

AMMONIUM LEACHING IN COASTAL PLAIN SOILS

by

HOLLY PETROVA BARLOW

(Under the Direction of David Kissel)

ABSTRACT

Because of the relatively low cost of production and their high N content, the vast majority of N fertilizers used in crop production are ammonium-based. Previous research on three soils representing the range of characteristics within a field in Crisp County, Georgia documented the presence of NH_4^+ -N to 120 cm in unfertilized plots at planting and after the growing season, indicating some potential for NH_4^+ -N leaching, especially in sandy soils. Based on these findings, a series of mass balance studies were performed in an attempt to duplicate the conditions that led to NH_4^+ -N movement into lower soil profile depths. Field and undisturbed soil column studies indicated that while each of the experimental soils differed in texture, percent carbon and CEC, each had some potential to transport NH_4^+ -N past the surface soil horizons and into lower soil horizons.

INDEX WORDS: Ammonium nitrogen, leaching, coastal plain region, soil fertility

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Chapter 1

INTRODUCTION

Much has been written about environmental hazards associated with nitrate (NO_3^-) leaching on sandy soils in the coastal plain region of the southeastern United States, however little has been written about leaching of other ions on these soils. Because of the relatively low cost of production and high N content, the vast majority of N fertilizers used in crop production are ammonium-based. Evidence indicates some potential for leaching of the ammonium (NH_4^+) ion, especially in sandy soils. Sandy soils have small amounts of clay, are typically low in organic matter, and are usually low in pH due to a leaching of basic cations. The effect of repeated applications of ammoniacal fertilizers tends to reduce pH because of nitrification. These conditions all contribute to a low CEC. In accordance with the lyotropic series, other cations adsorb more strongly to the available sites than NH_4^+ . Ions remaining in the soil solution are susceptible to leaching, particularly when soils rewet following conditions of low soil water content. Plant uptake and increased amounts of evapotranspiration during the growing season significantly decrease available soil water. In winter, heavy rains can progressively saturate the soil, leaching salts as wetting fronts proceed through the profile.

The coastal plain region of Georgia is distinguished from the rest of the state by age, topography, and parent material. Large portions of the parent material are marine sediments, a mixture of sands and sediments translocated from the upland Piedmont region. Although the area is considered relatively young in geologic terms, much of this material was already weathered at the time of deposition, allowing soil development to occur more rapidly. Typical of a young but maturing landscape, the topography transitions between flat to gently rolling.

Ultisols characteristic to the region are highly weathered and acidic due to extreme leaching of basic cations. Millions of years of the high temperatures and precipitation have intensely weathered primary and secondary clay minerals, forming the kaolinitic clays that dominate the state. Kaolinite (1:1) has low surface area and little isomorphous substitution, providing minimal CEC (2-10 $\text{cmol}_c \text{kg}^{-1}$).

Marine sediments are very sandy by nature. Sand both facilitates leaching and contributes little to CEC. Characteristic of an Ultisol, clays are concentrated in the subsurface horizons making their CEC of less benefit to most agricultural crops. In this highly acidic environment, nitrification rates decrease dramatically and adsorbed NH_4^+ ions can accumulate.

Minimal natural fertility and inability to retain plant nutrients in the rooting zone translates into high fertilizer requirements. Nutrients in the soil solution are subject to leaching, particularly after significant rainfall events and in the winter months when fields are bare (Mishra et al., 1988, Paramasivam, S. 2000, Wang, 2000). These conditions have both financial and environmental implications. Fertilizers that are applied but not plant available represent cost to the grower in terms of increased expenditure and decreased yield. Excess NH_4^+ -N reacting with chlorine reduces the effectiveness of the water treatment process creating public health risks. The risk of fish asphyxia increases at concentration levels of $<0.02 \text{ mg N L}^{-1}$. Taste and smell problems occur at concentrations of 0.1 mg N L^{-1} (Gangbazo, et al, 1995). A thorough understanding of the behavior of NH_4^+ -N in the soil is the key to maximizing profitability while reducing environmental impacts associated with N fertilization.

Chapter 2

REVIEW OF LITERATURE

Disturbed vs. undisturbed columns

Prior to the advent of the Haber-Bosch process, high cost and limited availability of N fertilizers limited their use to high-value crops. In the 1930's, attention was drawn to the problem of N leaching in sandy soils planted to citrus in Florida and California. Because nitrate (NO_3^- -N) leached quickly past the rooting zone, NH_4^+ -N was the preferred form of N fertilizer. As soil physical and chemical characteristics differ significantly in any given area, researchers sought to investigate the behavior and movement of NH_4^+ -N in soils.

Packed columns were used to simulate real world conditions. Soils were air-dried and sieved through a 2-mm mesh screen before being packed into columns of varying soil materials and varying depths. Ammonium leaching was greatest in the soils with the least amount of silt and clay. Babcock (1934) passed a 100 mg kg^{-1} solution of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ through soil columns 15 cm in length by 5 cm in diameter packed with either light sandy loam, medium clay loam or heavy clay loam textures. The two loam soils retained 99.1% and 100% of the NH_4^+ -N respectively, while the light sandy soil retained 72.2%. Additionally, a field experiment was executed on a light silty loam soil. A stream of 50 mg kg^{-1} $(\text{NH}_4)_2\text{SO}_4$ solution was applied to a shallow furrow until the water had penetrated to a depth of 90 cm and lateral distance of 30 cm on each side. A majority of the NH_4^+ -N was retained close to the point of application; approximately 5% had penetrated to 90 cm in depth and 30 cm laterally.

Influence of soil type on ammonium leaching

Seedling injury from banded N fertilizer applications in close proximity to the seed row led to a study of NH_4^+ -N movement at constant moisture conditions (Ray et. al, 1957). Four

soils representing Minnesota farming areas included a loamy fine sand, a silt loam and two loam soils. Soils were packed into acrylic clear plastic tubes (7.2 cm depth by 5 cm diameter) and held at a constant tension of 300 cm of water. Ammonium nitrate solution (60 mg N¹⁵-enriched NH₄⁺-N) was injected into the center of the column. The top of the column was exposed to the atmosphere and therefore subject to evaporation and capillary rise.

Vertical distribution of retained NH₄⁺-N was in a nearly symmetrical pattern to the injection point in all except the fine sandy loam soil, which indicated downward movement. Lateral distribution was most pronounced in the fine sandy loam soil and was more normally distributed in the loam and silt loam soils. The larger lateral movement was attributed to the texture and low CEC of the fine sandy loam. Dispersion depends on soil texture, moisture conditions, CEC and fertilizer concentration. Also under consideration were the differences in capillary forces that vary with soil texture, forces that decrease with increasing sand fraction.

Packed columns were used to evaluate the ability of slow-release N fertilizers to reduce N leaching losses on sandy soils in comparison to readily soluble ammonium nitrate (NH₄NO₃) (Wang and Alva, 1996). Candler fine sand (hyperthermic, uncoated Typic Quartzipsamment) and Wabasso sand (sandy, siliceous, hyperthermic Alfic Haplaquod) soils have different properties and dominate the central and East Coast Florida citrus production regions. Soil samples from were taken to 90 cm in 30-cm increments. Additionally, a hardpan layer (Bt) was sampled at 90 to 100 cm in the Wabasso soil with high organic C (13.6 g kg⁻¹).

Soil profiles of 94 cm ± 2 cm were simulated by packing air-dried soil samples in a PVC pipe 131 cm long by 10 cm in diameter. After pre-leaching with 2000 mL deionized water to bring the soils to field capacity, NH₄NO₃ (water soluble), isobutylidene diurea (IBDU) and a polyolefin resin-coated urea (Meister) were applied at the rate of 1 g N per column. The soil

columns were subjected to intermittent leaching-incubation conditions; eight leaching events (1000 mL each) were each followed by a four-day incubation period. The average N from a control soil column was subtracted from each respective leachate fraction from the treated columns to calculate the loss of added N.

Total N recovered in the leachate at the end of the experiment was 88 to 100% for the total N applied as NH_4NO_3 , 27 to 32% for IBDU, and 12% for Meister, reflecting the solubility characteristics of each fertilizer. For the Candler fine sand and Wabasso sand soils, the percent of NH_4^+ -N recovered in the leachate that was applied as NH_4NO_3 was 47.6% and 31.2% respectively. A plot of percent NH_4^+ -N over time indicates that the greatest concentrations leached during the first few leaching events (36% and 19% respectively).

Overall, the Wabasso sand retained a greater proportion of applied N than the Candler fine sand. The fact that the mechanism for the observed difference was not clear led to an examination of the exchange reactions of NH_4^+ -N in different horizons of these sandy soils (Wang and Alva, 2000). Samples were taken from the surface (0 to 30 cm) and subsurface (30 to 90 cm) layers of both soils and from a 90- to 100-cm hardpan layer in the Wabasso sand. Values of CEC, determined by neutral 1 M NH_4OAc and exchangeable acidity, were greater in the Wabasso sand than the Candler fine sand, being $12.4 \text{ cmol kg}^{-1}$ and $3.31 \text{ cmol kg}^{-1}$ from 0-30 cm in depth; $3.03 \text{ cmol kg}^{-1}$ and $1.15 \text{ cmol kg}^{-1}$ from 30 to 60 cm; $1.06 \text{ cmol kg}^{-1}$ and $0.72 \text{ cmol kg}^{-1}$ from 60 to 90 cm and $2.08 \text{ cmol kg}^{-1}$ from 90 to 100 cm in the Wabasso sand. Differences were attributed to the presence of hydroxyinterlayered vermiculite in the Candler sand and smectite in the Wabasso sand, which meant the differences in CEC of two closely related soils is significant in affecting NH_4^+ -N leaching.

Influence of soil management practices on ammonium leaching

Lack of soil N after heavy summer rains led to an investigation of N leaching in the sandy soils of South Africa (Merwe, 1942). A field experiment compared fertilizer treatments on one soil representative of the area under cultivation. The soil series name was unspecified; mechanical analysis determined it fit the classification of a sandy soil (49.8% coarse sand, 29.9% fine sand, 21.2% clay). A bare plot area was subdivided into four treatments: control, $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{SO}_4$ and lime application (liming agent unspecified), and calcium nitrate ($\text{Ca}(\text{NO}_3)_2$). No information was given regarding land preparation or method of fertilizer application. The first set of samples were taken before treatments were applied. The study was conducted during two consecutive years, for 7 and 6 months respectively.

Results presented are the average of the N concentration (mg kg^{-1}) in the first, second and third 30-cm increments. Unfortunately, the data were presented as total NH_4^+ plus NO_3^- -N. At no point is nitrification mentioned. Each plot started with approximately the same concentration of $\text{NH}_4^+ + \text{NO}_3^-$ -N, and the control plot remained constant over both experimental periods. Concentrations after fertilization in the treated plots were similar with the exception that approximately 20 mg kg^{-1} more $\text{NH}_4^+ + \text{NO}_3^-$ -N was found in the plot treated with $\text{Ca}(\text{NO}_3)_2$ in the first year. Total rainfall over the experimental period in 1941 was 170 cm, a majority of which fell in the last 4 months. In 1942, heavy rains occurred in the last 2 months of the experimental period. The percent decrease in concentration of NH_4^+ -N + NO_3^- -N from the time of fertilizer application and the experiment end was similar for both years in the $(\text{NH}_4)_2\text{SO}_4$ (decreases of 60 and 50% respectively) and $\text{Ca}(\text{NO}_3)_2$ treatments (decreases of 71 and 73%). In the $(\text{NH}_4)_2\text{SO}_4$ plus lime plot, there was a 39% decrease in the first year and a 73% decrease in the second year. Increased precipitation in the second year did not lead to an increased amount

of total N lost in the plots fertilized with $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}(\text{NO}_3)_2$. The difference between losses in the $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ with lime treatment was substantial. Although the author does not explicitly state a reason for the different treatments, it can be assumed that the lime was applied to offset the acidifying properties of ammonium sulfate. Increasing soil pH in acidic soils increases nitrification rates and CEC. More NH_4^+ ions retained in the surface soils in the presence of nitrifying organisms can translate into greater concentrations of highly leachable NO_3^- .

Noting that most leaching experiments were focused on packed soil columns under controlled conditions, researchers in India compared the retention and movement of $\text{NH}_4^+\text{-N}$ both through packed columns and natural field profiles of a Bhubaneswar sandy loam soil (Typic Haplustult), low in organic carbon (0.4%) and strongly acidic (pH 5) (Mishra and Misra, 1988). Packed columns 8 cm in diameter and 9 cm in length were leached with a 0.05M CaSO_4 solution before and after application of one of four ammonium salts ($(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , NH_4NO_3 and $(\text{NH}_4)_2\text{HPO}_4$) at the rate of $400 \text{ mg NH}_4^+\text{-N L}^{-1}$. Leachate samples were collected at hourly intervals for 24 hours and analyzed for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ using standard colorimetric methods. Six 3x3-m field plots were brought to near water saturation before adding pulses of NH_4 salts. One plot was leached with NH_4NO_3 containing $400 \text{ mg NH}_4^+\text{-N}$ and $402 \text{ mg NO}_3^-\text{-N}$ before and after being amended with paper mill sludge (PMS) as a liming material. Solution samples were collected for 20 hours. Five days later, maize was sown in the same plot. After 50 days, the same concentration of NH_4NO_3 was applied and followed with irrigation water for 20 hours. A second plot was treated in a similar manner, except for the application of lime. The third plot was amended with PMS. Solution pulses of $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl each containing $400 \text{ mg NH}_4^+\text{-N L}^{-1}$ were followed by irrigation water. The interval between these experiments

was five months. Samples were collected over a 32 hour and 24 hour period respectively by solution samplers installed at various depths. For each treatment, soil cores were collected from the top 10 cm of the surface soil for determination of NH_4^+ -N and NO_3^- -N. No NH_4^+ -N was found in the fractions collected during leaching of the packed soil columns. Distribution of NH_4^+ -N retained in the columns differed somewhat with treatment. Maximum concentration occurred at 3 to 4 cm in the NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ treatments and at 5 to 6 cm in the NH_4Cl treatment.

