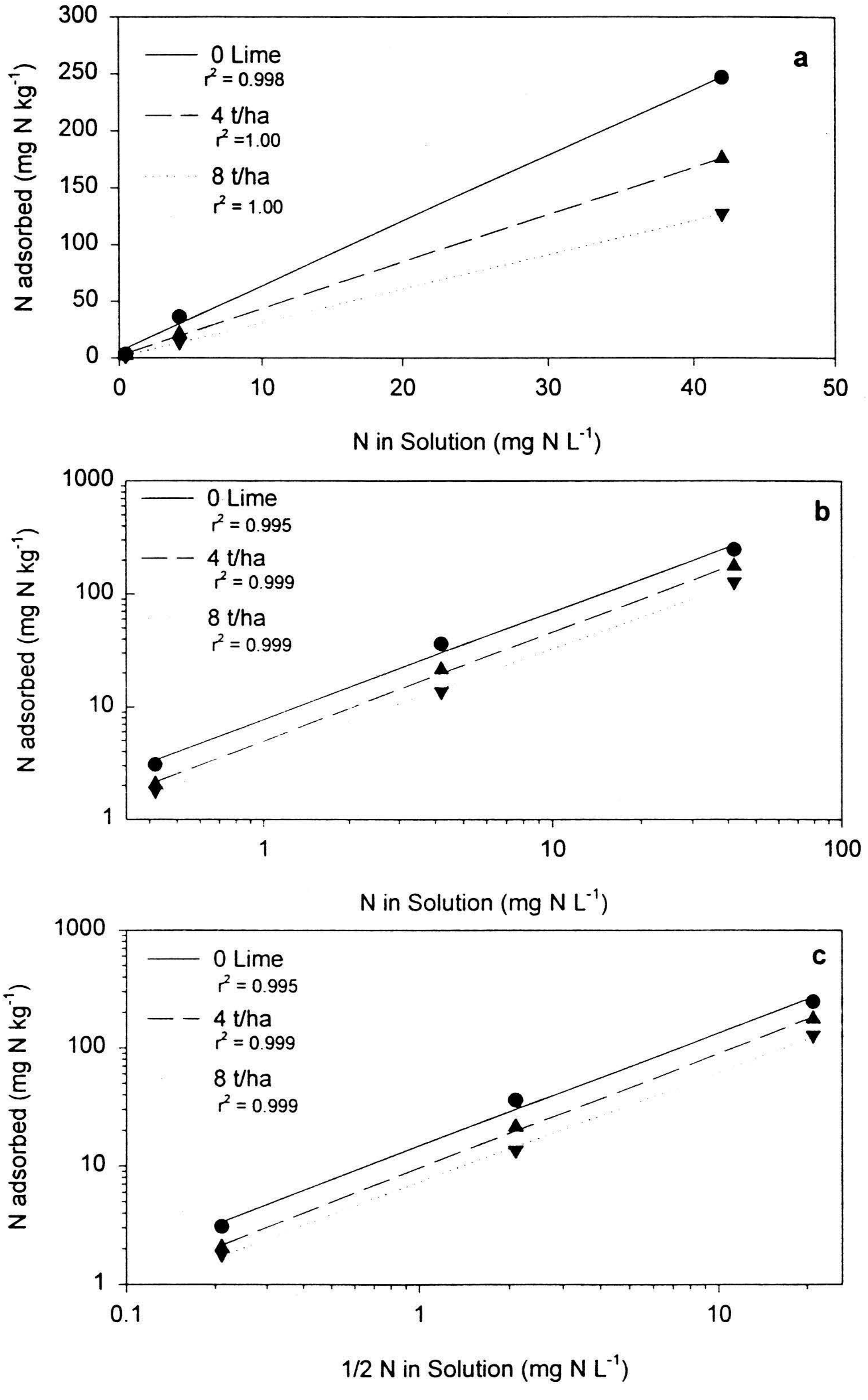


Figure 38. Nitrate adsorption data for Leilehua subsoil according to three models: (a) linear model, (b) linear form of the Freundlich model, and (c) the linear form of the Gouy-Chapman model.

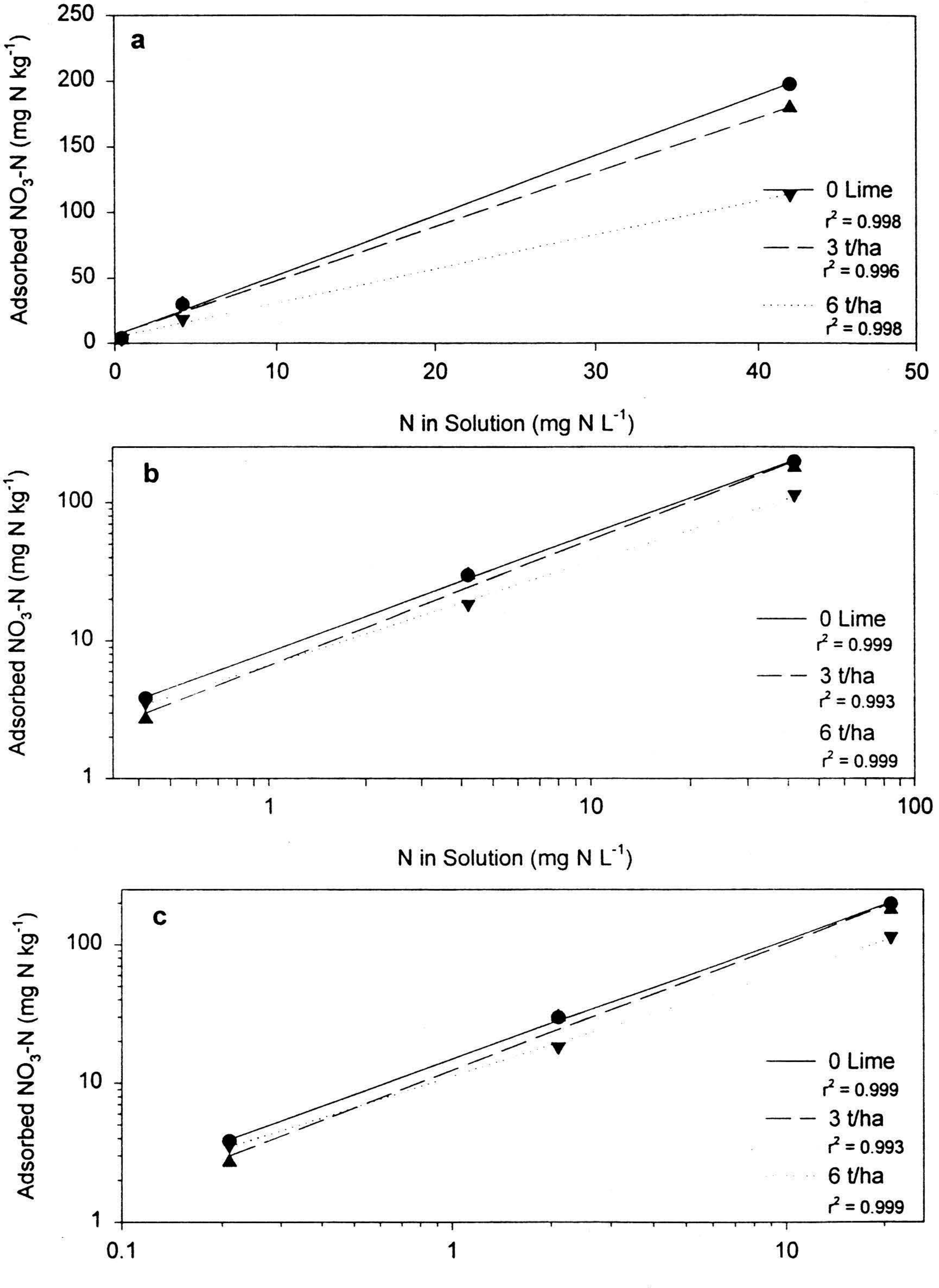


Figure 39. Nitrate adsorption data for the Wahiawa subsoil according to three models: (a) linear, (b) linear form of the Freundlich model, and (c) the linear form of the Gouy-Chapman model.

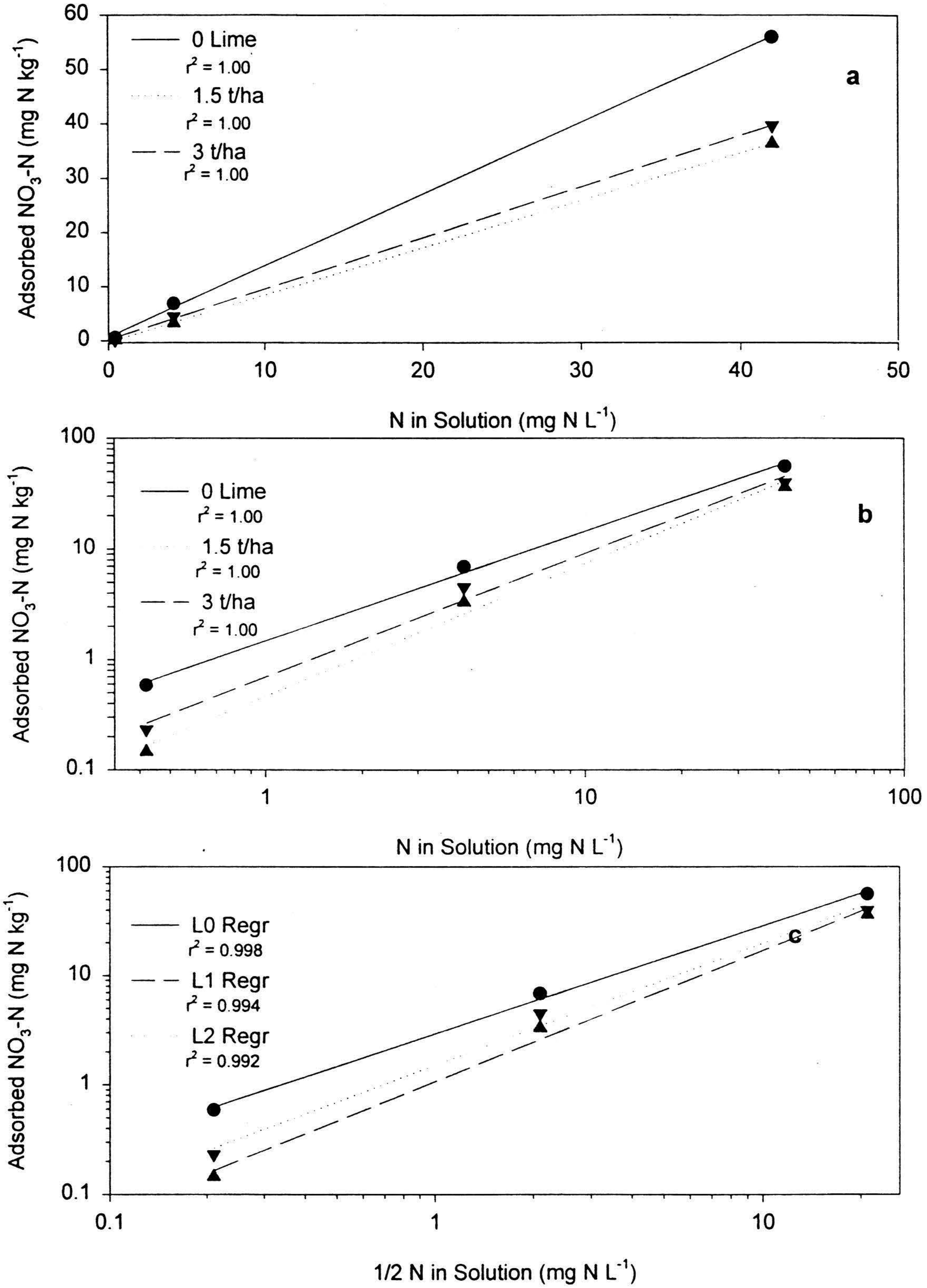


Figure 40. Nitrate adsorption data for the Kunia soil fit according to three models: (a) linear model, (b) linear form of the Freundlich model, and (c) the linear form of the Gouy-Chapman model.

Column Study

Nitrate Adsorption

Nitrate adsorption was measured in the subsoil (80 - 100 cm) of a *Wahiawa* and a *Leilehua* subsoil collected from recently harvested sugarcane fields prior to the installation of the soil columns. The *Wahiawa* subsoil had a significantly higher adsorption capacity, adsorbing two times more nitrate than the *Leilehua* at the highest concentration of the equilibrating solution (Fig. 41). The higher adsorption observed in the *Wahiawa* is related to important differences in chemical properties between the two subsoils (Table 12). Lower organic carbon content and a +0.14 reading for ΔpH correlate well with the higher adsorption observed in the *Wahiawa*. The *Leilehua* was sampled from a region with higher rainfall permitting organic matter to penetrate deeper into the subsoil where it neutralizes positive charge and a subsequent reduction in nitrate adsorption capacity.

Table 12. Some chemical properties of the *Leilehua* and *Wahiawa* subsoils (80-100 cm) used in the column study.

Property	Leilehua	Wahiawa
pH_{H2O}	4.06	5.67
ΔpH	-0.24	+0.14
Organic Carbon (%)	1.27	0.80
K_d	0.83	2.51

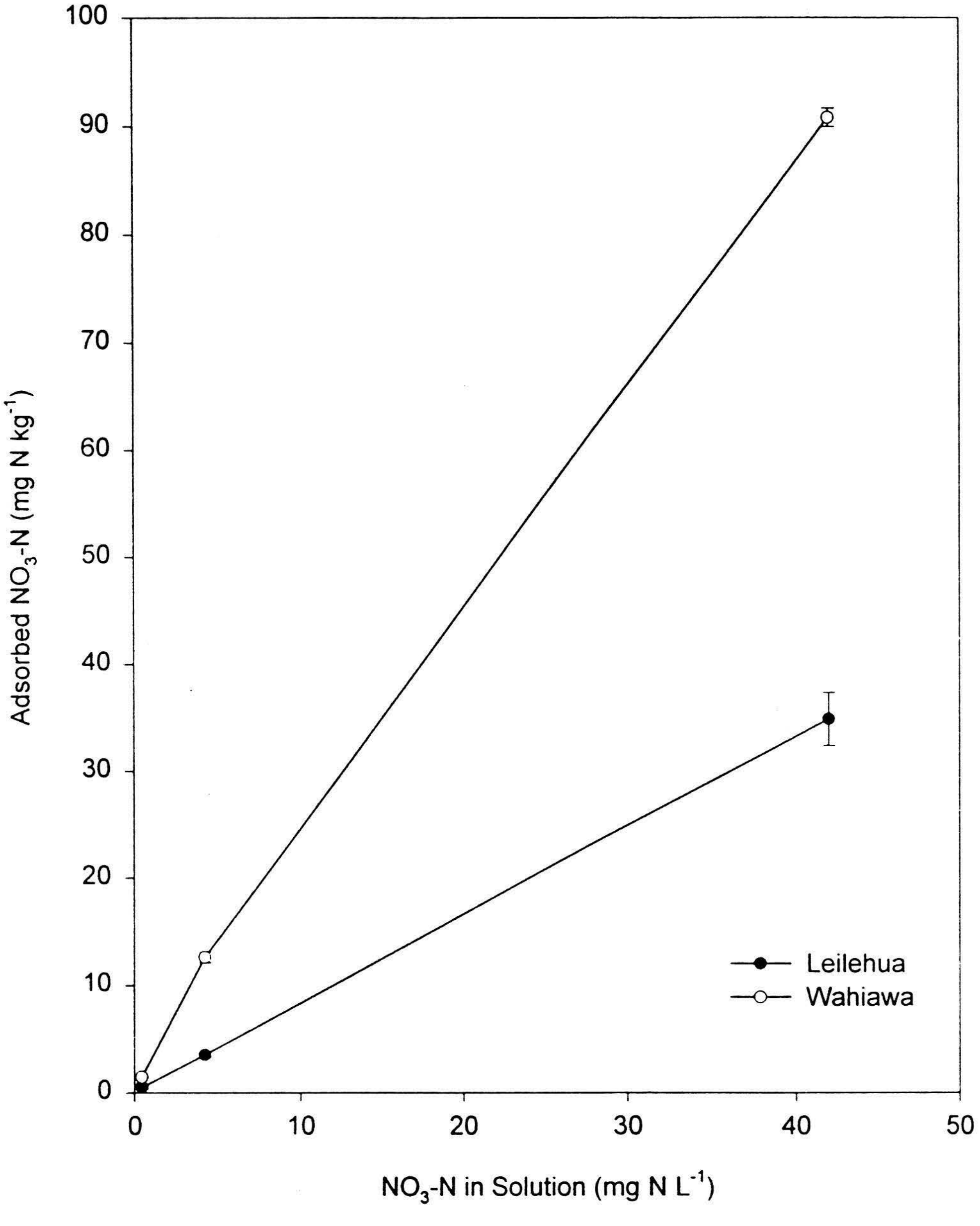


Figure 41. Nitrate-N adsorption isotherms for a Leilehua and Wahiawa subsoil (80 - 100 cm). Each point represents a mean of two replicates.

Nitrate Breakthrough Curves

Breakthrough curves are particularly suited to the evaluation of solute mobility in porous media. They provide a quick format from which one can quantitatively assess chemical interactions between the solute and the media it is passing through. Figure 42 shows idealized plots for breakthrough curves representing three general solute categories. Plot *b* represents the movement of an inert solute and shows that when the equivalence of one pore volume has passed through the column, half of the solute will have moved out of the column. Plot for solute *a* is an example of a solute that is being repulsed from the solid surface. In

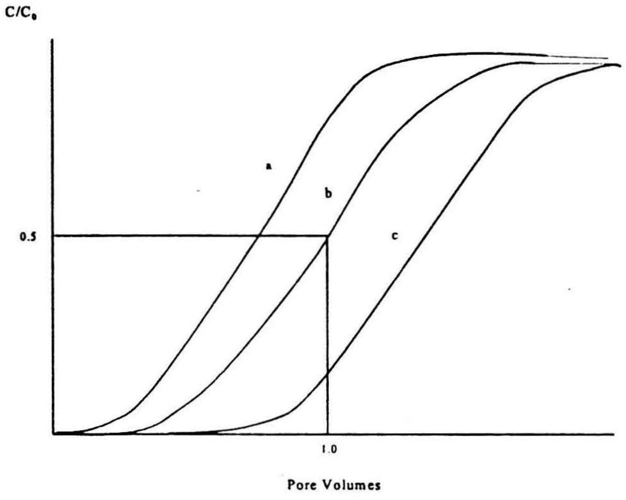


Figure 42. Solute outflow concentrations for three solutes with differing chemical properties: solute *a* exhibits negative adsorption, *b* shows no interaction, and *c* shows delayed arrival due to adsorption.

volume to reach $C/C_0 = 0.5$. The third case (plot *c*), illustrates attraction between charged solutes and colloid surfaces and the resulting retardation in the movement of the solute. The plot for adsorbing solutes moves progressively to the right as adsorption capacity increases.

Nitrate breakthrough curves for the present column study are presented in figures 43 through 46 (see Appendix 8 for raw data). Delayed movement of nitrate was observed in all the columns with the most delay occurring in the control columns of the *Wahiawa* soil. Nitrate was most mobile in the *Leilehua* soil that received lime and gypsum treatments. Results for analysis of variance on the pore volumes[1] associated with $N/N_0 = 0.5$ for each column are presented as mean comparisons in Table 13. Amending the

Table 13. Mean comparison for number of pore volumes required to achieve $N/N_0 = 0.5$ in the *Leilehua* and *Wahiawa* columns for all treatments.

Treatment	**Leilehua**	**Wahiawa**
	Mean Pore Volumes	
Control	2.20a	3.07a
Lime	2.05ab	2.43b
Gypsum	2.04b	2.24b
LSD_{05}*	0.15	0.26

*Comparisons were made between treatments within soils, means followed by the same letter are not statistically significant.

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[1] Defining a pore volume in systems that pass from a saturated state through varying states of unsaturation is arbitrary. Defining one pore volume as the total porosity of the media minimizes the number of pore volumes needed to displace the solute. On the other extreme, the pore volume as the difference between drained volumetric water content and residual water content maximizes the number of pore volumes.

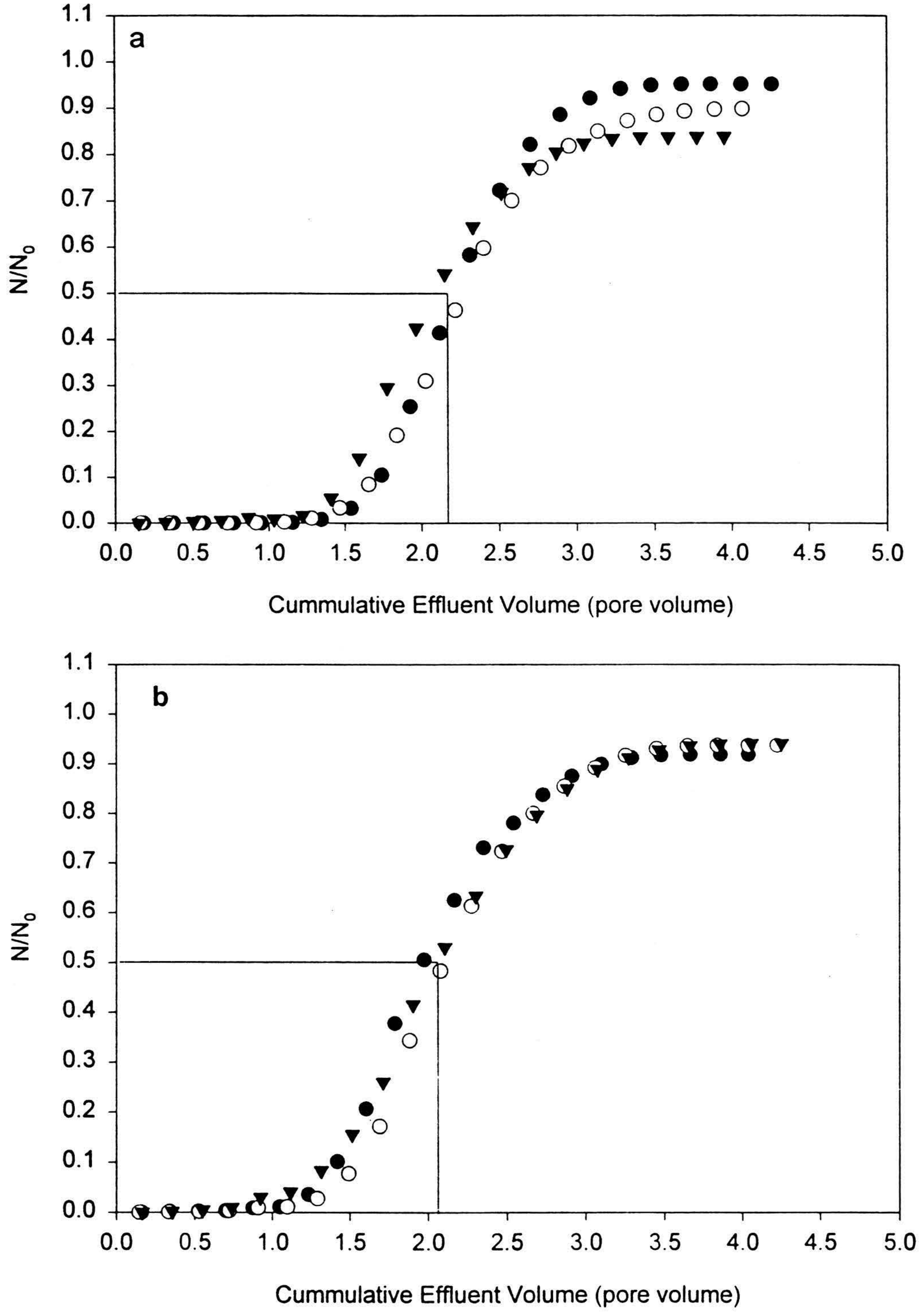
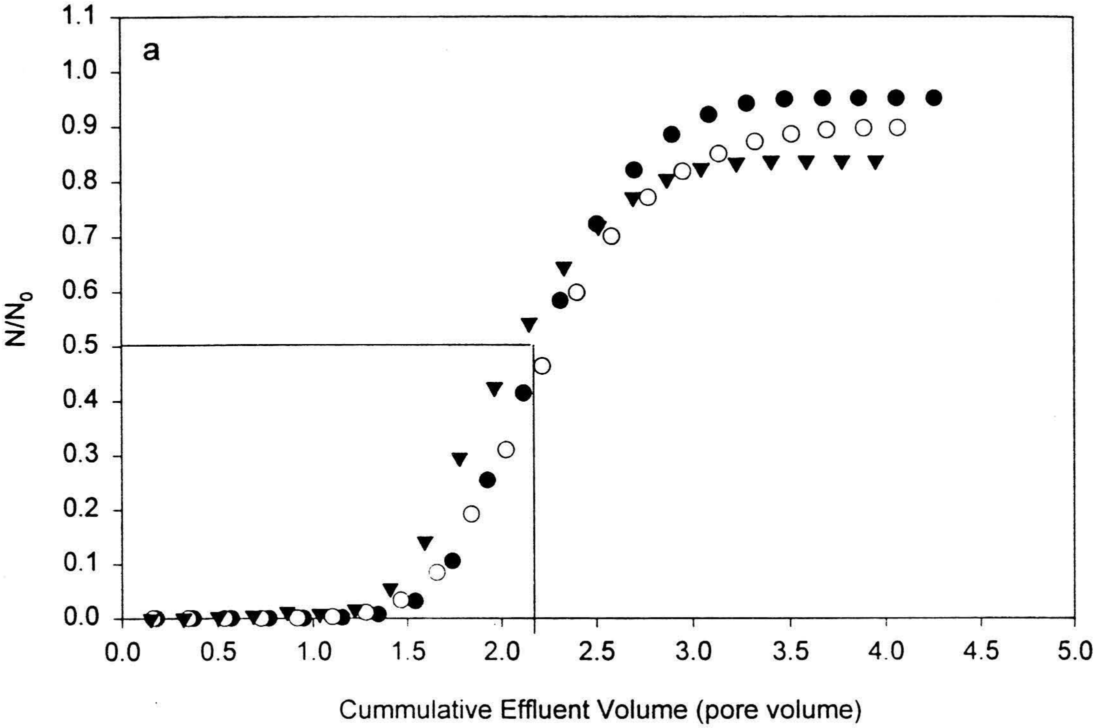