In each treatment of the limed and unlimed plots, the majority of NH_4^+ -N was retained in the top 4 cm of the field profile. The amount retained in surface 0 to 2 cm was lower in the lime amended soil. There was also a greater amount of NO_3^- stemming from nitrification at 50 cm in depth. Researchers suggest that the higher rate of nitrification in the limed soil left fewer NH_4^+ ions, reducing the chance of NH_4 exchange with adsorbed Ca^{2+} in the surface layer. An appreciable amount of NH_4^+ in the second pulse of N fertilizer was forced down into lower depths. The opposite was assumed to be true for the unamended acid soil. In leachate fractions from the bare amended plot, approximately 6.1% NH_4^+ -N was recovered. Only trace amounts were recovered from the plots under the growing crop. Following the $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl applications, the greatest amount of NH_4^+ -N was held in the 0- 4 cm layer initially, but decreased with time. Infiltration was more uniform and to a greater depth for the NH_4Cl treatment compared to $(\text{NH}_4)_2\text{SO}_4$. In contrast to the concentrations at depth, more adsorption was observed with $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl application in comparison to NH_4NO_3 .

Changes in cultural practices designed to reduce N losses in highly weathered soils in a humid tropical area led to a study of the downward movement of NH_4^+ -N and NO_3^- -N under different tillage and cropping conditions (Deare et al. 1995). Three field experiments were

conducted on a Picaro Series soil (*Aquoxic Tropudults*) in Central Trinidad. Soil chemical and physical characteristics are as follows. At 0 to 1 cm in depth, pH = 4.2, CEC = 4.30 cmol kg⁻¹, base saturation (BS) = 2.22 cmol kg⁻¹, 2.19% organic matter (OM), and sandy loam texture (14.6% clay). From 1 to 50 cm, pH = 3.9, CEC = 2.58 cmol kg⁻¹, BS = 0.78 cmol kg⁻¹, 0% OM, and sandy loam texture (19.1% clay). From 50 to 89 cm, pH = 4.0, CEC = 4.59 cmol kg⁻¹, BS = 0.29 cmol kg⁻¹, 0% OM, and sandy clay loam texture (23.1% clay). From 89 to 110 cm, pH = 4.2, CEC = 6.31 cmol kg⁻¹, BS = 0.27 cmol kg⁻¹, 0% OM, and sandy clay loam texture (32.2% clay).

The first experiment was conducted under bare-fallowed conditions during August and September, considered the early rainy season. Subsequently, the second and third experiments were cropped with okra (*Abelmoschus esculentus*) and carried out during the late (October to January) and early (July to September) rainy season. Prior to each experiment, the field was brush-cut, disc-ploughed and rotovated. In all cases, four treatments were tested: (1) no mulch, flat-tilled; (2) mulched, flat-tilled; (3) no mulch, ridge-tilled; (4) mulched, ridge-tilled. Each plot was fertilized with urea at a rate equivalent to 112 kg N ha⁻¹. Soil samples were collected weekly at 15 cm intervals between 0 and 60 cm in depth.

Movement of NH₄⁺-N was most dramatic in the bare-fallow plots. High levels (averaging 95 mg kg⁻¹ NH₄⁺-N) were observed in the 30 to 45 cm soil layer seven days after fertilization (DAF). At 14 DAF, most of the NH₄⁺-N had disappeared, suggesting further movement down the soil profile. At 7 DAF under cropped conditions in both the late and early rainy season, increased NH₄⁺-N levels were observed at the 15-30 cm soil layer. The maximum concentration in the 30 to 45 cm depth occurred at 28 DAF in the late rainy season and at 14

DAF in the early rainy season, which can be attributed in differences in precipitation, being 5.9 mm day⁻¹ and 10.7 mm day⁻¹ respectively.

Influence of soil type and fertilizer treatment on ammonium leaching

Soluble and insoluble fertilizer materials were used to compare N leaching in four Florida soils (Benson and Barnette, 1939). Packed columns of varying depths were intended to represent the first two soil layers of each soil (ranging from 0 to 51 cm to 0 to 76 cm in depth). Almost 100% of the NO₃ from the sodium nitrate (NaNO₃) treatment was leached in a Norfolk sand, Bladen fine sand, and Fellowship fine sandy loam in 7.5 cm of drainage. The Norfolk fine sandy loam was the exception at 72.2%. Significant NH₄⁺ leaching (40.3%) only occurred in the (NH₄)₂SO₄ treatment on the Norfolk sand. Little to no N was leached in the urea treatment (2.6% in the Norfolk sand, 1.0% in the Fellowship fine sandy loam, and 0.1% in the Norfolk fine sand loam). A variety of N fertilizers were applied to ten 23 cm columns packed with the Norfolk sand. Columns were allowed to incubate for 21 days; leachates were collected on days 1, 4, 10, and 21. The percentages recovered from the (NH₄)₂SO₄ treatment leachate were 32.0, 41.9, 33.1 and 39.7 respectively. Losses of NH₄NO₃ were fairly consistent (17.3, 15.4, 18.1 and 18.6); ammonium phosphate losses decreased over time (10.6, 14.0, 8.3 and 2.6). Percent N leached was calculated by subtracting the amount of N in the leachate of the treated column from the amount of N in the leachate of the control column, divided by the total N applied.

Noting that the good economic returns of a new type of fertilizer is no guarantee of lasting efficiency, Jenny et al (1945) set out to acquire a better understanding of the behavior of NH₃ and NH₄⁺ salts in soil. When adsorption isotherms were plotted for twenty-three California soils using NH₃ in water (NH₄OH) and (NH₄)₂SO₄, two outstanding features were noted. The amount of N adsorbed varied with soil type and the two fertilizers behaved differently in

different soils. The Yolo clay loam adsorbed more nitrogen from $(\text{NH}_4)_2\text{SO}_4$ than NH_4OH while the Aiken clay loam adsorbed less N overall but more from NH_4OH than $(\text{NH}_4)_2\text{SO}_4$. A Holland sandy loam adsorbed the least and behaved indifferently towards the two N compounds.

Differences in adsorption in the clayey and sandy soils were attributed to the relationship between adsorption with soil texture being greater in fine-textured soils and less in coarse-textured soils. The difference between the two clay soils was attributed to pH. It is likely that as a weak base, NH_4OH increases the CEC of the kaolinitic Aiken clay soils as hydrogen protons dissociate from organic matter and oxides on the outer edges of the clay particles. The exchange reaction between the NH_4^+ ion and H^+ ion is favored due to the affinity for hydrogen bonding; the product of which is a water molecule. Montmorillonite in the Yolo clay is rich in basic cations and has CEC that is not pH dependant. Not enough information is given to clearly explain the difference in adsorption of NH_4OH and $(\text{NH}_4)_2\text{SO}_4$. The explanation given by Jenny et al (1945), that the acidic fertilizer is more likely to be adsorbed by a basic soil, does concur with modern soil science. Certainly, NH_4OH would not have the same self-propelling effect as in the kaolinitic soil. The reason adsorption of $(\text{NH}_4)_2\text{SO}_4$ is somewhat higher than that of NH_4OH is unclear.

Packed columns were used by Jenny et al (1945) to observe the distribution of NH_4^+ in relation to depth. Brass cylinders 15 to 20 cm in length by 2.5 cm in diameter were filled with twelve soil types, ranging from sand to clay. Through each cylinder was passed a NH_4OH or $(\text{NH}_4)_2\text{SO}_4$ solution containing $127 \text{ mg kg}^{-1} \text{ NH}_3$ in a volume corresponding to 1028 m^3 of irrigation water. Nitrogen from both sources permeated more deeply in lighter soils. Distribution was fairly uniform in the Oakley sand soil and appreciable N was found in the leachate. In medium-textured soils, the bulk of N was held in the first 7.6 cm of the column,

with almost none found in the percolating solution. Infiltration of N was limited to the top 5 cm in heavy clay soils. Differences in N distribution in the two clay loam soils were attributed to differences in mineral composition. In the soil with kaolinitic clay particles, a majority of N applied as NH_4OH was retained in the top centimeter. The first and second cm of the column treated with $(\text{NH}_4)_2\text{SO}_4$ contained similar concentrations with N at 10 to 13 cm in depth. These results were related back to the acidic nature of kaolinitic soils and the preference for adsorption of N from NH_4OH over $(\text{NH}_4)_2\text{SO}_4$.

Influence of soil physical characteristics on solute leaching

Movement of soil water and solutes through a soil profile is affected by soil texture and soil structure, which contribute to large and continuous voids called macropores. Over the years, scientific literature has offered several different ranges for dimension limits. Some publications give a pore size range of 0.03 – 300 mm (Beven and Germann, 1982; White, 1985). In general, some pores in the lower part of the range would fill by capillarity, while pores in the upper part of the range would not fill by capillarity. Macropores are present in both structured and unstructured soils. Major types are distinguished as: (1) due to random packing of single grains; (2) compound voids that result from packing of natural aggregates such as peds; (3) vughs or voids significantly larger than (1) that appear as discrete entities; (4) channels significantly larger than (2) and generally cylindrical elongated in shape; and (5) planes that are planar according to the ratio of their principal axes (Bouma, 1991). Most macropore formation can be attributed to soil fauna, plant roots and cracks or fissures that result from desiccation, weathering, freeze/thaw cycles, as well as cultivation techniques like subsoiling. Under favorable conditions, macropores can be formed in one to two years; their effectiveness can be destroyed in one rain event by washed in sediments. The ability for a macropore-sized void to contribute to leaching losses is

dependant on the level of continuity and connectivity with other macropores. In fact, macropores that end abruptly serve as catchments for solutes in the soil solution (Bouma, 1981). While they disproportionately contribute to vertical flow in comparison with the rest of the soil matrix, they contribute little to total porosity.

Cultivation practices both create and destroy macropores. Plowing a soil produces many cracks in the plow layer, which may or not disappear during the growing season (Beven and Germann, 1982). It also cuts through existing macropores, thereby disrupting vertical continuity. Compaction by machinery and grazing animals increases density, destroys macropores and slows infiltration in the upper soil layers. Below plow depth, however, where soil structure is undisturbed, macropores have been found to be responsible for rapid flow in the subsoil (Quisenberry and Phillips, 1976). On five soils in England, subsoiling was determined to increase the number and continuity of macropores in the subsoil (Godwin et al, 1981).

Solute flow that is dominated by macropores and does not infiltrate into the soil matrix is known as preferential flow. Soil texture attributes to two types of preferential flow; fingering and funnel flow, which are not applicable to the scope of this research. However, soils with higher silt content, such as one type used in this study, will have a wetter soil moisture regime, slower wet/dry times and thus limited translocation (Radcliffe and West, 1999). Increasing soil structure similarly increases the soil moisture regime, but also causes preferential flow, which may result in the vertical movement of free water through the unsaturated matrix (Bouma, 1991). Non-equilibrium bypass flow (or channeling) can rapidly transport water to depths deeper than otherwise expected, particularly in soils with low hydraulic conductivities (K_s). In undisturbed soils, the extent depends on soil structure, water/solute application rate, K_s and soil water content.

It is important to note that just as soils are highly spatially variable in terms of soil texture and structure, physical parameters like K_s are also highly variable. Soil pores are characterized by differing sizes and irregular geometry, which affects the velocity (v) of the soil solution as it moves through the profile. Measured values of flow through a soil core are an average of flow through the entire soil matrix. A large portion of the soil matrix is composed of solid particles, which does not participate in flow.

In column experiments, nutrient breakthrough curves (BTC) are useful indicators of preferential flow. The shape of the curve is a measure of macroporosity; early breakthrough is due to fast movement of solute through larger voids. Mobile regions in the soil matrix develop more rapidly due to root penetration along planes of weakness. As microbial and faunal activity increases in these regions, so does water penetration and differentiation from the surrounding areas. Similarly, soil cation exchange capacity (CEC) must be considered in terms of “active” and “non-active”. Infiltrating soil water must come into contact with CEC sites in order for ions in solution to participate in exchange, differentiating “available” CEC from “accessible” CEC (Bouma, 1991).

The above techniques were used in this research. Following an field mass balance study on a sandy site in the coastal plain, disturbed and undisturbed soil columns experiments will be performed on three soils selected to represent the range of NH_4^+ -N leaching potential in a research field in Crisp County, Georgia. The movement of NH_4^+ -N through soils with varying soil texture, water holding capacity, pH and CEC will be measured in an attempt to describe the mechanisms of transport of NH_4^+ -N to lower soil profile horizons.

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Chapter 3

AMMONIUM LEACHING IN COASTAL PLAIN SOILS

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ABSTRACT

Because of the relatively low cost of production and their high N content, the vast majority of N fertilizers used in crop production are ammonium-based. Previous research on three soils representing the range of characteristics within a field in Crisp County, Georgia documented the presence of NH_4^+ -N to 120 cm in unfertilized plots at planting and after the growing season, indicating some potential for NH_4^+ -N leaching, especially in sandy soils. Based on these findings, a series of mass balance studies were performed in an attempt to duplicate the conditions that led to NH_4^+ movement into lower soil profile depths. Field and undisturbed soil column studies indicated that while each of the experimental soils differed in texture, percent carbon and CEC, each had some potential to transport NH_4^+ -N past the surface soil horizons and into lower soil horizons.

INTRODUCTION

The coastal plain region of Georgia is distinguished from the rest of the state by age, topography, and parent material. Large portions of parent material are marine sediments translocated from the upland Piedmont region. Although the area is considered relatively young in geologic terms, much of this material was already weathered at the time of deposition allowing soil development to occur more rapidly. Ultisols characteristic to the region are highly weathered and acidic due to extreme leaching of basic cations. Millions of years of high temperatures and precipitation have intensely weathered primary and secondary clay minerals, forming the kaolinitic clays that dominate the state. Marine sediments are low in basic cations from prior weathering and are very sandy by nature. Sand both facilitates leaching and contributes little to CEC. Characteristic of an Ultisol, clays are concentrated in the subsurface

horizons making their CEC of little benefit to most agricultural crops. In this highly acidic environment, nitrification rates decrease dramatically and adsorbed NH_4^+ ions can accumulate.

In cultivated areas, surface soils are routinely tilled to a depth of 30 cm, which disrupts the formation of soil structure. Conventional plowing can compress a layer of soil into a hardpan at about 15 cm. Annual subsoiling breaks up the hardpan, allowing greater water percolation and deeper root penetration. Increased clay content in the subsoils translates into better-developed soil structure. A typical coastal plain Ultisol has weak to medium subangular blocky structure in the Bt soil horizon. The spaces between the soil aggregates create pathways for preferential flow of the soil solution.

The Cabin field in Crisp County, Georgia has repeatedly been utilized for research at the University of Georgia. To further refine the science of precision agriculture, researchers investigated the influence of soil properties on N mineralization rates (Egelkraut, 1999). Three soils were selected to represent the continuum of N mineralization potential across the field. The soils were classified as the Norfolk coarse-loamy (a taxadjunct to the Norfolk series), a coarse-loamy, kaolinitic, thermic Typic Kandiudult, (designated North and Center locations respectively), and as the Norfolk depressional, a fine-loamy, kaolinitic, thermic, Typic Kandiudult (designated South). Four check plots selected at each study location were used to measure the N mineralized from soil organic matter. Samples were taken to a 120 cm depth at 15 cm intervals at the beginning and end of the study, in May and September respectively. Cotton (*Gossypium hirsutum* L.) (Delta Pineland 90) was grown in both the study year and the year preceding. Data analysis showed that NH_4^+ -N was present below the plow layer and to depths of 90-120 cm prior to planting and late in the growing season (Table 1). Interpretation of the results could not be attributed to one or any combination of known soil characteristics.

Yields tended to be higher at the South position, which means more residue and more potential N mineralization. In the late growing season, total $\text{NH}_4^+\text{-N}$ was comparable in the South (18.24 kg ha^{-1}) and Center (17.13 kg ha^{-1}) positions, and less in the North position (7.83 kg ha^{-1}). The difference between the North and Center locations is unexpected in soils with such similar characteristics. Concentrations tended to increase with depth, being significantly less in the plow layer (0 to 30 cm) than at lower depths. Peak concentrations occurred at 60 to 90 cm in the North and Center locations, and at 90 to 120 cm in the South location. Based on these findings, the following study was designed to investigate the effect of soil variability and cultural practices on the movement of $\text{NH}_4^+\text{-N}$ through the soil profile.

MATERIALS AND METHODS

Preliminary mass balance experiment

A mass balance experiment was conducted in Crisp County, Georgia, on a Fuquay soil (loamy, kaolinitic, thermic Arenic Plinthic Kandiodults) using ammonium sulfate fertilizer. A 12 x 24 m field area was divided into eight 6 x 6 m plots in a randomized complete block design, with two treatments (fertilized and unfertilized). In November 2003, AS was broadcast at a rate of 112 kg N ha^{-1} soil. In late May 2004, soil samples were collected in 15-cm intervals to a depth of 30 cm, and then in 30-cm depth increments to 120 cm. Four replicate samples at each depth were collected on a diagonal transect across each plot and composited. The soil was air-dried, ground and passed through a 2-mm screen. Soils were extracted with Melich 1 extract and analyzed for total S with a Thermo Jarrel Ash ICP, model 61E. Ammonium and nitrate was extracted using 5 g soil in 40 mL of 1 N KCl and analyzed on an Alpkem RFA 300 from Alpkem Corp., Clackamas, OR. Soil pH was measured using a 1:1 soil:solution ratio in a 0.01 M CaCl_2 solution while being stirred using the method described by Thomas (1996).

Bulk soil sample collection

Bulk soils were collected from the Cabin field in the NW corner Crisp County, Georgia in May 2004. Three soil series were selected to represent the range of variability of physical characteristics across the field, including Norfolk, Norfolk depressional (fine-loamy, kaolinitic, thermic Typic Kandiudults), and Bonifay (loamy, siliceous, subactive, thermic Grossarenic Plinthic Paleudults). A shovel was used to collect samples to 30 cm from the Norfolk and Norfolk depressional soils. In the Bonifay series, bulk soil was obtained separately from 0 to 15 cm and 15 to 30 cm in depth. Soils were air-dried, well mixed, and sieved using a 2-mm screen, then placed in a sealed bucket.

Soil characterization

Particle size distribution was determined by the pipette method (Kilmer and Alexander, 1949). Soil pH was measured in a 0.01 M CaCl₂ solution while being stirred (Thomas, 1996). Cation exchange capacity (CEC) was determined using the ammonium acetate (pH 7) method (Sumner & Miller; 1996). Subsamples were analyzed for C with a CNS-2000 elemental analyzer from LECO Corp., according to methods described by Kirsten (1983). Bulk densities were calculated from the oven dry weight of small soil cores (8.5 cm diameter x 6 cm depth) taken at a soil depth of 15 cm. A pressure chamber and 0.1 MPa ceramic plate was used to determine gravimetric water contents (w) at field capacity. Bulk samples were wetted with a 0.01 M solution of CaCl₂, then 0.1 MPa of pressure was applied for 3 days. Soil samples were weighed, then allowed to dry for 24 hours at 105°C. Gravimetric water content was calculated according to the following formula: (wet weight – dry weight)/ (dry weight – container weight). The following were calculated accordingly: volumetric water content (θ_v) = bulk density * w ; and porosity (ϕ) = 1 – (bulk density/2.65).

Adsorption Isotherms

Adsorption isotherms were developed for each of the four bulk soil types. Samples were prepared using 5 g soil in 40 mL of NH_4Cl prepared to concentrations between 0 to 4.5 meq L^{-1} , shaken for 2 hours, centrifuged and then poured into 20-mL scintillation vials. Results were compiled using Sigma Plot version 9.0 from Systat Software, Inc., Point Richmond, CA. Using Freundlich isotherms, the amount of $\text{NH}_4^+\text{-N}$ adsorbed ($\text{meq } 100 \text{ g soil}^{-1}$) vs. the concentration of $\text{NH}_4^+\text{-N}$ in solution (meq L^{-1}) was plotted. The distribution coefficient (K_d) is an isotherm parameter that defines the soils' capacity to adsorb organic and inorganic compounds. A greater value of K_d is indicative of a greater capacity to adsorb. When dealing with inorganic compounds, the Freundlich exponent (n) is primarily used to describe the shape of the isotherm, being concave when $n > 1$, linear when $n = 1$ and convex when $n < 1$.

Undisturbed soil core collection

Two types of soil cores were collected from the Bonifay, Norfolk and Norfolk depressional soils. After the top 12 cm of soil was cleared from several areas within a given soil type, small metal cores (7.5 cm diameter by 7.5 cm depth or 8 cm diameter by 6 cm depth) were driven into the soil using a rubber mallet and a block of wood. The area around the core was cleared of soil, and a flat shovel was inserted a few centimeters below the bottom in order to lift out the core. Both sides were shaved with a knife in order to level the volume of soil, then the cores were wrapped in cheesecloth. PVC sleeves (15.5 cm diameter) were similarly driven into the soil to a depth of 30 cm. Soil in the surrounding area was removed with a shovel, before a flat shovel was inserted into the soil 3 to 5 centimeters below bottom of the sleeve. A knife was used to shave the soil on the bottom to level, then the bottom of the column was secured with newspaper and duct tape. The columns were taken from areas between crop rows, with the

exception of those labeled ND7, ND8, ND9. These were taken from within a row that had been planted in cotton, after the crop had been harvested.

Determination of soil hydraulic properties

Saturated hydraulic conductivity (K_s) was determined using the small soil cores. Empty cores with the same dimensions were fitted to the top of the small core and sealed with parafilm. A dilute solution of CaCl_2 (0.01 M) was applied using a Mariotte siphon to maintain constant depth of ponding. Leachate volumes were collected and recorded in 5-minute intervals, until the flux rate stabilized. Values of K_s were calculated using the formula $K_s = (\text{vol} * L) / (\text{area} * t * (L + b))$; where vol = leachate collected (cm^3), L = length of core (cm), area = cross-sectional area of core (cm^2), t = time (h) and b = depth of ponding (cm). Other hydraulic properties were calculated as follows: Darcy flux (J_w) = $-K_s * ((L + b) / L)$; and velocity (v) = J_w / ϕ (ϕ assumed to be equal to θ_s).

In the larger intact soil cores, values of J_w were determined from the average rate of flow over the experimental period. From this average, K_s was calculated using the formula $K_s = J_w * ((L + b) / L)$ and velocity (v) = J_w / θ_s . Values of J_w were similarly determined in packed columns, while velocity was calculated using the volumetric water content (θ_v) calculated for each individual experiment. No values of K_s could be measured in the packed columns, as there was either no ponding or no specific value for depth of ponding (b).

Undisturbed soil - 15.5 diameter column preparation

Hose barbs (0.6 cm diameter) were inserted into the outside center of nine 15 cm wide PVC caps, which were inverted and placed on 20 cm tall ring-stands. Into each cap was placed a layer of cheesecloth, and then 1 cm of coarse sand. The 30 cm long undisturbed soil cores were saturated with DI water, allowed to drain for 2-3 days, and then placed inside the PVC caps. The

PVC sleeves were lifted up and removed. The bare soil columns were coated with several layers of liquid saran (1:7 dilution in Acetone) using a squeeze bottle. After the saran dried, poster board (waxy-side facing in) was secured tightly around the PVC caps and loosely around the soil core (minimum gap of 1 cm) with four to six ring clamps. A large funnel was inverted and set on top of the soil, before molten paraffin wax was poured down the sides to just below the top of the soil core. The funnel was removed and a PVC ring (15.5 cm diameter by 12 cm long) was pressed over the top of the core into the wax, in order to facilitate ponding at the soil surface. After 24 hours, the ring clamps and poster board were carefully removed, and any possible air holes were filled with warmed paraffin wax.

Prior to leaching experiments, the top 1 cm (273.9 g soil) was removed, mixed with NH_4Cl at a rate equivalent to 168 kg N ha^{-1} (1.012 g NH_4Cl), and returned to the top of the column. Distilled water was applied to the surface using a Mariotte siphon. Plastic buckets were used to collect drainage in approximately 1 cm (200 mL) increments. Total volume of each increment collected was well-mixed and a representative sample was poured into a 20-mL scintillation vial and frozen until analysis. Collection time and mass of leachate were recorded at each interval, and depth of ponding was measured at regular intervals.

Disturbed soil – 4.3 diameter column preparation

A plexiglass cylinder (4.3 cm diameter and 34 cm long) was built for the packed column experiments. At the base, a 1 cm thick detachable plate included an o-ring and a drainage hole was fitted with a 0.5 cm hose barb. Filter paper was placed between the column base and plate and washed diatomaceous earth was loosely packed to a 1-cm depth prior to packing. Loose soil was packed to varying bulk densities at 7.5-cm increments to 29 cm. Into the last cm of soil (~23 g) was mixed NH_4Cl at a rate equivalent to 168 kg N ha^{-1} (0.08 g NH_4Cl). Filter paper was

placed on top of the soil and covered with 1 cm of coarse sand. The column was suspended on a ring stand with a clamp. Using a peristaltic pump, water was applied to the top by a cylindrical plexiglass rainfall simulator cap fitted with nine 23 gauge syringes spaced 1.5 cm apart. At the first drop of solution from the bottom of the column, the column was weighed and wet weight was divided by dry weight to determine gravimetric water content (w), which was multiplied by the bulk density to calculate θ_v . When the column was returned to the ring stand, suction was applied to the bottom of the column via plastic tubing, which was attached to a fraction collector. Fractions of the solution were collected at various time intervals until at least one pore volume was collected. Samples were weighed in tared glass tubes, transferred into 20-mL scintillation vials and stored in a freezer. Samples were analyzed for NH_4^+ and Cl^- .

Soil samples were extracted using 5 g soil in 40 mL of 1 N KCl. All NH_4^+ analysis was performed using EPA method 350.1 Rev 2. on an AquaKem 200 by EST Analytical, Fairfield, OH. Chloride analyses were performed on both the Aquakem 200 and with a digital chloridometer (model 442-5000, Lanconoco, Kansas City, Missouri). Nitrate analysis was performed using a Dionex DX-120 ion chromatograph.

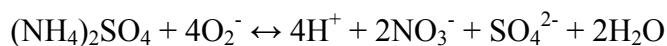
RESULTS AND DISCUSSION

Based on the findings of the Egelkraut study (1999), a mass balance study was carried out at a sandy site in an attempt to duplicate the conditions that led to NH_4^+ movement into lower soil profile depths. Those conditions were believed to be: 1. a sandy soil with low CEC that might not retain all NH_4^+ against leaching; and 2. a soil with low pH, which is known to greatly slow the rate of nitrification, thereby increasing both the time that applied N fertilizer remains in the soil as NH_4^+ and the opportunity for leaching rains to move NH_4^+ down to deeper depths in the soil.

Preliminary mass balance study

The amount of precipitation during the study period was 45 cm, enough to cause considerable leaching given that the plots were kept relatively free of vegetation during this time period. Major rainfall events that would have led to leaching took place during November 2003, January 2004, February 2004 and May 2004 (Table 2).

In the soil, ammonium sulfate reacts according to the following equation:



Acidity produced by the fertilizer resulted in lower average pH values in the 0-15 and 15-30 cm depths (Figure 1). Although average pH values indicate steady increases with depth, the individually measured values overlap considerably. Percent recovery of NH_4^+ -N, NO_3^- -N and S was calculated by subtracting the concentration found in the treated plot from the control. All of the NH_4^+ -N recovered (2.1%) was found in the top 15 cm of soil (Figure 2). In both the 0 to 15 and 15 to 30 cm depths, more acidic pH values in the treated plots may indicate slowed rates of nitrification. Of the 34% of the applied N recovered as NO_3^- -N, most was located in the 30 to 120 cm depths, although 8% was found in the 0 to 15 cm soil depth (Figure 3). In contrast, the recovery of S was much lower (4%), and all of it was measured in the 30 to 120 cm depths (Figure 4). The difference in the leaching of N and S was probably due to the fact that all S from the fertilizer was present in the highly leachable sulfate form beginning on the date of application, whereas there would have been a significant delay in nitrification, causing the N from the AS to remain in the much less leachable NH_4^+ form during a substantial time period between AS application and sampling of the soil. This is supported by the fact that 9 kg N ha⁻¹ of NO_3^- -N was found in the 0-15 cm depth, whereas no sulfate was found in the surface layer at the

time of sampling the soil. In both treatments, S concentrations increased in magnitude and variability with depth, particularly in the 90 to 120 cm depth. This was possibly due to the increase in clay content at this depth, which probably restricted downward movement of water. It is also quite likely that some anion exchange may have occurred at these depths due to higher iron oxide contents associated with the clays and the acidic pH.