Figure 43. Nitrate-N breakthrough curves for Leilehua (a) control columns and (b) lime columns. Different symbols represent the three replicates per treatment. Data on y-axis plotted as cummulative mass of nitrate-N in the effluent (N) as a fraction of total nitrate N in the column (N_0). Lines represent relationship of pore volumes required to displace half of the nitrogen in the columns.



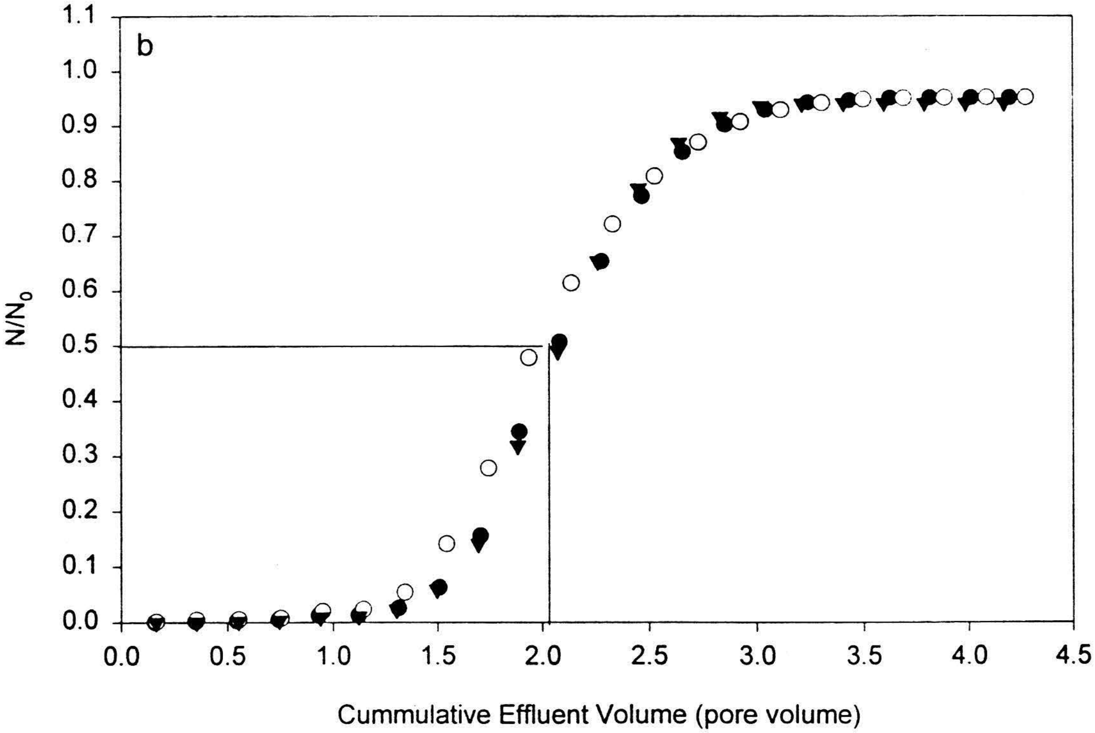


Figure 44. Nitrate-N breakthrough curves for Leilehua (a) control columns and (b) gypsum columns.

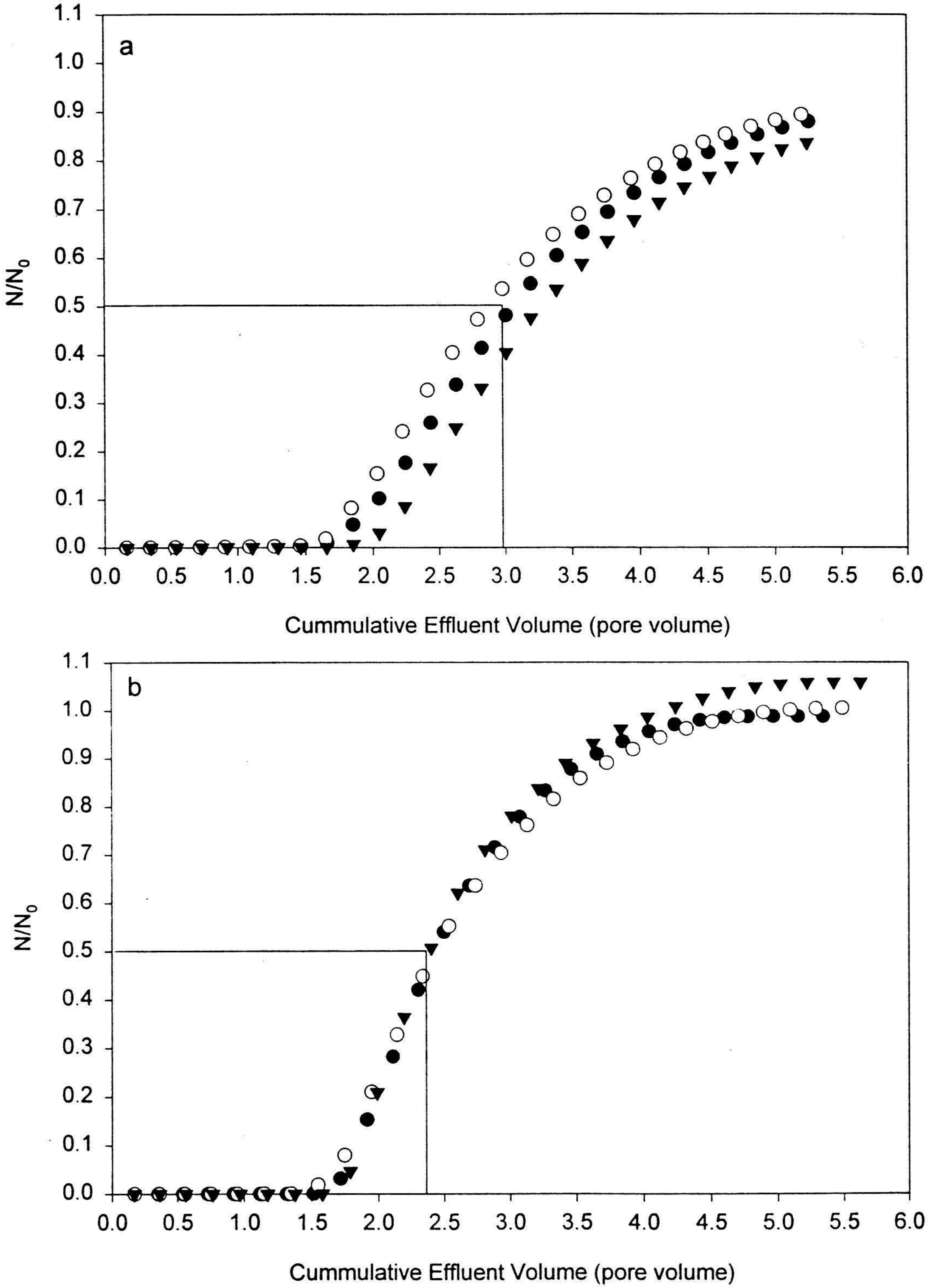
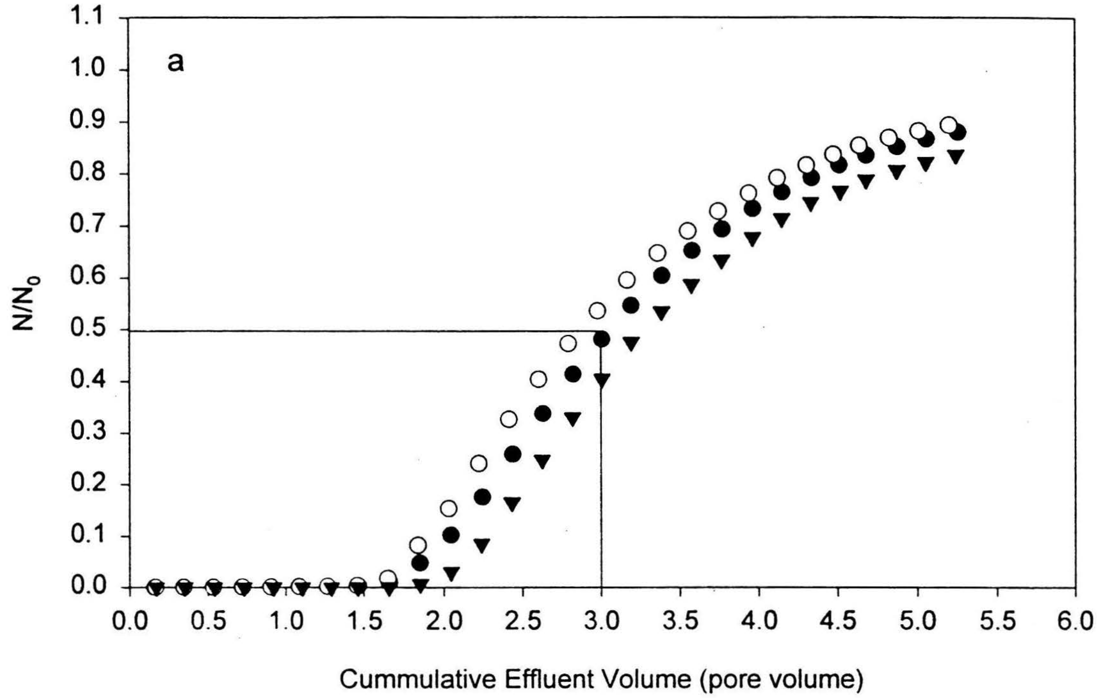


Figure 45. Nitrate-N breakthrough curves for Wahiawa (a) control columns and (b) lime columns.