Although there was no significant leaching of NH_4^+ to deeper soil layers observed in this study, it was noted in the study by Egelkraut et al (1999) that NH_4^+ can be found at the deeper depths. The movement of NH_4^+ to depths below 30 cm was noted in other crop production fields in the area (unpublished data). In order to better understand the process of NH_4^+ movement in coastal plain soils, some column leaching studies were initiated.

Column leaching studies

Some pertinent soil physical and chemical characteristics are given in Table 3. The Norfolk depressional soil contained the greatest amount of carbon, silt and clay. As a result, it had a greater CEC and water holding capacity than the other soils. The Norfolk soil and Bonifay subsoil were very similar, with the Bonifay subsoil being greater in clay content and CEC. The Norfolk has more sand, silt, and 50% more carbon, which at pH 4.6, contributes little to variable charge CEC but increases water holding capacity. The Bonifay topsoil is differentiated from the others by high sand content, low silt and clay content, low carbon and the highest pH (5.2).

Adsorption isotherms reflected the differences in CEC, with the Bonifay topsoil having the lowest value for K_d (0.267) (Figure 5). Greater in terms of adsorption capacity was the Norfolk soil (0.370) (Figure 6), the Bonifay subsoil (0.504) (Figure 7) and the Norfolk Depressional (0.748) (Figure 8). In all cases, r-square values were greater than 0.98. Only the

Bonifay topsoil had an n value greater than one, reflecting a tendency for this soil type to increase in adsorption capacity with increasing solution NH_4^+ -N concentration.

Little difference was found in the average bulk density of the undisturbed soil columns (Table 4). Average gravimetric water content (w_{fc}) and volumetric water content (θ_{fc}) at 0.033 MPa were greatest in the Norfolk depressional soil and equal in the Norfolk and Bonifay soils. Porosity, inversely related to bulk density, was the same in the Norfolk and Norfolk depressional soils (0.40), and only slightly greater in the Bonifay soil (0.42). Because the Norfolk depressional soil has a greater capacity to retain water, the same volume of pore spaces effectively contains different volumes of water. Structured clay soils can have lower bulk densities and higher porosity than sandy soils when structure has had the opportunity to develop. The opposite trend is shown to exist in these data, likely due to the recent interruption of soil structure development.

Soil hydraulic conductivity

Results of the small cores (7.5 cm diameter, 7.5 cm length or 8 cm diameter, 6 cm length) varied greatly from that of the large core (15.5 cm diameter, 30 cm length) (Table 5). Treatments differed in the chemical composition of the leaching solution. To prevent clay dispersion, a dilute solution of CaCl_2 (0.01 M) was used to measure saturated hydraulic conductivity (K_s) in the small cores. Distilled water used in the 30-cm cores most likely caused some dispersion, which could have slowed flow. More likely, differences can be attributed to the smaller volume and greater level of pore connectivity in the smaller core. Solute traveling through the smaller volume of soil for a shorter distance would have a more direct path to follow. Furthermore, the sidewalls of the longer core would block flow in a larger proportion of non-vertical pores. By nature, smaller cores are less representative of the actual hydraulic properties

of the soil. Additionally, soil texture was sandier towards the surface in all soils except for the Norfolk depressional (Table 1). Overall, measured values of K_s and J_w were fairly consistent in the small and large cores with rates in the larger cores being less than in the smaller cores due to differences of the physical volume and range of textural and structural qualities.

Intact soil columns – Differences among soil types

The Bonifay soil columns were distinguished by the presence of approximately 15 cm of sandy soil over 15 cm of loamy sand soil. In contrast to the Norfolk and Norfolk depressional soils, which have been moldboard plowed to a depth of 30 cm within the past two years, this portion of the field had not been moldboard plowed in approximately ten years. The more clayey lower layer had different hydraulic properties that offset the effect of the sand layer (Table 5). From this soil type, columns averaged the greatest amount of NH_4^+ -N recovered in leachate in the shortest amount of time (Table 6). Peak concentrations varied from 28.8 to 36.4 mg L^{-1} and occurred between 0.5 - 1 pore volume (Figure 5). For each column, chloride peaks were more closely centered around 0.5 pore volume (Figure 6). With the longest run time, chloride in column BF3 appeared gradually over 2.6 pore volumes, with a greater percent NH_4^+ -N recovered in comparison (18%). Lower velocity (44.0 cm hr^{-1}) in this column suggests a greater influence of the more clayey subsoil on this column and a greater water holding capacity, perhaps due to increased macroporosity and/or water retaining soil constituents. The greater percent NH_4^+ -N recovered is contrary to what would be expected, and appeared to be related to the earlier appearance and greater concentrations of NH_4^+ -N in the leachate (Figure 5). Rapid flow through macropores can account for the early part of the curve, while concentrations at the tail end could be due to more opportunities for base cation exchange reactions with adsorbed NH_4^+ ions in a slow moving system.

Of the Norfolk soil columns, NF2 and NF4 performed remarkably similarly (Table 7). Peak NH_4^+ -N concentrations occurred within a 0.1 difference in pore volume, with breakthrough curves that were virtually the same (Figure 7). In column NF2, 100% of the chloride was recovered earlier than in column NF4 (Figure 8), accompanied by an earlier breakthrough of NH_4^+ -N.

The NF3 column differed radically in flow time and hydraulic properties; experiment duration was about one third of NF2 and NF4, velocity was four times greater, and peak NH_4^+ -N concentration and percent NH_4^+ -N leached were dramatically larger (Table 7). Had the NF3 column not been included in the average values found on Table 7, the coefficient of variance for the flow rate data would be improved from 0.86 to 0.09. While the data suggested rapid solute flow through fewer macropores, the bulk of the chloride breakthrough curve was spread out over two pore volumes, and small amounts were still being measured at three pore volumes. One apparent explanation for this was the presence of anion exchange sites, which would delay the progress of the solute front. Being the most acidic of the experimental soils, variable charge AEC would be greatest in the Norfolk soil. Additionally, diffusion of soil solution into immobile regions could slow the progress of the solute front. Ions that diffuse into these regions would only slowly move back into the bulk solution where they would be available for leaching.

Results were variable for all three of the Norfolk depressional soil columns (Table 8). Because the ND5 column differed so dramatically from the others, it was not included in the averages presented in earlier tables. This soil type is differentiated by being higher in carbon, silt and gravimetric water content. The only discernable trends between ND4 and ND6 were NH_4^+ -N and Cl^- concentrations greater than zero in the first leachate fraction, and similar peak NH_4^+ -N concentrations and percent NH_4^+ -N leached (Figure 9 and Figure 10). After the first peak and

subsequent drop off of the ND4 column, the curve shadows that of the ND6 column with about one half of a pore volume lag time. Average velocity of the ND4 column was twice that of the ND6 column.

More clay, carbon and relatively higher pH result in more CEC in the Norfolk depressional soil. Solute interaction with water holding soil constituents can slow flow and increase interaction with CEC sites, making them more accessible. While less total NH_4^+ -N was recovered in leachate, small concentrations were still being leached between 2-3 pore volumes. Results indicate that while a small concentration of NH_4^+ -N flowed quickly and directly through the larger pores, the majority was adsorbed as soil water percolated through smaller pores and held by immobile regions that were unsaturated at the beginning of the experiment.

Slower velocity differentiates the ND5 column. Almost 20 hours were required to leach two pore volumes, over which the velocity dropped precipitously. Dispersion of clay and organic matter is likely responsible for blocking macropore flow. Both NH_4^+ -N and chloride were measured in the final leachate fractions at the end of the twenty hour period.

Experiments on columns taken from within rows in order to examine the effects of in row chisel at planting and cotton root channels in the Southern end of the field did not yield increased percent NH_4^+ -N recoveries as expected. While the ND7 column performed drastically differently than the other, it was included in the averaged results (Table 9) because it maintained a fairly constant rate of flow. It is likely that the difference can be attributed to natural variation. Slower velocity mirrors the behavior of the ND5 column, but flow velocity remained fairly constant over time. Like the Norfolk depressional soil columns from between rows, lower recoveries of NH_4^+ -N can be attributed to greater solute interaction with accessible CEC as the solution slowly percolates through the column and diffuses into immobile regions (Figure 11).

Unsaturated regions would function like a sponge; soil solution diffuses slowly into immobile regions where it is held by capillary forces. Like the previous ND columns, the chloride breakthrough curves were dispersed over the experimental period (Figure 12).

Packed column experiments – Differences between soil types and intact columns

In general, column experiments involving repacked soil were problematic. Except for the sandy Bonifay topsoil, it was virtually impossible to pack columns to bulk densities close to those of the intact columns. Constant flux was difficult to maintain in most cases, particularly when packed to higher bulk densities. The system frequently overflowed, likely due to clay dispersion. Destruction of soil structure destroyed all macropores but those that existed due to random arrangement of packed sand grains (Bouma, 1991.), and broke up immobile regions so that all regions participated equally in flow. Increased exposed surface area of clay particles increased the number of accessible CEC sites. With a few exceptions, 100% of the applied chloride was recovered in the leachate before or around one pore volume, reflecting uniformity and good connectivity in pore size distribution (Figure 14).

From several repetitions of packed column experiments with the sandy Bonifay topsoil, the two represented in this paper maintained the most constant flux. In both the BT P1 and BT P2 columns, NH_4^+ -N concentrations peaked after one pore volume (Table 10). After the peak, the concentration dropped but remained fairly consistent in subsequent leachate fractions, even increasing with time in the BT P2 column (Figure 13). Although this column had a percent NH_4^+ -N recovered in leachate comparable to that of the intact Bonifay columns, the Darcy flux was considerably slower (0.96 cm hr^{-1} vs. an average of 5.76 cm hr^{-1}). Peak concentrations were much lower and occurred later in the packed columns. Despite the fact that these were more

homogeneous in soil texture and structure, chloride breakthrough curves generally occurred later in relation to the intact columns (Figure 14).

Bonifay subsoil packed columns were typified by low percent NH_4^+ -N recoveries and low peak NH_4^+ -N concentrations (Table 10). Relative concentrations of NH_4^+ -N fluctuated over time (likely due to experimental error because of concentrations below detection limits), particularly in the BS P2 and BS P3 columns (Figure 15). In all cases, peak concentration corresponds with the initial leachate fraction, followed by a fairly steady flux in the BS P1 column, more erratic flux in the BS P2 column and apparent NH_4^+ -N pulses in the BS P3 column. The chloride breakthrough curve for the second column is distinguished by an abrupt beginning at 0.5 pore volumes and ending at 1.5 pore volume (Figure 16). Coupled with the 160% recovery of applied chloride, the presence of AEC is suggested. Chloride at the beginning of the solute front could have been delayed by available AEC. Once the sites were saturated, the breakthrough curve began almost instantly.

Only one experiment was performed using the Norfolk soil. Based on recoveries of total N and Cl⁻, it was presumed that this was a good representative of the behavior of NH_4^+ -N in a repacked Norfolk soil (Table 11). Although comparable to the averaged BS packed columns in percent NH_4^+ -N leached and early peak concentration (Figure 17), the chloride breakthrough curve started at a greater initial amount and reached its maximum in less than half a pore volume (Figure 18). By nature of increased surface area and accessible CEC in repacked soils, adsorption capacity could be more than enough to impede the movement of NH_4^+ -N through the column.

The Norfolk depressional soil was by far the slowest draining of the repacked soil columns. An average of forty-seven hours was required to leach 1.25 pore volumes (Table 12).

Leachate NH_4^+ -N concentrations either zero or slightly greater, with the exception of intermittent pulses from the ND P1 column (Figure 19). Like the repacked NF columns, chloride breakthrough curves started high and maxed out around 0.5 pore volumes (Figure 20). Apparently, CEC from clay minerals and organic matter was sufficient to adsorb 99% of applied NH_4^+ -N. A comparison of the average disturbed and undisturbed column percents NH_4^+ -N and Cl^- leached is found in Table 13.

Influence of soil structure on ammonium leaching

At the time the 30 cm intact soil cores were collected, the North end of the field had not been moldboard plowed in about ten years. Sufficient translocation of clays had resulted in two different soil textures above and below 15 cm. It is more than likely that soil structure had developed in the subsoil over this time. Although bulk Bonifay subsoil in packed columns effectively retained applied NH_4^+ -N, macropores in the intact columns allowed for relatively high velocities of solute flow, with relatively high NH_4^+ -N concentrations and high percent recoveries in leachate.

Having been plowed to a depth of 25 to 30 cm in the winter before collection, the Norfolk 30 cm intact cores would be more homogeneous in pore size distribution. Although comparable with the Bonifay soil series in θ_{fc} , solute traveled through less directly connected pores associated with unstructured soils resulting in longer experiment duration and lower velocities. Low values of pH reduces the effectiveness of CEC from clay materials and organic carbon, so appreciable amounts of NH_4^+ -N were conducted through the columns, albeit at a slower rate. At the time of collection, it was difficult to drive the PVC sleeve into the last few centimeters of the top 30 cm, suggesting that a few centimeters of hardpan were included in the columns. It is also

possible that the NF3 column was collected close enough to the row to include the effect of subsoiling and therefore conducted applied NH_4^+ -N more efficiently and effectively.

In the two winters since the Southern end of the field was turned, there would have been some opportunity for the development of structure in the Norfolk depressional soil. Although it would be mostly homogeneous, a few well connected macropores could be responsible for the relatively moderate velocities and experiment duration times. However, the organic carbon, clay and silt materials would act like a sponge, absorbing soil water and NH_4^+ -N which would only be slowly diffused back out into the bulk solution.

Regardless of how laboratory soil cores reproduce the behavior of solubilized NH_4^+ in the top 30 cm of cultivated field, what is going on below that depth is going to be more influential on the movement of NH_4^+ -N into deeper profile depths. A typical pedon of the Fuquay soil series has redox features starting at 120 cm. If the AS fertilizer applied in the preliminary mass balance study had encountered a raised water table, it could easily be removed as the water table dropped. Rising and falling water tables increase the rate of soil structure development. From 86 to 114 cm, the typical pedon has weak medium subangular blocky structure followed by weak medium angular blocky structure from 114 to 178 cm, providing distinct pathways for the movement of ions in the soil solution.

The Bonifay soil series is characterized as very deep, well drained and moderately slowly permeable. A typical Bonifay pedon has eluvial soil horizons to 120 cm with sand textures. Below 120 cm are loamy sand over sandy loam textures with of clay and iron accumulations and a weak to moderate medium angular blocky structure. In the cultivated soils of the Cabin field, the top 30 cm mimics this natural system, having a sandy over a loamy sand texture. In the field, the character of eluvial horizons to 120 cm are naturally conducive to solute leaching.

A typical pedon of the Norfolk series is similarly characterized as very deep, well drained and moderately permeable. It differs from the Bonifay series by having eluvial soil horizons to 35 cm with loamy sand texture. From 35 to 43 cm is a sandy loam B horizon with weak medium subangular blocky structure. Subsequently to 250 cm, are B, BC and C horizons with sandy clay loam texture with weak medium subangular blocky or massive structure. Redoximorphic features begin at 150 cm. Between 30 and 120 cm, increases in clay content would correspond with finer pores and more accessible CEC which could retain NH_4^+ -N. Norfolk depressional soils are distinguished by greater amounts of carbon, silt and clay, and a less acidic pH. Thus, while the Norfolk soil would appear to have more in common with the Bonifay series in terms of surface soil texture and CEC, in the field, this soil have a greater capacity to retain NH_4^+ -N like the Norfolk depressional.

Chapter 4

CONCLUSIONS

In all cases except the sandy Bonifay topsoil, bulk soils used in the packed column experiments effectively retained applied NH_4^+ -N. In the intact soil columns, increased amounts of leached NH_4^+ -N can be attributed to the presence of macropores associated with soil structure. However, these 15.5 cm diameter by 30 cm length cores apparently do not represent the natural systems adequately enough to reproduce the conditions that led to findings of the Egelkraut study. Further investigation of a larger section of the soil profile, including the outer limits of a row and the incision made by the subsoiling shank, would provide better clues to the movement of NH_4^+ -N in cultivated soil that has resulted in NH_4^+ -N accumulations with depth.

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Table 1. Average NH_4^+ -N concentration (kg ha^{-1}) with depth in May and September from unfertilized plots in the study by Engelkraut (1999).

Depth(cm)	May [†]			Sept [†]		
	North	Center	South	North	Center	South
	-----kg ha ⁻¹ -----			-----kg ha ⁻¹ -----		
0-15	0	0.77	0.07	0.18	0.32	0.35
15-30	0	0.20	0.00	0.64	0.60	1.51
30-45	0	0.59	0.39	1.42	2.44	3.07
45-60	0	0.34	0.51	1.17	3.36	2.89
60-90	0.14	1.22	0.44	2.55	5.43	3.70
90-120	1.50	0.43	1.14	1.87	4.98	6.74
Total	1.63	3.56	2.54	7.83	17.13	18.24

[†]Determined by colorimetric methods using Perstorp Analytical Autoanalyzer (500 series) after extraction with 2 M KCl.

Table 2. Rainfall data for the study period from the Crisp County Power Commission in Cordele, GA.

Month	Rainfall (cm)
November	7.1
December	5.1
January	6.8
February	13.8
March	0.6
April	3.1
May	8.8

Table 3. Particle size distribution, CEC, %C, initial NH_4^+ -N concentration and pH of the study soils.

Soil	Depth	Soil texture	Sand [†]	Clay [†]	Silt [†]	ECEC [‡]	%C [§]	NH_4^+ -N [¥]	pH [¶]
	cm		-----g kg ⁻¹ -----			cmol ⁺ kg ⁻¹		mg kg ⁻¹	
Bonifay topsoil	0-15	Sand	911	45	44	3.27	0.28	0.000	5.2
Bonifay subsoil	15-30	Loamy sand	816	120	64	4.99	0.18	0.000	4.9
Norfolk topsoil	0-30	Loamy sand	861	64	75	3.57	0.40	8.46	4.6
Norfolk subsoil	30	Loamy sand	835	90	70	4.20	0.44	6.41	4.8
Norfolk depressional topsoil	0-30	Sandy loam	558	190	252	10.72	1.37	12.72	5.0
Norfolk depressional subsoil	30	Sandy loam	745	151	105	8.91	0.69	11.20	4.6

[†] Particle size distribution determined with pipette method (Kilmer and Alexander, 1949).

[‡] Determined using the ammonium acetate (pH 7) method (Sumner & Miller; 1996).

[§] Analyzed with a CNS-2000 elemental analyzer from LECO Corp., according to methods described by Kirsten (1983).

[¥] Analyzed using EPA method 350.1 Rev 2. with AquaKem 200 by EST Analytical, Fairfield, OH.

[¶] Measured in a 0.01 M CaCl_2 solution while stirring, according to methods described by Thomas (1996).

Table 4. Physical and hydrological characteristics of undisturbed soil columns.

Soil Series	Soil texture [†]	Bulk density [‡]	w_{fc} [§]	θ_{fc}	ϕ
		g cm^{-3}	g g^{-1}	$\text{cm}^3 \text{cm}^{-3}$	
Bonifay	Sand/Loamy sand	1.55	0.06	0.09	0.42
Norfolk	Loamy sand	1.60	0.06	0.10	0.40
Norfolk depressional	Sandy loam	1.59	0.16	0.25	0.40

[†]Texture determined by particle size distribution with pipette method (Kilmer and Alexander, 1949).

[‡]Determined using ring method on small soil cores (7.5 cm diameter by 7.5 cm length, or 8 cm diameter by 6 cm length).

[§]Determined at in pressure chamber at 0.033 MPa.

Table 5. Average flow data from small cores (7.5 cm diameter by 7.5 cm length, or 8 cm diameter by 6 cm length) and large cores (15.5 cm diameter by 30 cm length).

Soil series	7.5-cm cores			30-cm cores		
	K_s^{\ddagger} cm hr ⁻¹	J_w^{\S} cm hr ⁻¹	v^{\dagger} cm hr ⁻¹	K_s^{\parallel} cm hr ⁻¹	$J_w^{\text{¥}}$ cm hr ⁻¹	v^{\dagger} cm hr ⁻¹
Bonifay surface soil	23.95	30.00	72.29	-	-	-
Bonifay subsoil	12.52	16.70	40.22	-	-	-
Bonifay average	18.23	23.35	56.25	5.88	5.76	13.88
Norfolk	18.88	25.81	65.13	2.16	1.99	5.01
Norfolk depressional	18.14	25.16	62.90	4.19	3.85	9.62

[‡]Calculated using the formula $K_s = (\text{vol} * L) / (\text{area} * t * (L+b))$; where vol = leachate collected (cm³), L = length of core (cm), area = cross-sectional area of core (cm²), t = time (h) and b = depth of ponding (cm);

[§]Calculated using the formula $J_w = K_s * ((L+b)/L)$.

[†]Calculated using volumetric water content at saturation or porosity.

[¥]Determined from the average rate of flow over the experimental period.

Table 6. Physical characteristics and results of leaching experiments in Bonifay intact soil columns.

Column ID	Run time	Bulk density [†]	K _s	J _w	v	NH ₄ ⁺ -N leached [‡]	Peak concentration [‡]	Cl ⁻ leached [§]	Total pore volumes
	h:min	g cm ⁻³	cm hr ⁻¹	cm hr ⁻¹	cm hr ⁻¹	%	mg L ⁻¹	%	
BF2	3:52	1.55	8.14	7.94	19.14	14.35	36.38	114.6	2.6
BF3	7:40	1.55	3.94	3.87	9.33	17.98	33.11	99.4	2.6
BF4	6:00	1.55	5.56	5.46	13.14	12.11	28.88	101.0	2.6
AVG		1.5	5.88	5.76	13.88	14.81	32.79	105.0	2.6
SD		0.00	2.12	2.05	4.94	2.96	4.11	8.35	0
CV		0.00	0.36	0.36	0.36	0.20	0.12	0.08	0

[†]Determined using ring method on small soil cores (7.5 cm diameter by 7.5 cm length, or 8 cm diameter by 6 cm length).

[‡]NH₄⁺-N determined using EPA method 350.1 Rev 2. with AquaKem 200 by EST Analytical, Fairfield, OH.

[§]Analyzed using colorimetric methods with AquaKem 200 by EST Analytical, Fairfield, OH., and by and redox reactions using digital chloridometer (model 442-5000, Lanconoco, Kansas City, Missouri).

Table 7. Physical characteristics and results of leaching experiments in Norfolk intact soil columns.

Column ID	Run time	Bulk density [†]	K _s	J _w	v	NH ₄ ⁺ -N recovered [‡]	Peak concentration [‡]	Cl ⁻ leached [§]	Total pore volumes
	h:min	g cm ⁻³	cm hr ⁻¹	cm hr ⁻¹	cm hr ⁻¹	%	mg L ⁻¹	%	
NF2	14:17	1.60	1.99	1.86	4.70	7.94	18.45	113.0	2.5
NF3	4:39	1.60	8.57	7.45	18.81	11.41	37.04	95.0	3.1
NF4	14:24	1.60	2.34	2.12	5.36	6.38	18.24	95.0	2.1
AVG		1.60	4.30	3.81	9.62	8.58	24.58	101.0	2.5
SD		0.00	3.70	3.15	7.96	2.57	10.79	10.4	0.5
CV		0.00	0.86	0.83	0.83	0.30	0.44	0.1	0.2

[†]Determined using ring method on small soil cores (7.5 cm diameter by 7.5 cm length, or 8 cm diameter by 6 cm length).

[‡]NH₄⁺-N determined using EPA method 350.1 Rev 2. with AquaKem 200 by EST Analytical, Fairfield, OH.

[§]Analyzed using colorimetric methods with AquaKem 200 by EST Analytical, Fairfield, OH., and by and redox reactions using digital chloridometer (model 442-5000, Lanconoco, Kansas City, Missouri).

Table 8. Physical characteristics and results of leaching experiments in Norfolk depressional between row intact soil columns.

Column ID	Run time	Bulk density [†]	K _s	J _w	v	NH ₄ ⁺ -N leached [‡]	Peak concentration [‡]	Cl- leached [§]	Total pore volumes
	h:min	g cm ⁻³	cm hr ⁻¹	cm hr ⁻¹	cm hr ⁻¹	%	mg L ⁻¹	%	
ND5	18:59	1.59	1.40	1.24	3.10	0.50	0.99	94.9	1.9
ND4	7:00	1.59	5.66	5.23	13.07	2.90	3.28	116.0	3.0
ND6	11:09	1.59	2.72	2.47	6.18	2.51	3.36	91.5	2.7
AVG		1.59	4.19	3.85	9.62	2.71	3.32	104.7	2.8
SD		0.00	2.08	1.95	4.87	0.28	0.06	18.7	0.2
CV		0.00	0.50	0.51	0.51	0.10	0.02	0.2	0.1

[†]Determined using ring method on small soil cores (7.5 cm diameter by 7.5 cm length, or 8 cm diameter by 6 cm length).

[‡]NH₄⁺-N determined using EPA method 350.1 Rev 2. with AquaKem 200 by EST Analytical, Fairfield, OH.

[§]Analyzed using colorimetric methods with AquaKem 200 by EST Analytical, Fairfield, OH., and by and redox reactions using digital chloridometer (model 442-5000, Lanconoco, Kansas City, Missouri).

Table 9. Physical characteristics and results of leaching experiments in Norfolk within row intact soil columns.

Column ID	Run time	Bulk density [†]	Ks	Jw	v	NH ₄ ⁺ -N leached [‡]	Peak concentration [‡]	Cl-leached [§]	Total pore volumes
	h:min	g cm ⁻³	cm hr ⁻¹	cm hr ⁻¹	cm hr ⁻¹		mg L ⁻¹	%	
ND7	18:06	1.59	1.26	1.22	3.05	0.50	1.19	104.0	2.2
ND8	9:17	1.59	2.75	2.42	6.06	1.00	1.36	98.6	2.2
ND9	9:23	1.59	2.25	2.11	5.28	1.50	3.83	101.0	2.1
AVG		1.59	2.09	1.92	4.80	1.00	3.19	101.2	2.2
SD		1.59	0.76	0.62	1.56	0.50	1.48	2.7	0.1
CV		0.00	0.36	0.33	0.33	0.50	0.06	0.0	0.0

[†]Determined using ring method on small soil cores (7.5 cm diameter by 7.5 cm length, or 8 cm diameter by 6 cm length).

[‡]NH₄⁺-N determined using EPA method 350.1 Rev 2. with AquaKem 200 by EST Analytical, Fairfield, OH.

[§]Analyzed using colorimetric methods with AquaKem 200 by EST Analytical, Fairfield, OH., and by and redox reactions using digital chloridometer (model 442-5000, Lanconoco, Kansas City, Missouri).

Table 10. Physical characteristics and results of leaching experiments in Bonifay packed soil columns.

Column ID	Run time	Bulk density [†]	θ_v	J_w	v	NH ₄ ⁺ -N leached Leachate [‡]	Total N recovered Soil extraction [‡]	Peak concentration [‡]	% Cl-leached [§]	Total pore volumes
	h:min	g cm ⁻³		cm hr ⁻¹	cm hr ⁻¹	%	%	mg L ⁻¹		
BT P1	20:15	1.57	0.39	1.36	3.48	6.8	64.48	9.8	103.0	2.8
BT P2	122:00	1.57	0.38	0.56	1.44	10.2	60.99	10.2	108.0	4.3
AVG		1.57	0.38	0.96	2.46	8.5	62.73	12.3	105.9	3.5
SD		0	0.01	0.56	1.44	2.4	2.47	3.4	2.9	0.7
CV		0	0.01	0.58	0.59	0.3	0.04	0.3	0.0	0.2
BS P1	105:30	1.51	0.31	0.55	1.77	0.41	85.87	0.7	102.0	2.5
BS P2	20:15	1.49	0.40	0.25	0.64	0.70	95.31	0.5	160.0	2.5
BS P3	28:45	1.47	0.31	1.04	0.55	0.23	91.03	0.4	91.0	2.2
AVG		1.49	0.34	0.45	0.99	0.45	90.73	0.5	117.7	2.4
SD		0.02	0.05	0.17	0.68	0.24	4.73	0.1	37.07	0.2
CV		0.02	0.15	0.38	0.69	0.53	0.05	0.3	0.32	0.1

[†]Calculated using mass of soil divided by volume.