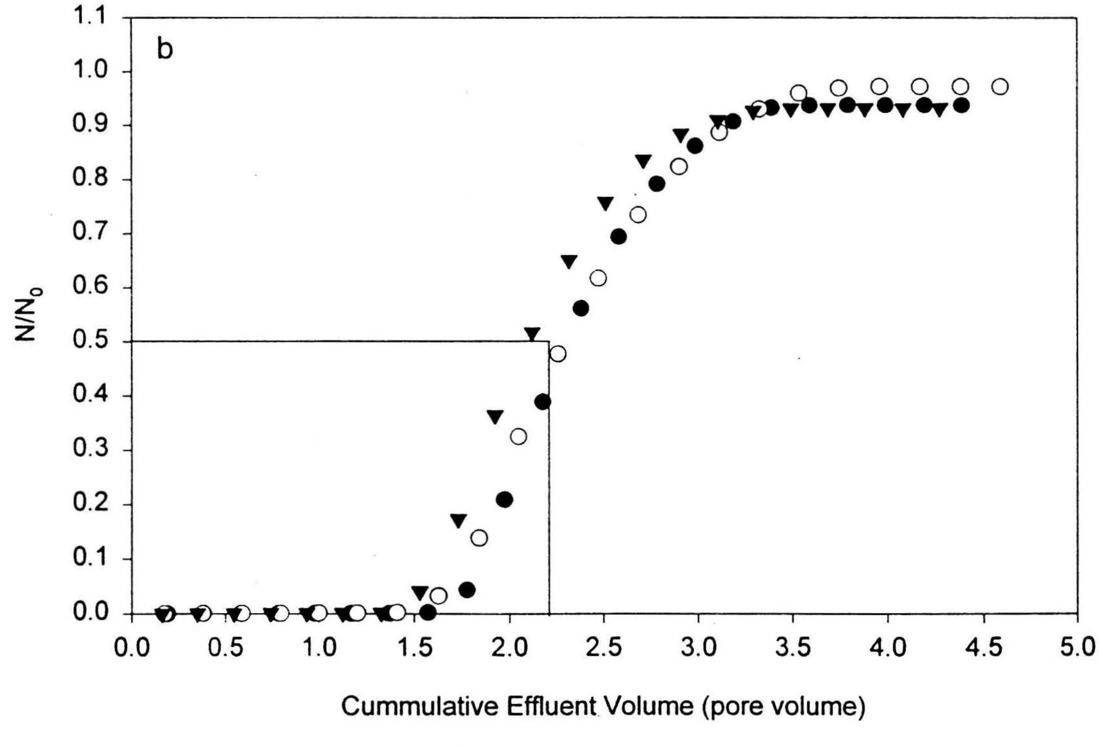


Figure 46. Nitrate-N breakthrough curves for Wahiawa (a) control columns and (b) gypsum columns.

surface layer in the *Leilehua* soil with gypsum increased the mobility of nitrate through the column. However, liming the *Leilehua* soil did not increase nitrate movement compared with the control columns. In the *Wahiawa* soil, the difference between the control columns and the lime and gypsum columns was much more pronounced. Arrival of nitrate in the lime and gypsum columns was significantly increased compared with the control. This early arrival of nitrate is apparent in the shift to the left in the breakthrough curves for both the lime and gypsum columns. No statistical difference in nitrate mobility existed between the lime and gypsum treatments despite the presence of a trend of increasing mobility in the gypsum treatment.

Applying lime to the surface of the *Wahiawa* soil reduced the number of pore volumes required to displace half of the resident nitrate from 3.07 in the control to 2.43 in the columns receiving lime. This reduction in pore volumes is equivalent to a reduction in the nitrate adsorption capacity of the soil. In an earlier experiment it was demonstrated that increasing soil pH decreased nitrate adsorption in a *Wahiawa* subsoil. In the columns that received lime the increase in nitrate mobility is related to increases in soil pH below the layer of application (Fig. 47a). Soil pH was measured at three depths below the 15 cm layer, and pH measured in the limed columns was significantly higher (by ANOVA) at the 20 and 30 cm increments than in the control columns at the same depths (Table 14). A measured increase in calcium was also observed at the 20 and 30 cm depth increments providing further evidence that the lime effect migrated below the layer of application (Fig. 47b).

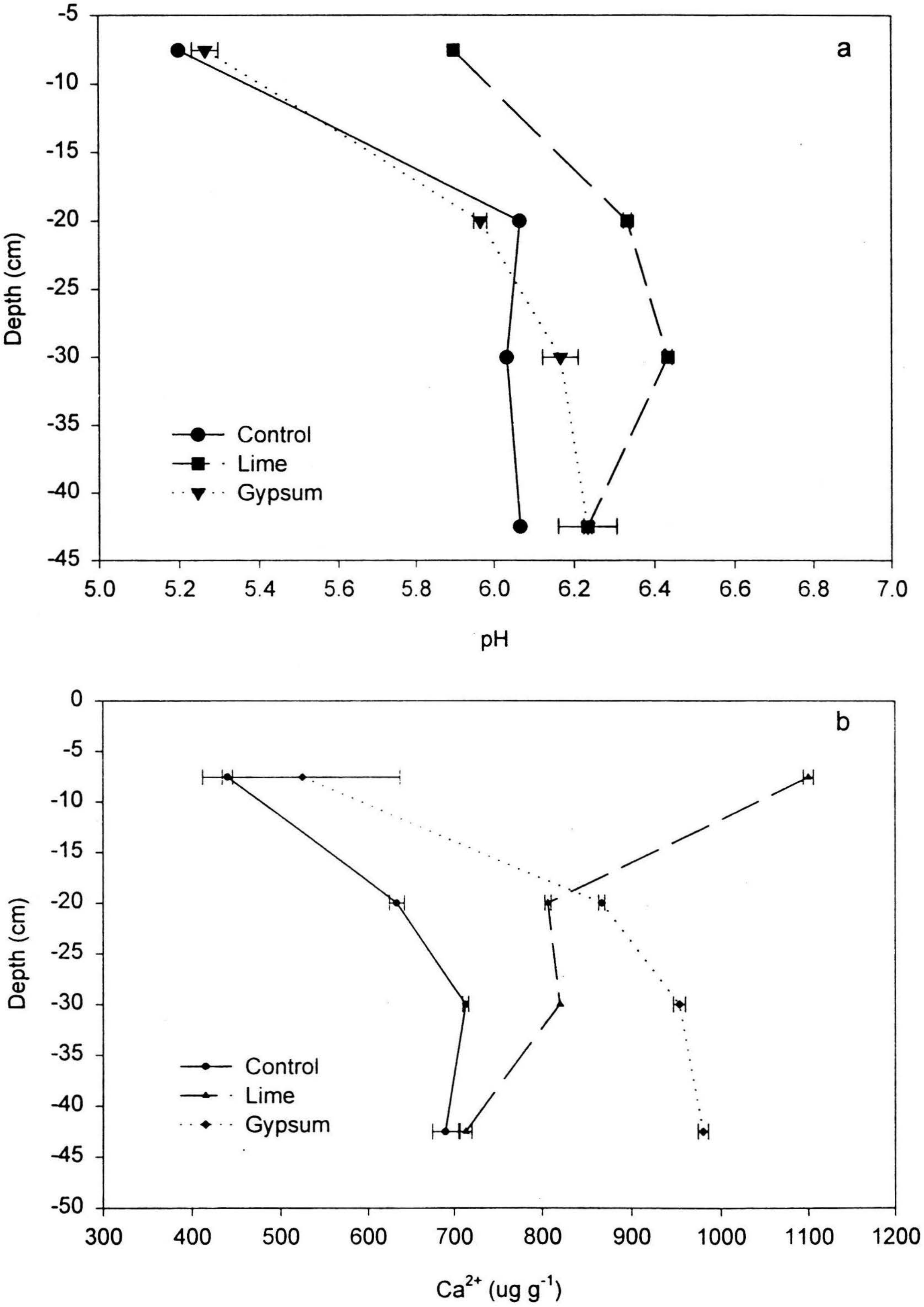


Figure 47. Wahiawa soil columns after leaching with approximately 5 pore volumes of water: (a) pH (1:5) and (b) Ca^{2+} distribution.

Table 14. Mean pH_{H2O} (1:5) values with increasing depth in the *Wahiawa* columns for all treatments. ANOVA performed separately for each depth.

Treatment	**Depth (cm)**		
	20	30	42.5
		mean pH	
Control	6.07a	6.03a	6.07a
Lime	6.33b	6.43b	6.23a
Gypsum	5.97a	6.17a	6.23a
LSD_{05}*	0.12	0.20	NA

*Comparisons were made between treatments for each depth, means followed by the same letter are not statistically significant.

The lime effect in the *Wahiawa* soil was significant down to a depth of 30 cm indicating that liming the surface soil will also cause increases in subsoil pH. Figure 47b shows that surface applied lime increased Ca^{2+} levels well below the layer of application. These results disagree with the findings of Liu and Hue (1996) who reported that surface applied $CaCO_3$ did not supply Ca^{2+} to the subsoil and had no effect on pH below the layer of application. Data reported in the literature indicates that calcitic lime does not move much beyond the layer of application in highly acidic soils (Friessen et al, 1982; Pavan et al, 1984; van der Watt, 1991; van raij, 1991; Sumner, 1995).

There exists substantial evidence showing that surface applied gypsum is an effective ameliorant of infertility associated with highly weathered acid subsoils (Ritchey et al, 1980; Sumner et al, 1986; Pavan et al, 1984; Farina and Channon, 1988; Alva et al, 1990; Sumner et al, 1995). Gypsum has been proposed as an effective means to overcome fertility problems in acid subsoils because it provides the subsoil with calcium and sulfate. Calcium and sulfate ions can reduce aluminum toxicity to crop roots in the subsoil (Hue et al, 1985). In addition to these beneficial effects, however, sulfate is readily adsorbed on positively charged sites in the subsoil. Sulfate is preferentially adsorbed over nitrate in the subsoil (Mekaru and Uehara, 1972; Kinjo and Pratt, 1971; Black and Waring, 1979) and therefore amending the surface with gypsum will increase nitrate mobility as adsorbed nitrate is replaced by sulfate on positively charged sites.

The gypsum treatments in both the *Leilehua* and *Wahiawa* soils increased the mobility of nitrate through the soil columns. Figures 48b and 49b show that sulfate readily leached out of the surface layer and accumulated in the subsoil. Sulfate-S in the leachate of all columns was measured twice during the leaching period - once after three weeks of leaching and again at the end of the leaching period. Only 4% of the added sulfate-S leached out of the *Leilehua* columns and even less, at 2%, was removed from the *Wahiawa* columns. In column experiments on a Hawaiian Oxisol, Wann and Uehara (1978*b*) demonstrated that specific adsorption of sulfate and phosphate anions increased negative charge in the subsoil by lowering the isoelectric point (pH_0). Recalling that the expression (pH_0 - pH) determines the sign of σ, it follows that decreases in pH_0 will cause σ to become more negative. Measured values

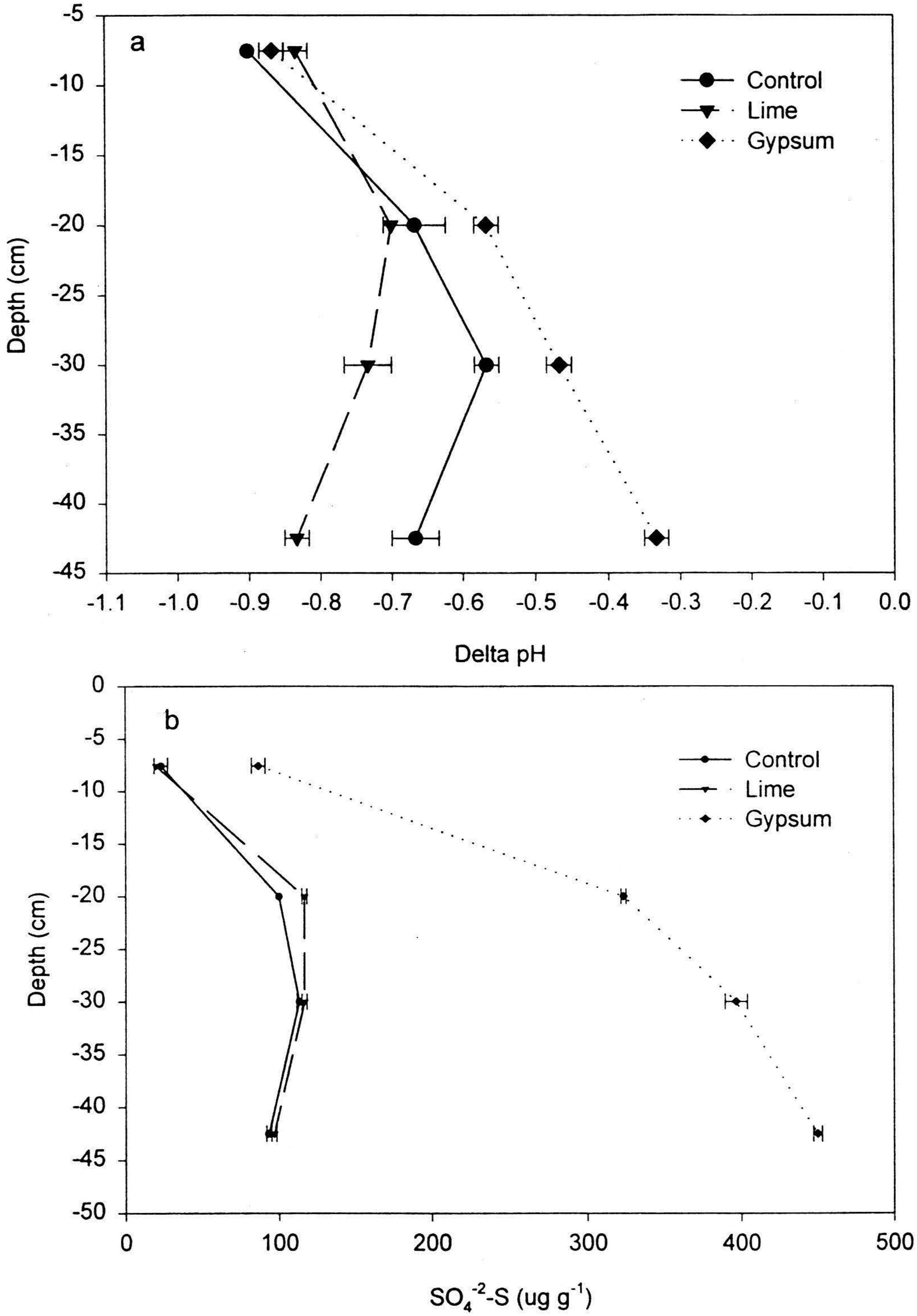


Figure 48. Leilehua soil columns after leaching with approximately 4 pore volumes of water: (a) delta pH and (b) SO_4^{-2}-S distribution.