[‡]NH₄⁺-N determined using EPA method 350.1 Rev 2. with AquaKem 200 by EST Analytical, Fairfield, OH., NO₃⁻-N determined using a Dionex DX-120 ion chromatograph.

[§]Analyzed using colorimetric methods with AquaKem 200 by EST Analytical, Fairfield, OH., and by and redox reactions using digital chloridometer (model 442-5000, Lanconoco, Kansas City, Missouri).

Table 11. Physical characteristics and results of leaching experiment in Norfolk packed soil column.

Column ID	Run time	Bulk density [†]	θ_v	J_w	v	NH ₄ ⁺ -N leached Leachate [‡]	Total N recovered Soil extraction [‡]	Peak concentration [‡]	Cl ⁻ leached [§]	Total pore volumes
	h:min	g cm ⁻³		cm hr ⁻¹	cm hr ⁻¹	%	%	mg L ⁻¹	%	
NF P1	37:30	1.5	0.39	0.71	1.83	0.37	97.35	0.86	101.3	2.0

[†]Calculated using mass of soil divided by volume.

[‡]NH₄⁺-N determined using EPA method 350.1 Rev 2. with AquaKem 200 by EST Analytical, Fairfield, OH., NO₃⁻-N determined using a Dionex DX-120 ion chromatograph.

[§]Analyzed using colorimetric methods with AquaKem 200 by EST Analytical, Fairfield, OH., and by and redox reactions using digital chloridometer (model 442-5000, Lanconoco, Kansas City, Missouri).

Table 12. Physical characteristics and results of leaching experiments in Norfolk depressional packed soil columns.

Column ID	Run time	Bulk density [†]	θ_v	J_w	v	NH ₄ ⁺ -N leached Leachate [‡]	Total N recovered Soil extraction [‡]	Peak concentration [‡]	Cl ⁻ leached [§]	Total pore volumes
	h:min	g cm ⁻³		cm hr ⁻¹	cm hr ⁻¹	%	%	mg L ⁻¹	%	
ND P1	42:44	1.43	0.44	0.51	1.15	0.37	95.92	3.45	101.0	1.5
ND P2	51:15	1.47	0.54	0.23	0.42	0.16	82.32	0.81	86.9	1.0
AVG		1.45	0.49	0.37	0.79	0.27	89.12	2.13	93.9	1.3
SD		0.03	0.07	0.20	0.52	0.15	9.62	1.87	9.9	0.3
CV		0.02	0.14	0.55	0.66	0.56	0.11	0.88	0.1	0.3

[†]Calculated using mass of soil divided by volume.

[‡]NH₄⁺-N determined using EPA method 350.1 Rev 2. with AquaKem 200 by EST Analytical, Fairfield, OH., NO₃⁻-N determined using a Dionex DX-120 ion chromatograph.

[§]Analyzed using colorimetric methods with AquaKem 200 by EST Analytical, Fairfield, OH., and by and redox reactions using digital chloridometer (model 442-5000, Lanconoco, Kansas City, Missouri).

Table 13. Comparison of average NH_4^+ -N and Cl^- leached in disturbed and undisturbed columns by soil type.

Soil type	Undisturbed columns		Disturbed columns	
	NH_4^+ -N leached %	Cl^- leached %	NH_4^+ -N leached %	Cl^- leached %
Bonifay	14.8	105.0	.045-8.5	105.0-117.0
Norfolk	8.6	101.0	0.4	101.3
Norfolk depressional	2.7	104.7	0.3	93.9

Figure 1. Average values and standard deviation of pH in preliminary mass balance experiment.

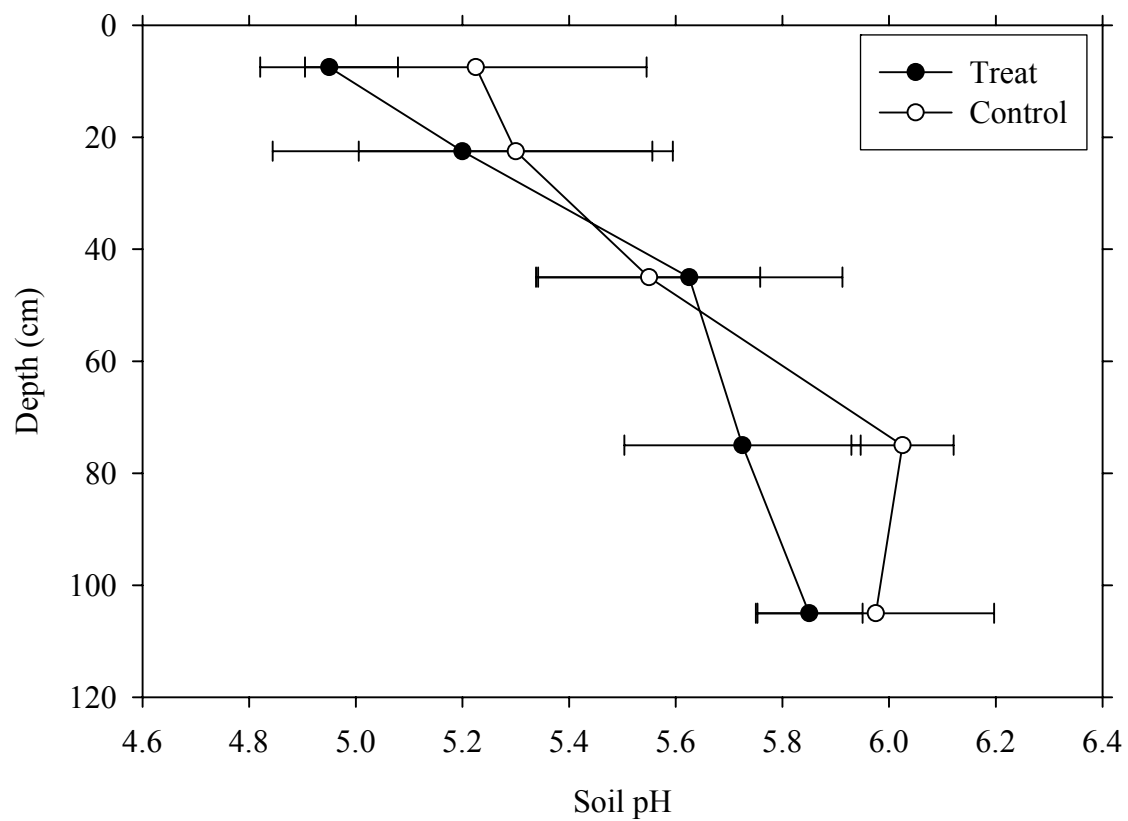


Figure 2. Average concentration and standard deviation of $\text{NH}_4^+\text{-N}$ (kg ha^{-1}) in preliminary mass balance experiment.

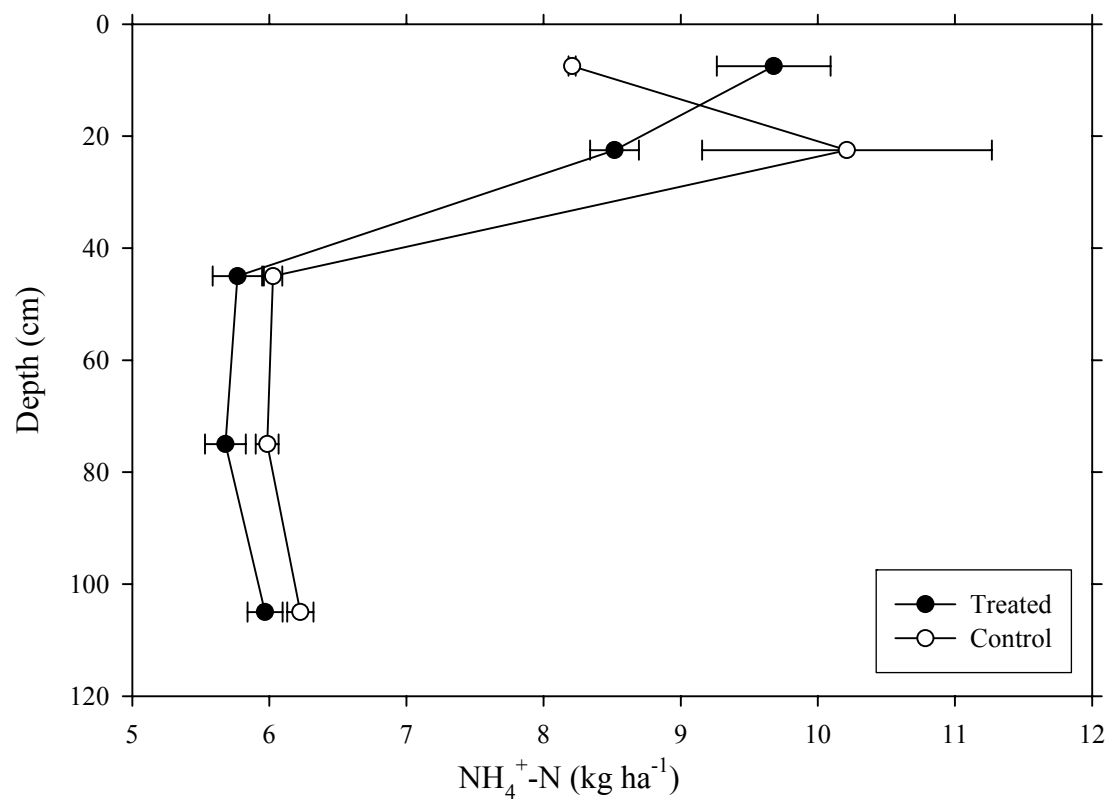


Figure 3. Average concentrations and standard deviation of NO_3^- -N (kg ha^{-1}) in preliminary mass balance experiment.

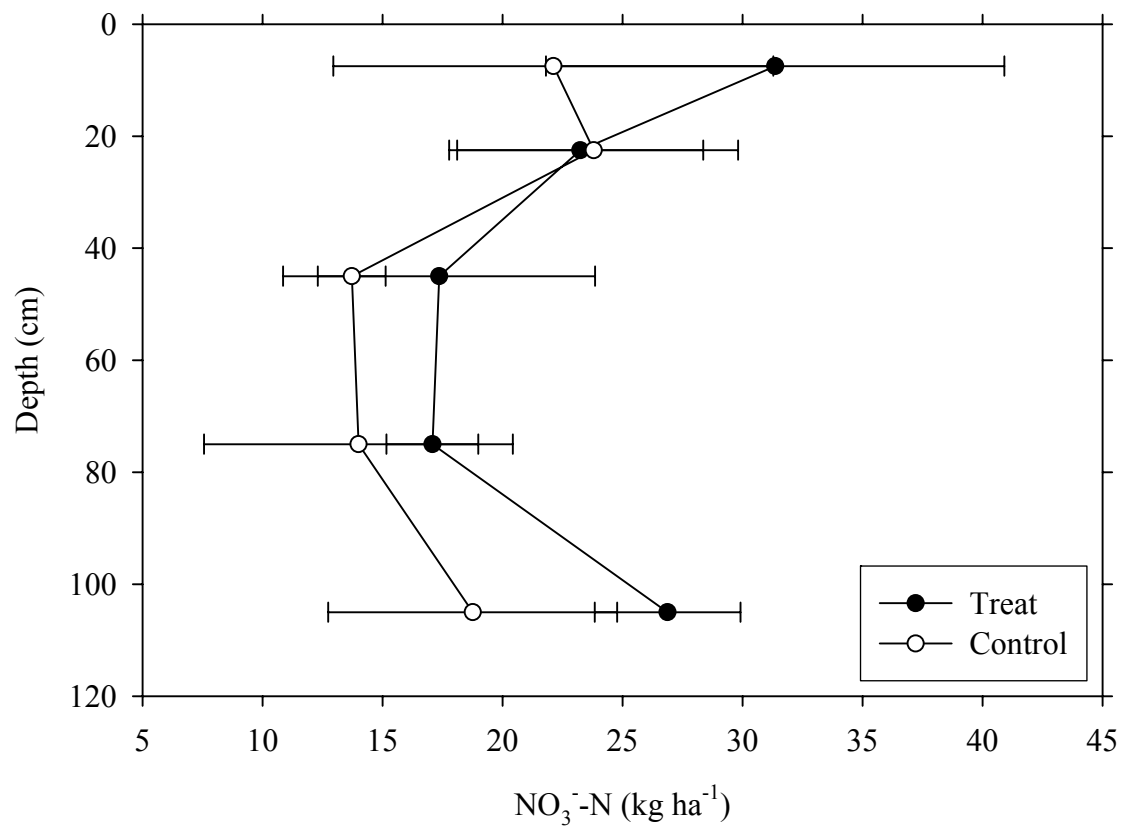


Figure 4. Average concentration and standard deviation of extractable S (kg ha^{-1}) in preliminary mass balance experiment.