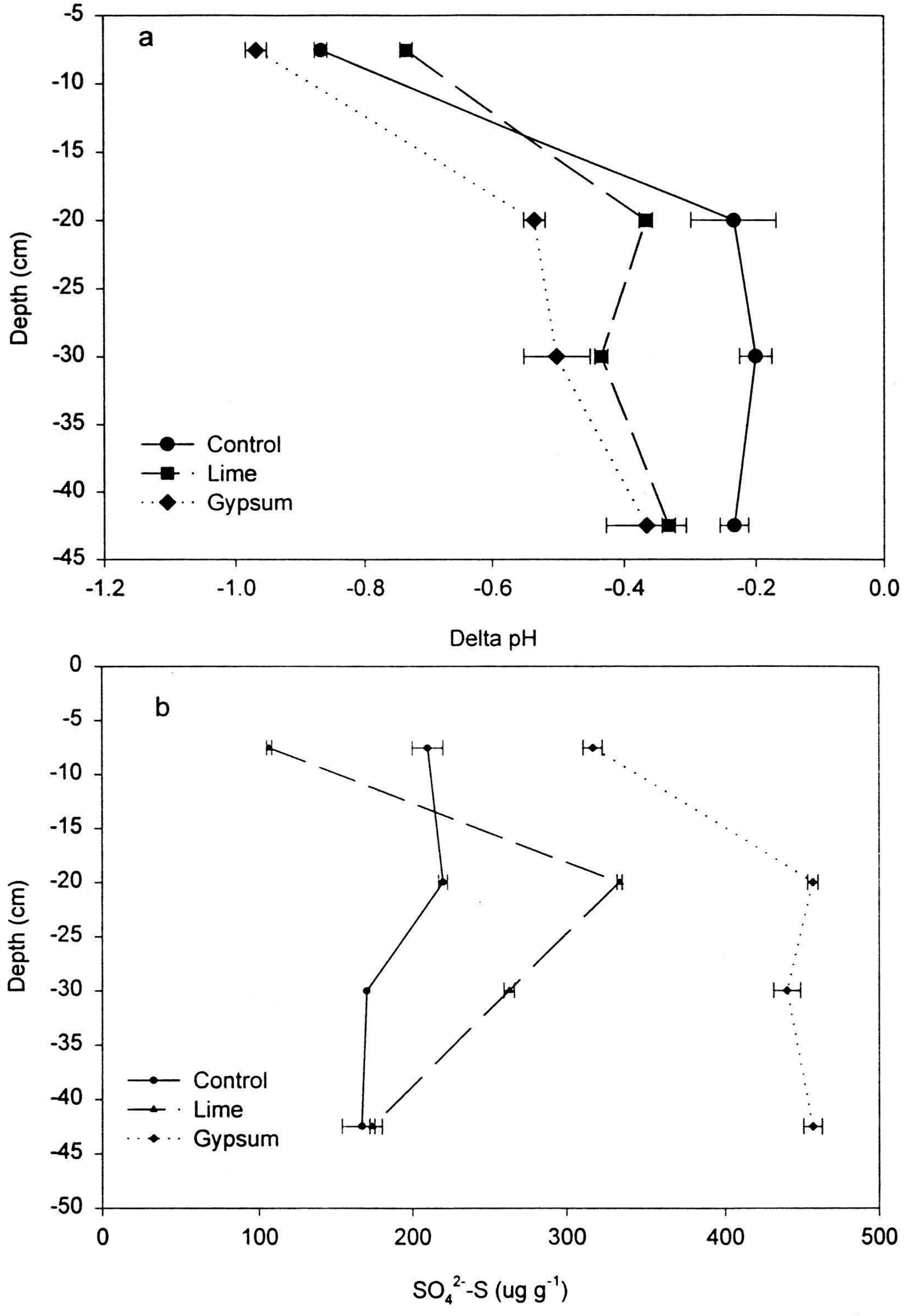


Figure 49. Wahiawa soil columns after leaching with approximately 5 pore volumes of water: (a) delta pH and (b) SO_4^{2-}-S distribution.

for ΔpH in the subsoil of the *Wahiawa* columns illustrate how negative charge increases with rises in sulfate adsorption (Fig. 49a). Specific adsorption of sulfate caused a significant increase in negative charge to the 30 cm depth (Table 15) and explained the increased mobility of nitrate through the soil column. Kinjo and Pratt (1971) reported that nitrate movement in an Andisol increased in the presence of sulfate.

Table 15. ΔpH with depth in the *Wahiawa* soil. ANOVA was performed on each depth increment as a separate group.

Treatment	Depth (cm)		
	20	30	42.5
		Mean ΔpH	
Control	-0.23a	-0.20a	-0.23a
Lime	-0.37a	-0.43ab	-0.33a
Gypsum	-0.53b	-0.50b	-0.37a
LSD_{05}*	0.16	0.29	NA

*Comparisons were made between treatments for each depth, means followed by the same letter are not statistically significant.

Nitrate mobility in the *Leilehua* columns was also enhanced significantly by treating the surface layer with gypsum. Sulfate accumulation in the lower depths of the soil columns is evident from Figure 48b. Unlike the data for the *Wahiawa* soil, ΔpH values in the *Leilehua* soil do not indicate an increase in negative charge as one would expect with specific adsorption of sulfate (Fig. 48a). Instead, ΔpH values for the gypsum treatment become increasingly less negative as sulfate adsorption rises. The lime treatment has the same effect on charge characteristics observed in the

Wahiawa soil. In fact, lime mobility rises as it significantly increases negative charge in the two lowest depths (Table 16). The discrepance between increased nitrate mobility in the presence of sulfate and higher values for ΔpH in the columns treated with gypsum remains puzzling with no satisfactory explanation available.

Table 16. ΔpH changes with depth in the *Leilehua* soil. ANOVA was performed on each depth increment as a separate group.

Treatment	**Depth (cm)**		
	20	30	42.5
		Mean ΔpH	
Control	-0.67a	-0.57a	-0.67a
Lime	-0.70a	-0.73b	-0.83b
Gypsum	-0.57a	-0.47a	-0.33c
$LSD_{.05}$*	NA	0.16	0.16

*Comparisons were made between treatments for each depth, means followed by the same letter are not statistically significant.

Earlier in this study nitrate adsorption was characterized in some soils collected from the island of Oahu. We used K_d, the anion distribution coefficient, as a means to compare soils regarding their relative capacity to adsorb nitrate anions. Our definition for K_d was the same as that assigned by Ketelle and Boyd (1947) and can be stated as:

$$K_d = \text{mg ion kg}^{-1}\text{ soil/mg ion L}^{-1}\text{ solution} \tag{7}$$

While K_d determined using equation 7 is measured directly using either the batch method or the flow equilibration method, values for K_d can also be estimated in a column system from the equation of Ketelle and Boyd (1947)

$$K_d = \frac{(V - 1)f}{\rho} \tag{8}$$

where V is the number of pore volumes required to reach the point where $C/C_0 = 0.5$, f is the proportion of pore space in the column, and ρ is the bulk density of the soil in the column. Employing equation 8 for the control columns of the *Leilehua* soil with mean values for $V = 2.2$, $f = 0.67$ ($f = 1$ - bulk density/particle density, assuming particle density = 3.0) and $\rho = 0.97$ we obtain a $K_d = 0.83$, which corresponds exactly to the K_d measured using the procedure corresponding to equation 8. For the control columns of the *Wahiawa* soil where $V = 3.02$, $f = 0.67$ and $\rho = 0.96$ calculated $K_d = 1.44$ which is considerably less than the measured K_d of 2.51.

In the case of the *Wahiawa* soil, calculated and measured values for K_d are in disagreement because the flow equilibration method for determining K_d may significantly overestimate K_d. Wong et al (1990) reported a similar discrepance between measured delay and predicted delay of nitrate in a Nigerian Ultisol. They employed a rearrangement of equation 8 to calculate delayed arrival of nitrate. The equation had the form

$$V = 1 + K_d \rho/\theta \tag{9}$$

where θ is volumetric water content instead of total pore space. Values for $V > 1$ meant delayed arrival for nitrate. They concluded that the overestimation of V was a result of high values for K_d obtained using a flow equilibration method similar to that employed in the present research. The high values for K_d were attributed to the removal of sulfate during the initial washing of the soil sample with $CaCl_2$. The removal of sulfate by mass action opened up charged surfaces for nitrate adsorption that were not available in the column study where nitrate was not able to displace native sulfate occupying exchange sites. In the present study, the *Wahiawa* soil had significantly more native sulfate than the *Leilehua* (Figs. 48 and 49) that was removed in the initial step of the flow equilibration measurement for nitrate adsorption. In the *Leilehua*, the discrepancy was not manifested presumably because initial sulfate levels were too low to make a difference.

The results indicate that running a column study to calculate K_d using equation 8 is a more meaningful measure of K_d than conducting an adsorption study. The flow equilibration method and the batch method give unrealistic values for K_d because they force complete saturation of charge. In the batch method, saturation is attained by shaking the soil in a solution of nitrate and in the flow equilibration method, charged sites were "saturated" because between 15 and 23 pore volumes passed through the soil. The movement of the water and solute through the soil columns is more consistent with what may occur in the field and thus provides for a better estimate of the AEC or K_d associated with the soil.

Data generated from the column study and equation 8 can be used to illustrate how adding amendments to the surface layer changes adsorption capacity in the subsoil. Changes in K_d as a function of surface treatment are presented in Table 17.

The column study provided evidence that surface applied lime and gypsum will migrate into the subsoil and alter charge characteristics sufficiently to increase the movement of nitrate through the subsoil. The use of gypsum has more far reaching implications for nitrate transport through the subsoil because sulfate has high vertical mobility. Gypsum and phosphogypsum have been proposed as effective neutralizers of subsoil aluminum toxicity, a ubiquitous problem in acid soils of the tropics carrying variable charge. Based upon the findings of this research, use of these two amendments will increase the vertical mobility of nitrate, phosphogypsum much more than gypsum, and could lead to a much higher risk of increased nitrate contamination of groundwater resources.

Table 17. Changes in K_d in the *Leilehua* and *Wahiawa* soils in relation to surface amendments. K_d estimated by equation 8. Since K_d is calculated using mean pore volumes for each treatment, differences between treatments will follow data presented in Table 2.

Treatment	K_d	
	Leilehua	Wahiawa
Control	0.83	1.44
Lime	0.73	1.00
Gypsum	0.73	0.87

CONCLUSION

This study set out to answer two important questions related to the potential for nitrate contamination of the Pearl Harbor aquifer. First, how much nitrate has accumulated in the subsoil and saprolite below agricultural land within the watershed area? Second, after measuring nitrate adsorption in these soils, how do some common liming practices change their adsorption characteristics, and what are the consequences of applying surface amendments to neutralize acidity as they relate to nitrate mobility?

Analysis of material from four deep bore holes in pineapple fields in the Pearl Harbor watershed area show that between 3.5 and 11 T/ha of nitrate-N have accumulated in the vadose zone. In all four bore holes, the nitrate level in the deepest sample of each hole corresponded to the "lower tail" of the nitrate-N distribution curve, inferring that the nitrate peaks are still well above the water table. Nitrate adsorption isotherms confirmed that the subsoil materials carry significant positive charge and a high nitrate retention capacity. They also validate the predictive capability of the Gouy-Chapman equation and double layer theory in soils with variable charge clays. Given that significant portions of the watershed are mantled by Oxisols or Ultisols with high nitrate retention capacity, these results indicate that nitrate retention in the vadose zone plays a significant role inhibiting the movement of nitrate into the groundwater body.

Recently, a small but significant rise in nitrate levels in wells located in the Pearl Harbor area has been detected (El-Kadi, 1996). Modeling studies using conventional approaches that assume that nitrate leaving the root zone travels unimpeded to the water table consistently over predict nitrate levels in the basal aquifer (Ling, 1996). According to a recent modeling effort based upon field data from corn and pineapple plots in the Kunia area, El-Kadi (1996) found that measured nitrate concentration in the soil layer immediately below the root zone was ten times higher than the nitrate concentration above the water table. The deficit between nitrate leaving the root zone and entering the water table suggests that the nitrate is being retained in the subsoil and deep saprolite above the aquifer. Prior to the work presented in this thesis, little was known about nitrate distribution and movement through the vadose zone. The nitrate distribution profiles from the deep bore holes and the associated nitrate adsorption isotherms provide evidence that nitrate does not pass unimpeded through the unsaturated zone and explain the deficit apparent in El-Kadi's modeling study.

The second question hinges on the fact that charge properties in variable charge systems are easily altered by farming practices. Liming, a common practice to amend soil acidity in the soils of the humid tropics, reduces the nitrate retention capacity by raising the pH. Gypsum, a soil amendment used to detoxify aluminum in acid subsoils, reduces nitrate adsorption by lowering the isoelectric point without substantially changing the soil pH. In the incubation study, liming subsoils from field samples reduced nitrate retention by as much as one half. In the column study, it was shown that an Oxisol receiving no soil amendment significantly retarded the movement of nitrate through the subsoil while surface application of lime and gypsum increased the mobility of nitrate through the subsoil. Nitrate mobility in the columns receiving lime was increased by raising the pH in the subsoil layers. In the columns receiving gypsum, nitrate mobility increased because sulfate was adsorbed preferentially causing nitrate desorption.

The findings related to the first question begin to fill the knowledge gap regarding nitrate distribution and behavior in the unsaturated zone. First, they confirm the occurrence of a large underground reservoir of nitrate-N sitting above the water table. Second, they point out that modeling efforts can no longer assume that nitrate does not react with the solid phase as it is transported through the subsoil and underlying saprolite. Models must incorporate an adsorption term to estimate retardation due to nitrate adsorption. By convention the linear adsorption parameter, K_d, has been determined by batch or flow equilibration studies conducted under equilibrium conditions in the laboratory. Findings from the column experiment, however, indicate that using K_d's obtained from the flow equilibration method tended to be high and overestimated the retardation of nitrate movement through the column. When K_d was calculated from data generated in the column study the values were lower and probably a more realistic estimate of adsorption capacity. In addition, this study provides further evidence that K_d is inversely proportional to pH. The data present strong evidence in support of the fundamental effect pH has on nitrate adsorption; high adsorption can be expected with low pH in the weathered subsoils of Ultisols and Oxisols. On the other hand, while the relationship between K_d and ΔpH is statistically significant, the correlation is weak and ΔpH may not be a reliable indicator of nitrate adsorption in soils with varying mineralogical properties.

In general, soil column studies usually provide useful information regarding the physical and chemical processes active in solute transport. However, since they are conducted in the laboratory under highly controlled and artificial conditions, using results from a column study to predict behavior under natural conditions in the field is not advisable. Nevertheless, results from the column study presented in this research raise important questions regarding the effect of surface applied amendments on nitrate transport. If charge characteristics of soils packed into a 50 cm column are altered by surface applied lime and gypsum in the short term, what would the effects be under long term field conditions? Would the lime and gypsum effect persist over time and continue to move further into the subsoil? Results from the column study justify further examination of these questions under field conditions.

At present a number of important questions remain unanswered regarding the status of nitrate in the unsaturated zone and the possibility of groundwater contamination in the future.

1) *Is the underground nitrate anthropogenic or do similar concentrations exist under natural vegetation?* While the four bore holes show that nitrate has

accumulated in the subsoil and saprolite, the source of the nitrate remains disputable. Sampling the subsoil and saprolite under former sugarcane land, alternative crop land and natural vegetation will provide a clearer picture as to the source of subsoil nitrate and the extent of its accumulation.

2) *How much more nitrate can the underground reservoir of positive charge adsorb?* The present study showed that subsoils dominated by variable charge minerals can adsorb nitrate anions. It did not give any indication of maximum adsorption capacity. If these soils are nearing their maximum adsorption capacity, additional nitrate may reach the groundwater at a much faster rate. Recently reported rises in groundwater nitrate may be a result of this.

3) *What is the long term effect of surface applied liming amendments on nitrate transport in the field?* In a comprehensive review paper, Sumner (1995) tabulates numerous short and long term liming studies that demonstrate that surface applied lime usually moves less than 50 cm, but has been reported to move up to 1 meter. Applied gypsum, on the other hand, can deliver sulfate anions to much greater depths. Trees planted eight years ago as part of a controlled liming experiment at the Waiawa Correctional Facility (central Oahu) on former pineapple land provides a timely opportunity to examine long term effects of surface applied lime and gypsum on an acidic Ultisol. A comparison of subsoil pH, charge characteristics and nitrate distribution under each plot will permit a better assessment of nitrate adsorption and mobility under different management practices.

4) *What will be the long term fate of the underground nitrate as land use patterns shift from pineapple and sugarcane to diversified agriculture and urban development?* The future of large areas of agricultural land in central Oahu once devoted exclusively to sugarcane and pineapple cultivation is questionable. While the acreage devoted to pineapple has decreased, both Dole and Del Monte do not plan to discontinue production in the foreseeable future. Sugarcane production has ceased completely in central Oahu and large segments of land in Ewa and upper Waipahu have been converted to residential areas. However, agriculture continues to dominate land use in the Kunia and Mililani areas. A number of diversified crops including potato, watermelon and vegetable crops are presently being grown on former sugarcane and pineapple land. The production of diversified crops will necessitate new management practices that will impact nitrate distribution in the subsoil.

5) *Are there suitable methods for extracting adsorbed nitrate from the subsoil to reduce probability of nitrate contamination of Oahu's groundwater?* Data from the four bore holes indicate that a significant fraction of the subsurface nitrogen is within five to ten meters of the surface. Trees are known to send roots to great depths in search of water, but less is known about nutrient uptake deep in the subsoil (Ong, 1994; Ong and Khan, 1993; Young, 1989). In a recent study conducted on an Oxisol in western Kenya with a known reservoir of adsorbed subsoil nitrate, tree roots

extended to depths below 4 meters and could utilize subsoil nitrogen (Buresh et al, 1995). Local and foreign investors and the Hawai‘i state government are interested in promoting the use of a variety of trees for long term investment on former sugarcane land. This is an area that will need further investigation.

APPENDIX 1. SOIL DATA FOR SOIL COLUMNS.

SOIL	TREATMEN	COLUMN Wt g	DRY Wt g	Wet Wt g	H2O Wt g	Vol Water	FINAL Wt g	SAND HEIGHT cm	SUBSOIL HEIGHT cm	TOTAL HEIGHT cm	SOIL HEIGH cm	BULK DENSIT g/cm3
LEILEHUA	*Control 1*	474.34	1805	2354	549	0.446	2396	0.5	37.2	52	51.5	0.97097
	Control 2	468.15	1798	2353	555	0.451	2407	0.7	37.5	52.1	51.4	0.97286
	Control 3	467.98	1800	2350	550	0.447	2389	0.5	38.2	52.4	51.9	0.96349
	CaCO3 1	458.6	1803	2359	556	0.452	2418	0.5	37.8	52.7	52.2	0.95795
	CaCO3 2	461.76	1795	2348	553	0.449	2396	0.7	38	51.8	51.1	0.97857
	CaCO3 3	485.95	1816	2353	537	0.436	2415	1	36.8	52.5	51.5	0.97097
	CaSO4 1	478.66	1811	2351	540	0.439	2405	1	38.5	52.4	51.4	0.97286
	CaSO4 2	459.01	1788	2321	533	0.433	2371	0.5	38	53	52.5	0.95247
	CaSO4 3	465.42	1799	2345	546	0.444	2407	0.5	38.4	53	52.5	0.95247
WAHIAWA	*Control 1*	452.46	1779	2320	541	0.439	2370	0.5	37.3	52.7	52.2	0.95795
	Control 2	493.86	1821	2358	537	0.436	2409	1	37.3	53	52	0.96163
	Control 3	479.09	1805	2337	532	0.432	2389	1	37.2	52.3	51.3	0.97475
	CaCO3 1	464.67	1793	2348	555	0.451	2387	0.8	37.1	52.7	51.9	0.96349
	CaCO3 2	464.86	1793	2336	543	0.441	2391	0.7	36.9	53	52.3	0.95612
	CaCO3 3	470.45	1800	2328	528	0.429	2388	1	37.5	53	52	0.96163
	CaSO4 1	472.44	1800	2340	540	0.439	2385	1	37.1	52.7	51.7	0.96721
	CaSO4 2	470.42	1799	2312	513	0.417	2370	1	37.5	52.9	51.9	0.96349
	CaSO4 3	468.77	1797	2342	545	0.443	2400	0.5	37.5	53	52.5	0.95247

APPENDIX 2. pH OF LEACHATE COLLECTED FROM COLUMNS DURING THE 6 WEEK LEACHING PERIOD.

SOIL	Trt	pH																			
		8/21	*8/23*	*8/26*	*8/27*	*8/29*	*8/31*	*9/2*	*9/4*	*9/6*	*9/8*	*9/10*	*9/12*	*9/14*	*9/16*	*9/18*	*9/20*	*9/22*	*9/24*	*9/26*	*9/28*
Le	*Control 1*	4.42	4.76	4.65	4.47	4.31	4.14	4.44	4.01	3.96	4.06	3.65	3.61	3.95	3.83	3.62	3.84	4.10	4.19	3.92	4.02
	Control 2	4.31	4.69	4.58	4.46	4.31	4.16	4.42	4.05	4.18	4.25	3.78	3.70	4.03	3.89	3.74	4.04	4.20	4.26	3.94	4.02
	Control 3	4.23	4.87	4.72	4.59	4.62	4.34	4.62	4.21	4.16	4.16	3.80	3.81	4.16	4.03	3.92	4.20	4.35	4.42	4.24	4.24
	CaCO3 1	4.37	4.73	4.60	4.52	4.45	4.19	4.42	3.98	3.97	4.04	3.71	3.70	4.07	3.94	3.81	4.06	4.19	4.23	3.98	4.04
	CaCO3 2	4.26	4.87	4.63	4.54	4.41	4.05	4.30	4.01	3.86	4.03	3.67	3.64	4.00	3.85	3.72	3.97	4.14	4.17	3.94	4.03
	CaCO3 3	5.62	5.03	4.72	4.68	4.60	4.19	4.36	3.93	3.93	4.11	3.77	3.76	4.14	4.06	3.82	4.05	4.18	4.23	3.97	4.04
	CaSO4 1	4.65	4.82	4.61	4.77	4.65	4.27	4.43	4.01	3.87	3.97	3.62	3.62	3.98	3.95	3.78	4.11	4.23	4.19	3.99	3.94
	CaSO4 2	4.63	4.56	4.63	4.44	4.16	3.89	4.12	3.74	3.77	3.94	3.65	3.66	4.05	3.99	3.85	4.08	4.11	4.09	3.92	3.95
	CaSO4 3	4.83	4.78	4.61	4.48	4.55	4.12	4.36	3.98	4.04	4.05	3.70	3.64	4.00	3.93	3.76	4.20	4.37	4.21	3.95	3.91
Wa	*Control 1*	5.02	5.41	5.71	5.92	5.91	5.31	6.03	5.68	6.03	6.33	5.94	6.17	6.23	6.35	5.87	6.51	6.33	6.70	6.16	6.48
	Control 2	5.12	5.13	5.72	6.07	5.58	5.39	6.18	5.92	6.15	6.55	6.00	6.43	6.33	6.58	5.78	7.24	6.65	6.90	6.43	6.88
	Control 3	6.45	5.66	6.23	6.38	6.31	6.06	6.45	6.16	6.39	6.55	5.94	6.34	6.65	6.81	6.28	7.12	6.80	6.91	6.57	6.86
	CaCO3 1	5.77	5.25	5.65	6.20	5.99	5.61	6.26	6.05	6.39	6.87	6.56	6.79	7.03	7.12	6.68	7.25	7.12	7.19	6.93	7.12
	CaCO3 2	5.57	5.64	5.66	6.10	5.81	5.38	6.24	5.51	6.17	6.63	6.21	6.57	6.75	6.85	6.39	6.98	6.53	6.89	6.28	6.71
	CaCO3 3	6.71	5.58	5.74	6.00	5.70	5.15	5.97	5.67	5.99	6.45	5.90	6.33	6.54	6.73	6.32	6.96	6.67	6.95	6.61	6.82
	CaSO4 1	5.72	5.56	5.75	6.15	5.94	5.45	6.11	5.70	6.12	6.36	5.95	6.18	6.34	6.43	5.62	6.62	6.71	7.23	7.15	7.49
	CaSO4 2	6.53	5.12	5.45	5.98	5.72	5.18	6.10	5.60	6.22	6.56	6.24	6.45	6.63	6.78	6.51	7.11	7.19	7.56	7.34	7.52
	CaSO4 3	6.27	5.18	5.01	5.16	4.98	5.59	5.74	6.01	6.42	6.58	6.34	6.66	6.68	6.81	6.76	7.60	7.37	7.83	7.37	7.77