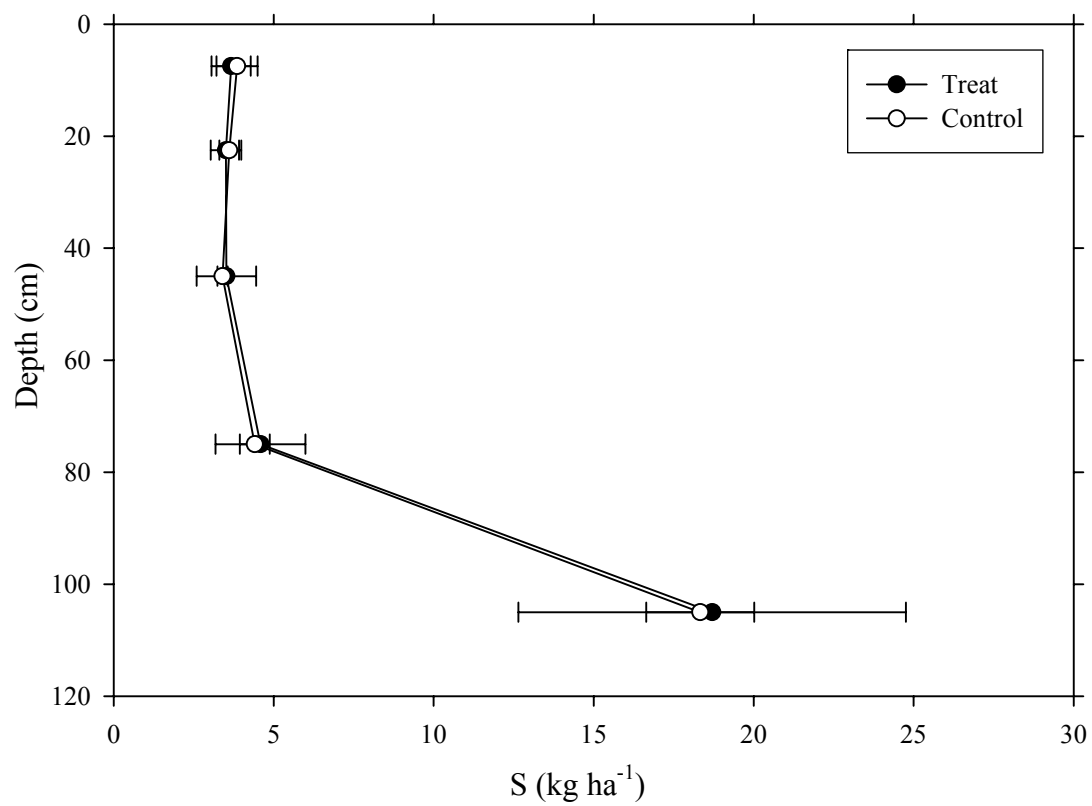


Figure 5. Adsorption isotherm for Bonifay top soil (0 to 15 cm).

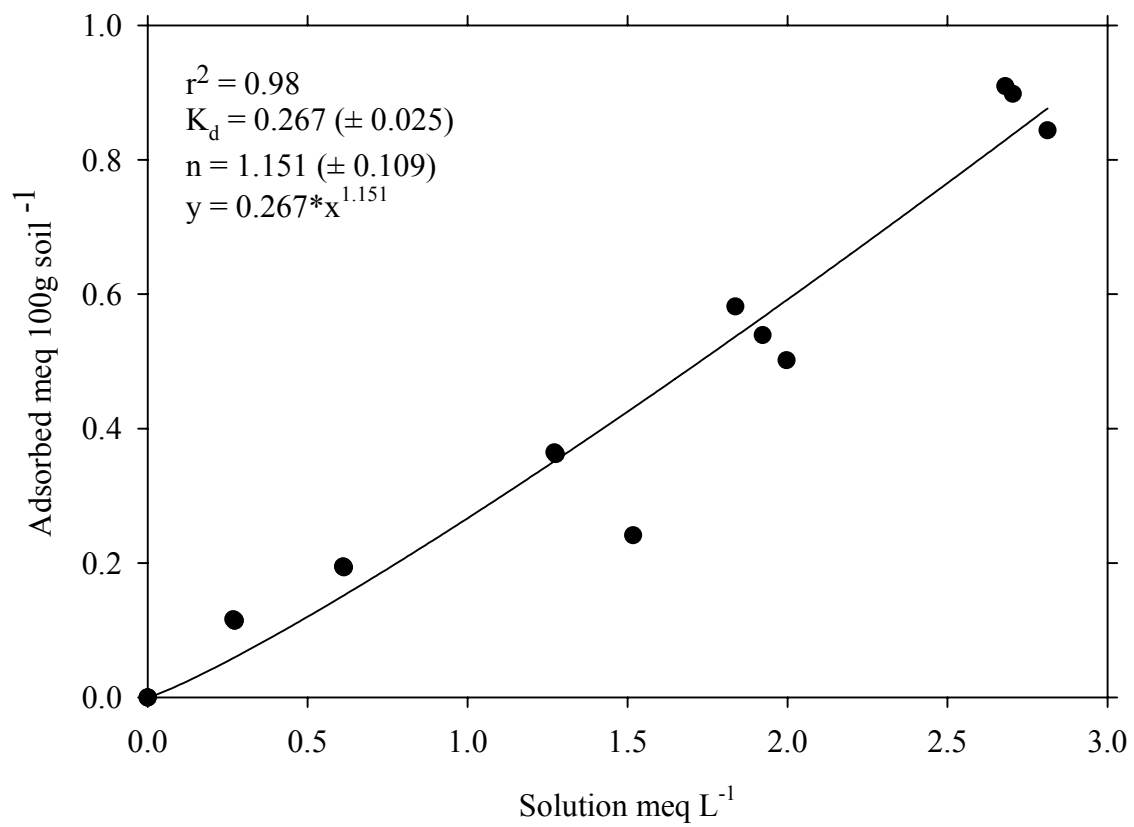


Figure 6. Adsorption isotherm for Bonifay subsoil (15 to 30 cm).

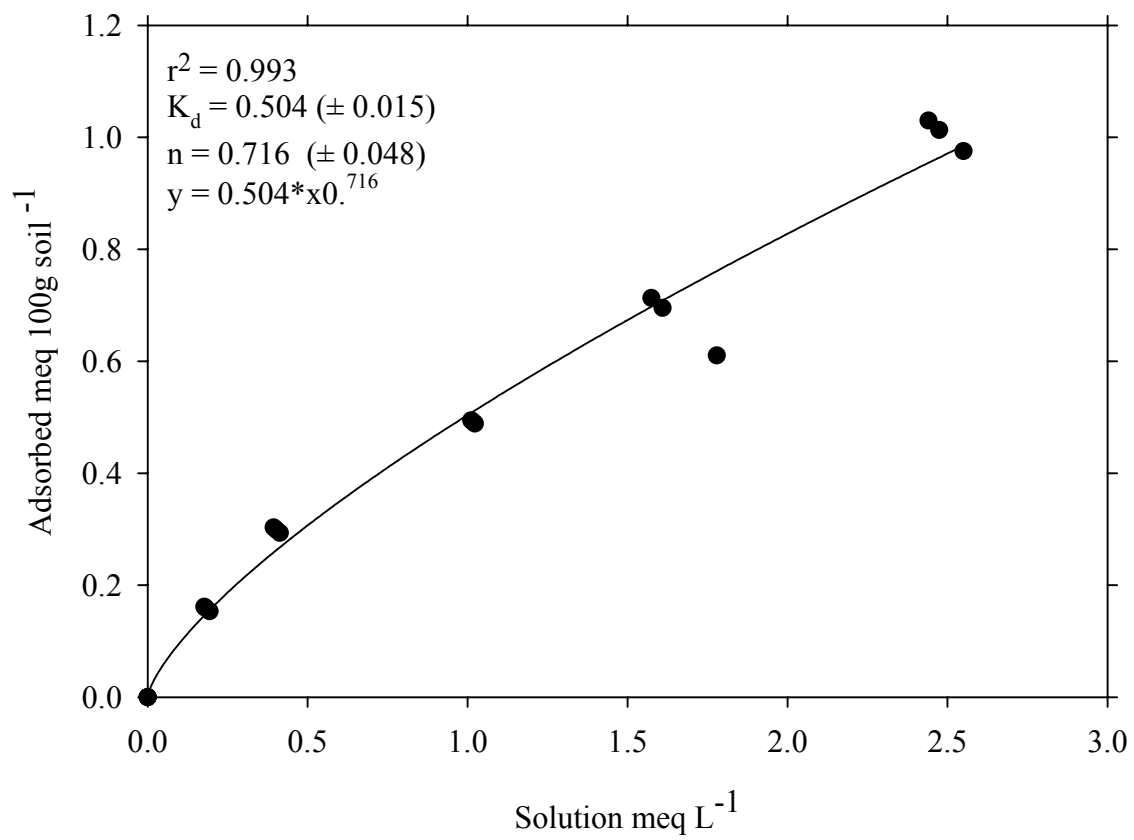


Figure 7. Adsorption isotherm for Norfolk soil.

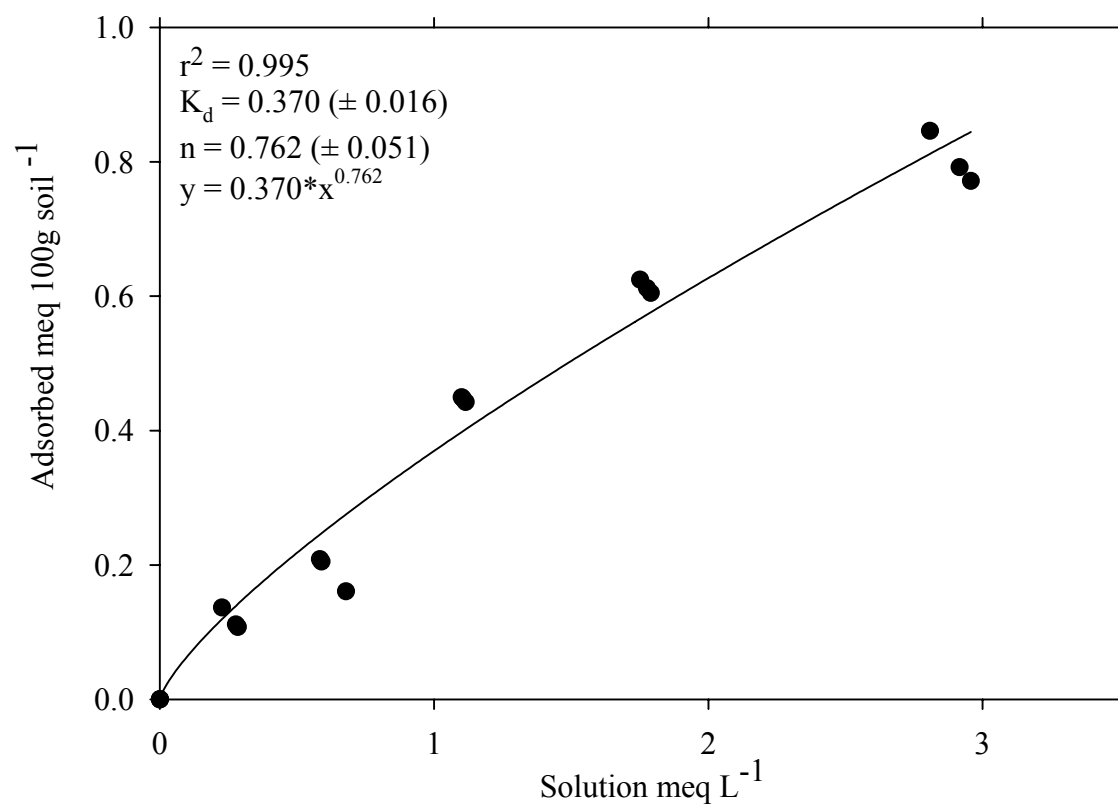


Figure 8. Adsorption isotherm for Norfolk depressional soil.

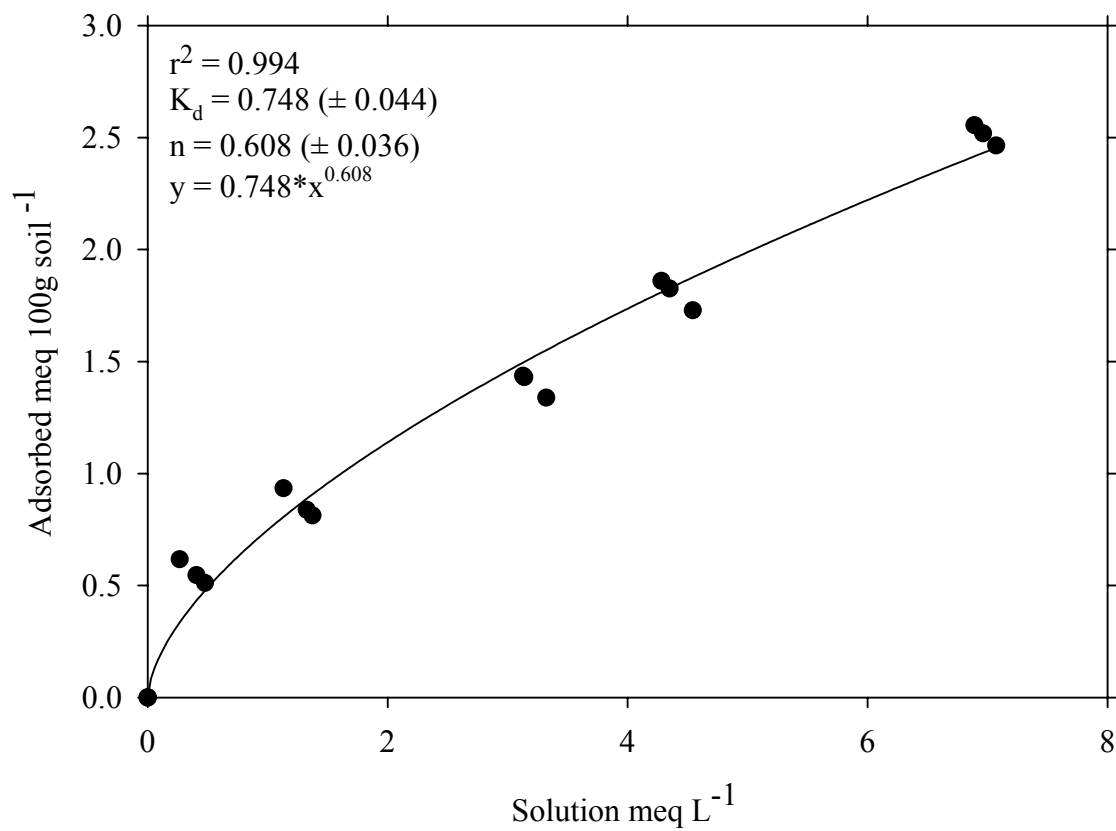


Figure 9. Ammonium-N breakthrough curves in Bonifay intact soil cores.