APPENDIX 3. ELECTRICAL CONDUCTIVITY (EC) OF LEACHATE COLLECTED FROM COLUMNS DURING 6 WEEK LEACHING PERIOD

SOIL	Trt	EC																			
		8/21	*8/23*	*8/26*	*8/27*	*8/29*	*8/31*	*9/2*	*9/4*	*9/6*	*9/8*	*9/10*	*9/12*	*9/14*	*9/16*	*9/18*	*9/20*	*9/22*	*9/24*	*9/26*	*9/28*
Le	*Control 1*	43	44	5	68	0	117	162	267	522	793	1003	1001	842	675	483	339	246	175	132	102
	Control 2	44	48	5	86	1	144	187	263	415	6	785	905	852	715	516	391	310	237	193	148
	Control 3	44	84	5	135	5	149	177	321	563	800	837	764	667	563	423	320	246	180	140	108
	CaCO3 1	55	62	5	97	7	147	244	477	744	880	835	759	684	590	450	352	270	193	146	105
	CaCO3 2	55	65	5	97	7	137	206	382	627	816	889	804	696	567	426	324	252	191	145	103
	CaCO3 3	62	81	5	128	33	226	340	523	712	805	773	671	606	545	431	350	276	209	156	113
	CaSO4 1	51	78	5	113	10	149	196	336	618	991	1068	949	794	636	447	396	524	614	685	709
	CaSO4 2	68	95	5	132	13	179	301	571	886	992	892	723	591	541	592	753	878	891	897	836
	CaSO4 3	NA	56	5	116	8	159	204	314	550	891	1102	1035	844	647	416	250	259	467	651	742
Wa	*Control 1*	43	57	6	78	1	95	99	105	157	332	499	563	598	622	580	529	486	423	371	341
	Control 2	43	46	6	76	2	103	109	120	237	485	617	646	634	626	554	503	460	407	436	327
	Control 3	50	51	6	70	0	84	91	96	106	156	310	497	620	674	632	580	544	480	437	379
	CaCO3 1	42	37	6	52	0	72	84	107	379	820	1021	962	848	757	618	507	441	378	331	279
	CaCO3 2	44	44	6	59	0	74	88	231	563	845	927	845	730	656	542	458	405	348	316	269
	CaCO3 3	37	36	6	47	0	63	71	85	478	1058	1130	948	797	677	547	457	390	335	298	259
	CaSO4 1	39	31	6	40	0	58	68	98	429	1072	1293	1148	955	804	630	487	369	275	326	460
	CaSO4 2	47	52	5	67	1	82	96	314	838	1125	1118	983	864	780	658	603	564	581	632	625
	CaSO4 3	52	56	5	71	1	81	88	371	945	1156	1151	1011	877	779	672	728	758	764	764	715

APPENDIX 4. NITROGEN BALANCE FOR SOIL COLUMNS.

Leilehua

	Control 1	Control 2	Control	Lime 1	Lime 2	Lime 3	Gypsum	Gypsum	Gypsum
Total N in Colum	51.17	51.17	51.17	51.17	51.17	51.17	51.17	51.17	51.17
Leachate N	48.7026	45.9528	42.8801	47.02	47.97	48.14	48.6641	48.68696	48.15647
Soil N**	0.20259	0.08925	0.16712	0.167	0.076	0.104	0.04145	0.047378	0.04812
Recovered N	48.9052	46.042	43.0472	47.18	48.05	48.24	48.7056	48.73434	48.20459
Unaccounted N	2.26481	5.12798	8.1228	3.987	3.122	2.928	2.46442	2.435662	2.965407

Wahiawa

	Control 1	Control 2	Control	Lime 1	Lime 2	Lime 3	Gypsum	Gypsum	Gypsum
Total N in Colum	50.54	50.54	50.54	50.54	50.54	50.54	50.54	50.54	50.54
Leachate N	38.6355	40.008	36.0608	49.06	48.62	51.86	47.3887	49.14672	47.09394
Soil N**	3.60504	2.92725	3.97533	0.267	0.338	0.508	0.03258	0.054643	0.042877
Recovered N	42.2406	42.9353	40.0362	49.32	48.96	52.37	47.4212	49.20136	47.13682
Unaccounted N	8.29944	7.60475	10.5038	1.217	1.579	-1.83	3.11877	1.338642	3.403181

* Total N: Input N = 49.18 mg
Initial N: Le surf. = 0.838 mg
Le sub = 1.147 mg
Wa surf = 0.716 mg
Wa sub = 0.647 mg

**N remaining in the soil after the columns were dismantled

APPENDIX 5. CALCIUM AND SULFATE DATA FOR SOIL COLUMNS FOLLOWING THE COMPLETION OF THE LEACHING PERIOD.

SOIL	Depth cm	*Control 1* Ca ug/g	*Control 2* Ca ug/g	*Control 3* Ca ug/g	*CaCO3 1* Ca ug/g	*CaCO3 2* Ca ug/g	*CaCO3 3* Ca ug/g	*CaSO4 1* Ca ug/g	*CaSO4 2* Ca ug/g	*CaSO4 3* Ca ug/g
LEILEHUA	0-15	160	160	160	940	920	960	360	360	400
	15-25	80	80	80	160	140	180	340	300	340
	25-35	60	60	80	120	120	100	300	280	300
	35-50	60	60	100	100	100	80	360	360	400
WAHIAWA	0-15	440	460	420	1080	1100	1120	740	74	760
	15-25	640	660	600	800	800	820	880	860	860
	25-35	720	720	700	820	820	820	980	940	940
	35-50	720	630	720	700	700	740	1000	960	980

SOIL	Depth cm	*Control 1* SO4-S ug/g	*Control 2* SO4-S ug/g	*Control 3* SO4-S ug/g	*CaCO3 1* SO4-S ug/g	*CaCO3 2* SO4-S ug/g	*CaCO3 3* SO4-S ug/g	*CaSO4 1* SO4-S ug/g	*CaSO4 2* SO4-S ug/g	*CaSO4 3* SO4-S ug/g
LEILEHUA	0-15	10	40	20	20	20	20	90	70	100
	15-25	100	100	100	110	120	120	320	320	330
	25-35	110	120	110	120	120	110	420	370	400
	35-50	90	100	90	100	90	100	460	450	440
WAHIAWA	0-15	230	230	170	110	110	100	340	310	300
	15-25	220	210	230	330	340	330	470	450	450
	25-35	170	170	170	270	270	250	470	410	440
	35-50	170	210	120	180	170	170	480	450	440

SOLUTION CALCIUM AND SULFATE DATA FOR LEACHATE FROM COLUMNS ON 2 DATES.

				Solution	
SOIL	**Trt**	**Ca (ppm)**	**SO4 (ppm)**	**Ca**	**SO4**
		9/13	**9/13**	**10/2**	**10/2**
LEILEHUA	*Control 1*	9.7	8	3.5	2
	Control 2	8.3	8	7.6	2
	Control 3	11.8	8	4.4	2
	CaCO3 1	19.2	8	5	2
	CaCO3 2	12.8	8	4.3	2
	CaCO3 3	26.9	8	5.2	2
	CaSO4 1	9.8	8	47.5	120
	CaSO4 2	25.5	8	80.3	196
	CaSO4 3	9.7	6	30.2	94
WAHIAWA	*Control 1*	7	6	23.3	2
	Control 2	7.5	6	24.4	2
	Control 3	5.7	6	28.9	2
	CaCO3 1	8.5	6	28.2	2
	CaCO3 2	16.1	6	25.1	2
	CaCO3 3	11.7	6	23.1	2
	CaSO4 1	8.4	6	13.6	4
	CaSO4 2	20.4	6	45.3	80
	CaSO4 3	26.7	6	71.3	120

pH (H2O) AND pH(KCl) DATA FOR SOIL COLUMNS

SOIL	**Depth**	***Control 1***	***Control 1***	***Control 2***	***Control 2***	***Control 3***	***Control 3***
	cm	**pH KCl**	**pH H2O**	**pH KCl**	**pH H2O**	**pH KCl**	**pH H2O**
Le	0-15	3.8	4.7	3.9	4.8	3.8	4.7
	15-25	3.6	4.4	3.9	4.4	3.7	4.4
	25-35	3.7	4.3	3.8	4.4	3.8	4.3
	35-50	3.7	4.3	3.8	4.4	3.8	4.6
Wa	0-15	4.3	5.2	4.4	5.2	4.3	5.2
	15-25	5.9	6	5.8	6.1	5.8	6.1
	25-35	5.7	6.1	5.9	6	5.9	6
	35-50	5.7	6.1	5.9	6.1	5.9	6
		CaCO3 1	*CaCO3 1*	*CaCO3 2*	*CaCO3 2*	*CaCO3 3*	*CaCO3 3*
Le	0-15	4.4	5.3	4.4	5.2	4.4	5.2
	15-25	3.8	4.5	3.8	4.5	3.9	4.6
	25-35	3.8	4.4	3.7	4.5	3.7	4.5
	35-50	3.7	4.5	3.7	4.6	3.7	4.5
Wa	0-15	5.1	5.9	5.2	5.9	5.2	5.9
	15-25	6	6.4	5.9	6.3	6	6.3
	25-35	6	6.5	6	6.4	6	6.4
	35-50	5.9	6.3	5.9	6.2	5.9	6.2
		CaSO4 1	*CaSO4 1*	*CaSO4 2*	*CaSO4 2*	*CaSO4 3*	*CaSO4 3*
Le	0-15	3.9	4.8	3.9	4.8	3.8	4.6
	15-25	3.8	4.4	3.8	4.4	3.8	4.3
	25-35	3.7	4.2	3.7	4.2	3.8	4.2
	35-50	3.7	4	3.7	4	3.8	4.2
Wa	0-15	4.3	5.2	4.2	5.2	4.4	5.4
	15-25	5.4	5.9	5.4	6	5.5	6
	25-35	5.6	6.2	5.7	6	5.7	6.3
	35-50	5.9	6.2	5.8	6	5.9	6.5

APPENDIX 6. NITRATE-N DATA FOR DEEP BORE HOLES.

Bore Hole 4111		Bore Hole 4101	
Depth (m)	NO3-N (mg/kg)	Depth (m)	NO3-N (mg/kg)
-1.064	6.16	-0.775	177.31
	6.11		175.37
	6.06		173.28
-2.28	13.56	-2.17	129.14
	11.89		125.38
	14.56		124.10
-3.04	10.01	-2.95	91.57
	9.08		89.21
	10.22		86.43
-5.32	28.40	-5.12	121.73
	31.13		120.39
	26.92		118.65
-6.84	37.82	-6.76	145.60
	33.37		148.78
	43.74		151.06
-8.36	25.82	-10.08	32.56
	26.44		32.80
	26.03		31.64
-11.4	20.19	-14.42	15.55
	19.89		16.38
	20.03		16.41
-15.2	15.08	-17.36	4.92
	14.76		4.81
	14.43		4.99
-17.024	8.67	-20.46	4.60
	8.75		4.44
	9.01		4.47
-17.48	7.55	-26.04	3.58
	7.61		3.37
	7.51		3.56
-19.456	4.22	-28.37	2.44
	4.07		2.66
	4.55		2.67

NITRATE-N DATA FOR DEEP BORE HOLES.

Bore Hole 4213		Bore Hole 4201	
Depth (m)	NO3-N (mg/kg)	Depth (m)	NO3-N (mg/kg
-0.775	62.59	-1.24	14.72
	64.99		11.76
	56.93		11.91
-1.86	15.95	-2.17	19.64
	15.13		20.17
	15.45		19.03
-2.64	6.86	-3.1	21.22
	7.94		21.90
	6.87		21.38
-3.41	7.53	-5.27	21.07
	8.27		20.08
	8.39		20.64
-11.16	13.79	-8.37	15.32
	13.24		15.29
	15.76		15.54
-13.33	22.81	-11.16	19.64
	21.88		21.51
	22.85		19.87
-19.53	23.42	-14.26	18.23
	23.80		14.82
	23.10		15.52
-24.18	20.53	-17.67	12.39
	20.48		12.18
	20.79		12.09
-31.62	1.82	-20.46	14.16
	1.51		13.89
	2.07		13.87
-37.51	0.93	-23.56	14.85
	0.69		14.62
	0.74		15.01
		-28.52	11.02
			11.18
			11.36
		-38.13	1.73
			1.99
			2.01

APPENDIX 7. pH(H2O) AND pH(KCl) IN SAMPLES FROM THE DEEP BORE HOLES.

Core #	Depth (m)	pH(H2O)	pH(KCl)
4111	-1.064	6.05	6.09
	-2.28	6.37	6.19
	-3.04	6.56	6.29
	-5.32	6.44	5.56
	-6.84	6.29	5.21
	-8.36	6.92	5.11
	-11.4	7.07	4.73
	-15.2	8.15	5.61
	-17.024	8.15	5.68
	-17.48	8.3	5.61
	-19.456	7.93	5.5
4101	-0.775	6.2	5.74
	-2.17	6.17	5.86
	-2.95	4.88	4.66
	-5.12	4.36	4.06
	-6.76	4.34	3.84
	-10.08	4.76	3.84
	-14.42	4.86	4.07
	-17.36	5.59	3.96
	-20.46	6.81	4.08
	-26.04	7.82	4.97
	-28.37	7.87	5.06
4213	-0.775	5.39	5.83
	-1.86	5.71	5.54
	-2.64	5.03	5.02
	-3.41	4.51	4.12
	-11.16	5.3	3.71
	-13.33	4.25	3.66
	-19.53	4.15	3.62
	-24.18	4.15	3.61
	-31.62	4.25	3.59
	-37.51	4.78	3.62
4201	-1.24	4.09	4.04
	-2.17	4.09	4.06
	-3.1	4.11	3.99
	-5.27	4.53	3.89
	-8.37	4.5	3.57
	-11.16	4.58	3.91
	-14.26	4.6	3.42
	-17.67	4.65	3.8
	-20.46	4.55	3.84
	-23.56	4.63	3.91
	-28.52	4.67	3.91
	-38.13	4.79	3.82

APPENDIX 8. NITRATE IN LEACHATE FROM SOIL COLUMNS

SOIL	Trt	Nitrate (mg)															
		8/21	*8/23*	*8/26*	*8/27*	*8/29*	*8/31*	*9/2*	*9/4*	*9/6*	*9/8*	*9/10*	*9/12*	*9/14*	*9/16*	*9/18*	*9/20*
Le	*Control 1*	0.00	0.01	0.00	0.00	0.03	0.28	1.32	5.53	16.68	33.81	36.22	38.33	31.60	22.32	14.56	8.14
	Control 2	0.00	0.01	0.00	0.00	0.09	0.56	1.78	5.07	11.57	24.37	26.83	34.77	30.45	23.21	16.15	10.65
	Control 3	0.00	0.18	0.47	0.57	0.35	0.32	1.93	8.58	19.66	34.86	29.31	26.69	23.18	16.70	11.96	7.52
	CaCO3 1	0.03	0.14	0.26	0.30	0.45	1.32	5.47	14.93	23.97	38.74	28.92	27.17	23.84	11.38	12.87	8.52
	CaCO3 2	0.00	0.13	0.24	0.36	0.48	1.14	3.83	11.26	21.42	38.89	31.72	29.50	24.97	17.37	12.36	8.45
	CaCO3 3	0.02	0.21	0.70	1.25	2.27	4.68	9.78	16.32	23.74	35.27	26.07	23.34	21.02	15.86	12.07	8.79
	CaSO4 1	0.02	0.16	0.36	0.55	0.69	1.08	2.91	8.47	21.08	42.61	36.89	33.25	27.02	18.10	11.37	6.12
	CaSO4 2	0.14	0.37	0.55	0.66	0.98	2.44	6.97	19.90	30.99	45.39	30.70	24.30	19.80	13.90	8.48	4.82
	CaSO4 3	0.00	0.03	0.22	0.47	0.56	1.03	2.83	8.04	18.74	40.28	38.79	37.11	29.94	18.80	10.70	4.57
Wa	*Control 1*	0.03	0.06	0.08	0.09	0.08	0.09	0.09	0.16	1.42	8.63	12.17	16.54	18.53	17.68	17.04	15.12
	Control 2	0.00	0.02	0.06	0.10	0.11	0.10	0.10	0.29	3.29	14.33	16.00	19.57	19.21	17.39	15.34	14.08
	Control 3	0.00	0.01	0.02	0.02	0.03	0.03	0.03	0.02	0.05	1.39	5.17	12.23	18.07	18.50	18.41	16.56
	CaCO3 1	-0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.16	6.87	27.20	28.94	30.94	26.66	21.57	17.87	14.08
	CaCO3 2	-0.00	0.01	0.02	0.02	0.02	0.01	0.15	3.92	13.62	29.22	26.42	27.03	23.16	18.90	15.16	12.85
	CaCO3 3	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.06	10.31	36.27	34.81	32.01	25.55	20.07	15.62	12.81
	CaSO4 1	-0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.50	9.23	36.97	40.36	38.62	29.67	21.83	15.71	10.03
	CaSO4 2	0.00	0.02	0.04	0.06	0.06	0.05	0.23	6.80	23.76	41.75	34.17	31.25	26.09	20.07	14.13	9.62
	CaSO4 3	-0.00	0.02	0.05	0.05	0.05	0.05	0.12	8.85	29.65	42.75	34.17	29.86	24.13	17.38	10.75	5.80

NITRATE IN LEACHATE FROM SOIL COLUMNS.

SOIL	Trt	Nitrate (mg)											
		9/22	*9/24*	*9/26*	*9/28*	9/30	10/2	10/4	10/6	10/8	10/10	10/12	10/14
Le	*Control 1*	4.69	1.67	0.36	0.07	0.03	0.03						
	Control 2	7.23	5.04	2.98	1.75	0.84	0.17						
	Control 3	4.60	2.16	0.67	0.14	0.03	0.02						
	CaCO3 1	5.48	2.89	1.22	0.24	0.07	0.01						
	CaCO3 2	5.59	3.15	1.27	0.27	0.04	0.01						
	CaCO3 3	5.47	3.52	1.81	0.73	0.23	0.03						
	CaSO4 1	2.83	0.89	1.07	0.01	0.01	0.02						
	CaSO4 2	3.03	1.47	0.44	0.16	0.06	0.04						
	CaSO4 3	1.05	0.06	0.02	0.01	0.01	0.02						
Wa	*Control 1*	14.62	12.81	10.76	9.28	8.76	7.05	6.07	5.59	4.24	3.84	3.23	2.83
	Control 2	13.41	11.56	9.45	8.47	7.80	6.51	5.47	4.59	3.91	3.43	3.00	2.54
	Control 3	15.98	13.17	11.76	10.56	9.67	8.01	7.00	4.94	4.86	4.22	3.52	3.03
	CaCO3 1	12.12	10.01	7.17	5.74	4.60	3.30	2.06	1.28	0.38	0.06	0.03	0.02
	CaCO3 2	11.95	9.70	7.25	6.31	5.34	4.27	3.28	2.59	1.68	1.26	0.48	0.31
	CaCO3 3	11.72	9.16	6.65	5.68	4.96	3.95	2.95	2.20	1.22	0.75	0.11	0.04
	CaSO4 1	5.75	1.11	0.03	0.00	0.00	0.01						
	CaSO4 2	6.75	2.20	0.50	0.06	0.02	0.01						
	CaSO4 3	3.73	0.98	0.14	0.00	0.01	0.01						

Cummulative volume of water leached through soil columns.

SOIL	Trt	Cummulative Leachate Volume (ml)															
		8/21	*8/23*	*8/26*	*8/27*	*8/29*	*8/31*	*9/2*	*9/4*	*9/6*	*9/8*	*9/10*	*9/12*	*9/14*	*9/16*	*9/18*	*9/20*
Le	*Control 1*	69	143	219	295	365	443	517	592	668	740	814	889	964	1039	1115	1188
	Control 2	62	134	208	282	356	428	497	570	644	715	787	862	933	1005	1078	1148
	Control 3	58	124	194	264	332	398	470	542	613	684	757	828	899	969	1039	1106
	CaCO3 1	62	132	204	272	340	408	479	553	624	696	770	843	916	990	1064	1136
	CaCO3 2	56	129	204	280	352	425	500	578	655	729	805	881	957	1034	1110	1186
	CaCO3 3	61	134	207	278	347	420	495	569	644	716	792	866	939	1012	1085	1157
	CaSO4 1	60	132	206	280	353	425	497	570	644	714	787	861	933	1005	1079	1150
	CaSO4 2	62	132	206	281	355	428	501	576	650	722	797	870	944	1019	1092	1161
	CaSO4 3	62	135	211	285	359	430	498	572	647	719	792	864	937	1009	1082	1154
Wa	*Control 1*	60	130	201	273	343	411	481	555	628	701	775	850	923	996	1069	1139
	Control 2	62	130	201	272	341	409	477	549	620	691	763	835	907	979	1050	1121
	Control 3	63	131	202	273	343	412	482	545	617	690	762	833	905	977	1050	1120
	CaCO3 1	66	138	210	284	358	435	511	588	666	743	819	895	971	1046	1121	1196
	CaCO3 2	66	138	211	286	361	436	512	588	664	740	813	889	964	1041	1116	1191
	CaCO3 3	63	134	208	283	358	433	508	584	661	735	811	888	963	1039	1114	1189
	CaSO4 1	71	144	220	295	370	443	518	594	671	747	823	900	976	1053	1130	1205
	CaSO4 2	62	136	211	286	360	432	507	584	661	736	812	888	965	1043	1119	1194
	CaSO4 3	62	133	208	283	357	430	507	583	660	735	809	884	959	1035	1111	1185

Cummulative volume of water leached through soil columns.

SOIL	Trt	Cummulative Leachate Volume (ml)											
		9/22	*9/24*	*9/26*	*9/28*	9/30	10/2	10/4	10/6	10/8	10/10	10/12	10/14
Le	*Control 1*	1263	1337.6	1413.3	1485.7	1561.4	1637						
	Control 2	1220	1293.2	1365.6	1436.7	1511.9	1581						
	Control 3	1174	1243.9	1312.9	1382.6	1453.6	1522						
	CaCO3 1	1208	1282.1	1355.7	1428.6	1503.2	1572						
	CaCO3 2	1261	1337	1412.9	1487.2	1563.8	1636						
	CaCO3 3	1231	1304.2	1378.5	1450.5	1526.2	1599						
	CaSO4 1	1224	1297.5	1370.8	1442.4	1516.3	1586						
	CaSO4 2	1233	1306.1	1377.5	1449.8	1524	1594						
	CaSO4 3	1227	1302	1375.3	1448.6	1523	1594						
Wa	*Control 1*	1210	1284.1	1356.7	1427.9	1501.2	1572	1643	1709	1773.7	1846.6	1916.8	1990.3
	Control 2	1192	1264.5	1336.7	1408.1	1481.2	1550	1619	1683	1744.4	1815	1883.8	1955.3
	Control 3	1190	1261	1331.8	1402.4	1476.1	1545	1614	1683	1744	1815.3	1883	1953
	CaCO3 1	1270	1346.4	1421.3	1495.6	1572.1	1646	1718	1789	1857.3	1931.1	2003.7	2078.5
	CaCO3 2	1267	1343.5	1417.9	1492.5	1569.4	1643	1716	1791	1862	1937.9	2012.3	2088.2
	CaCO3 3	1265	1341.9	1417.6	1491.2	1568.3	1642	1714	1788	1857.1	1932	2006.8	2082.3
	CaSO4 1	1281	1358	1433.8	1508.9	1585.9	1659						
	CaSO4 2	1270	1346.1	1422.1	1497.7	1574.4	1648						
	CaSO4 3	1256	1332.2	1407.6	1481.9	1557.4	1630						

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