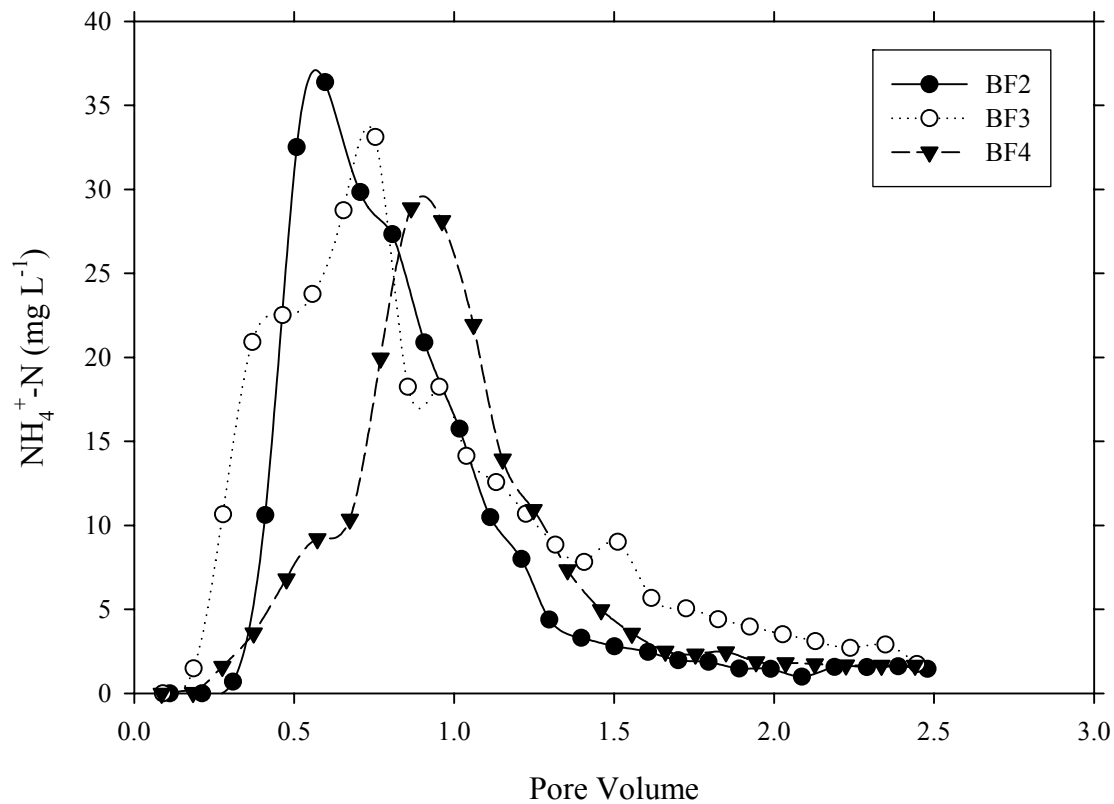


Figure 10. Chloride breakthrough curves in Bonifay intact soil cores.

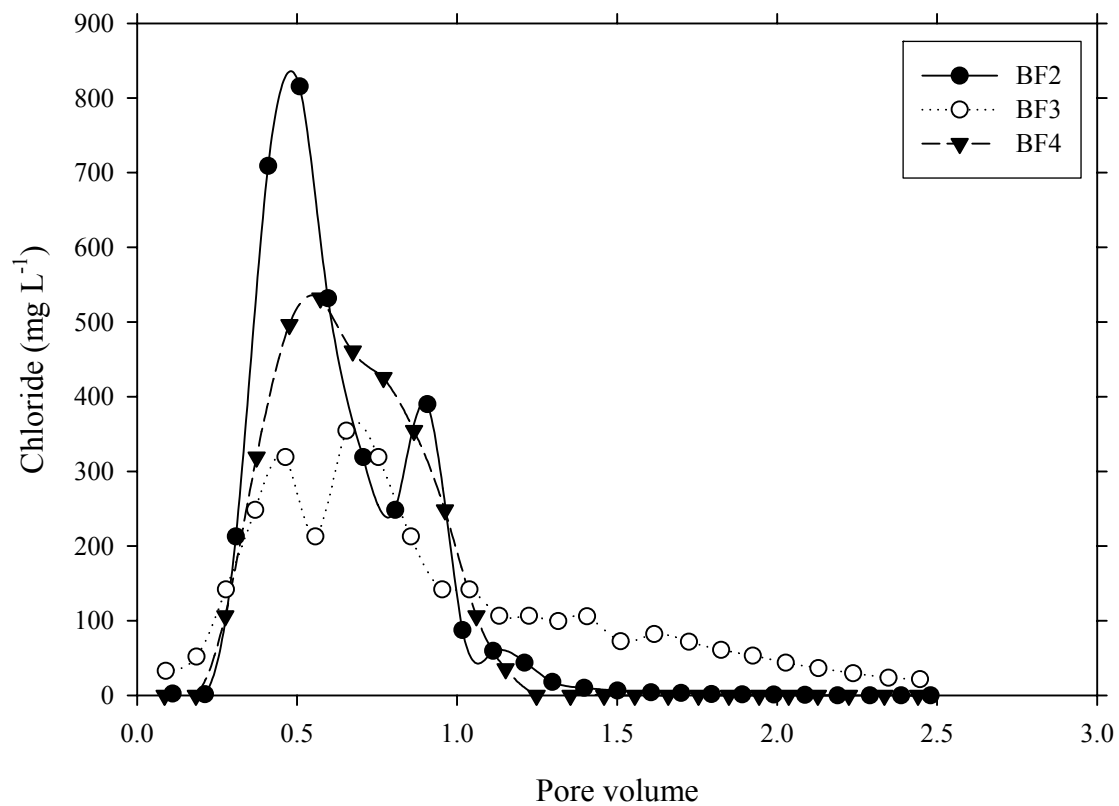


Figure 11. Ammonium-N breakthrough curves in Norfolk intact soil cores.

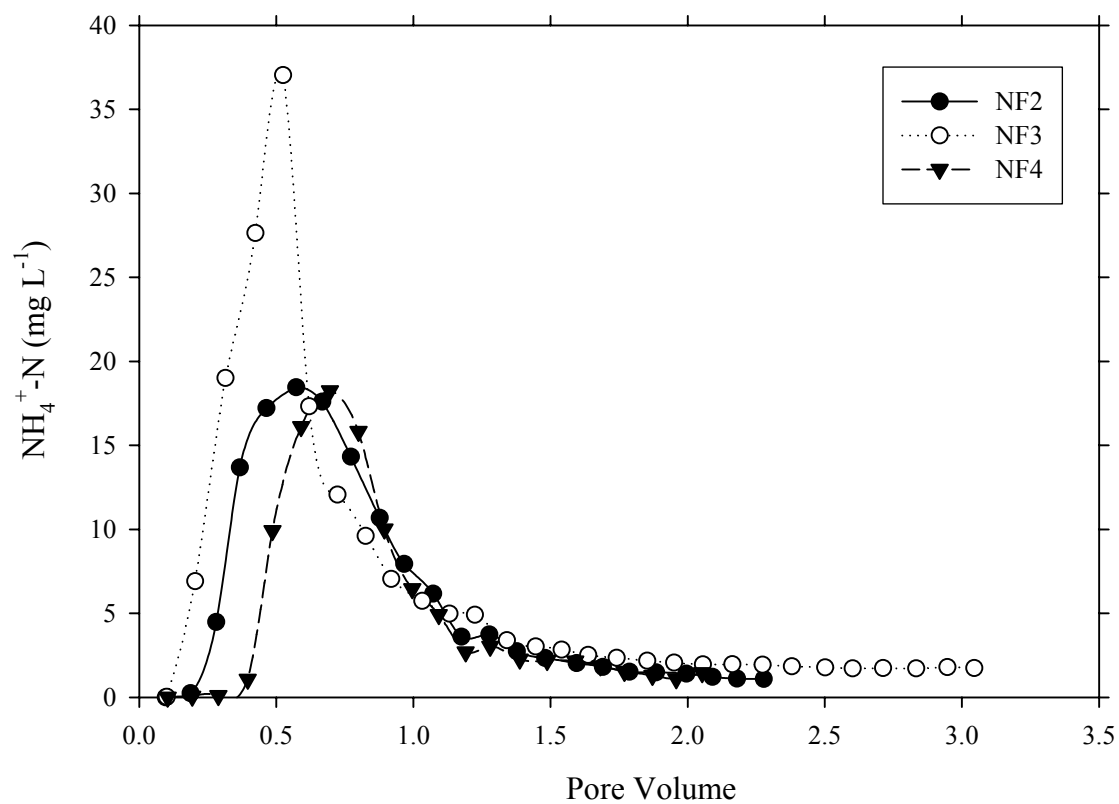


Figure 12. Chloride breakthrough curves in Norfolk intact soil cores.

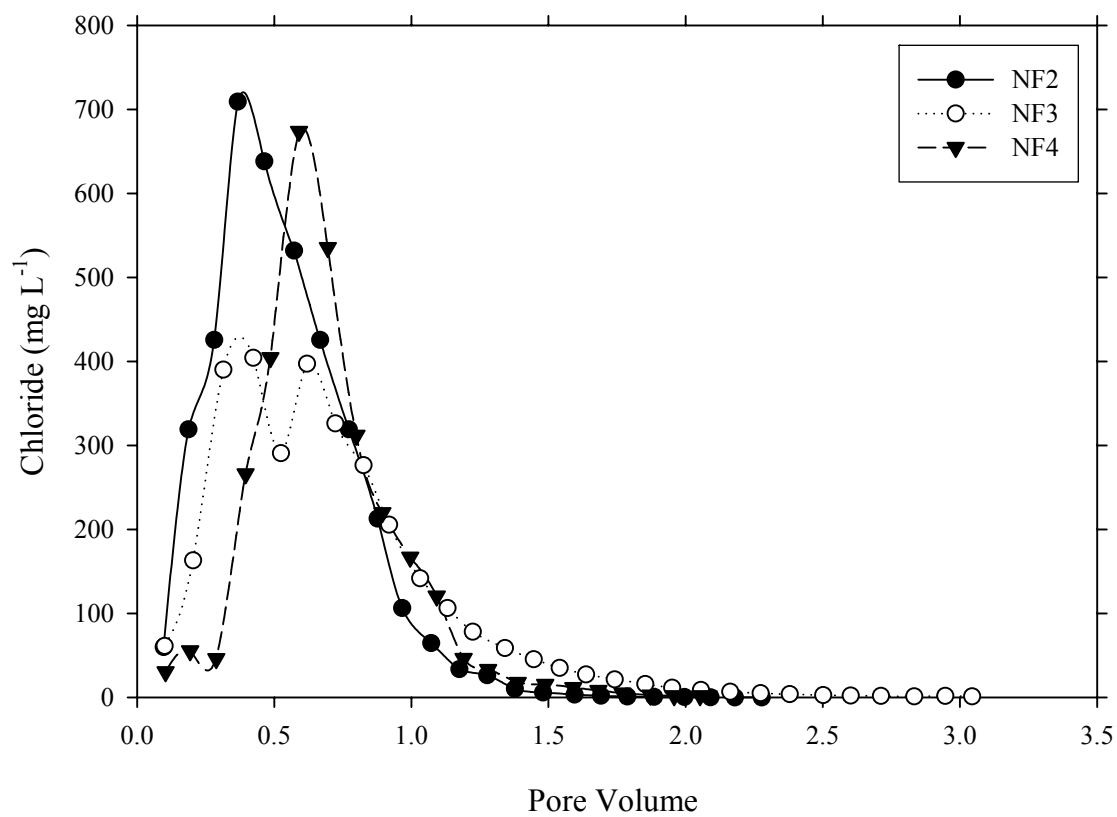


Figure 13. Ammonium-N breakthrough curves Norfolk depressional between row soil cores.

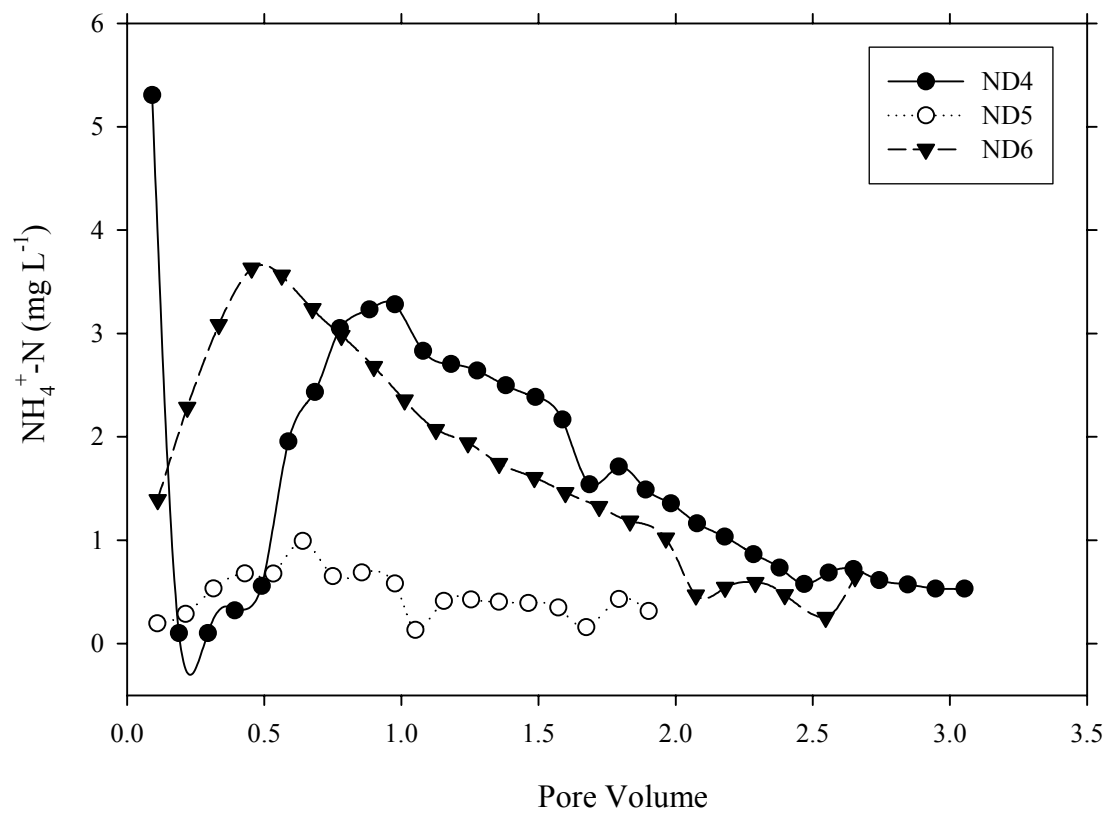


Figure 14. Chloride breakthrough curves in Norfolk depositional between row soil cores.

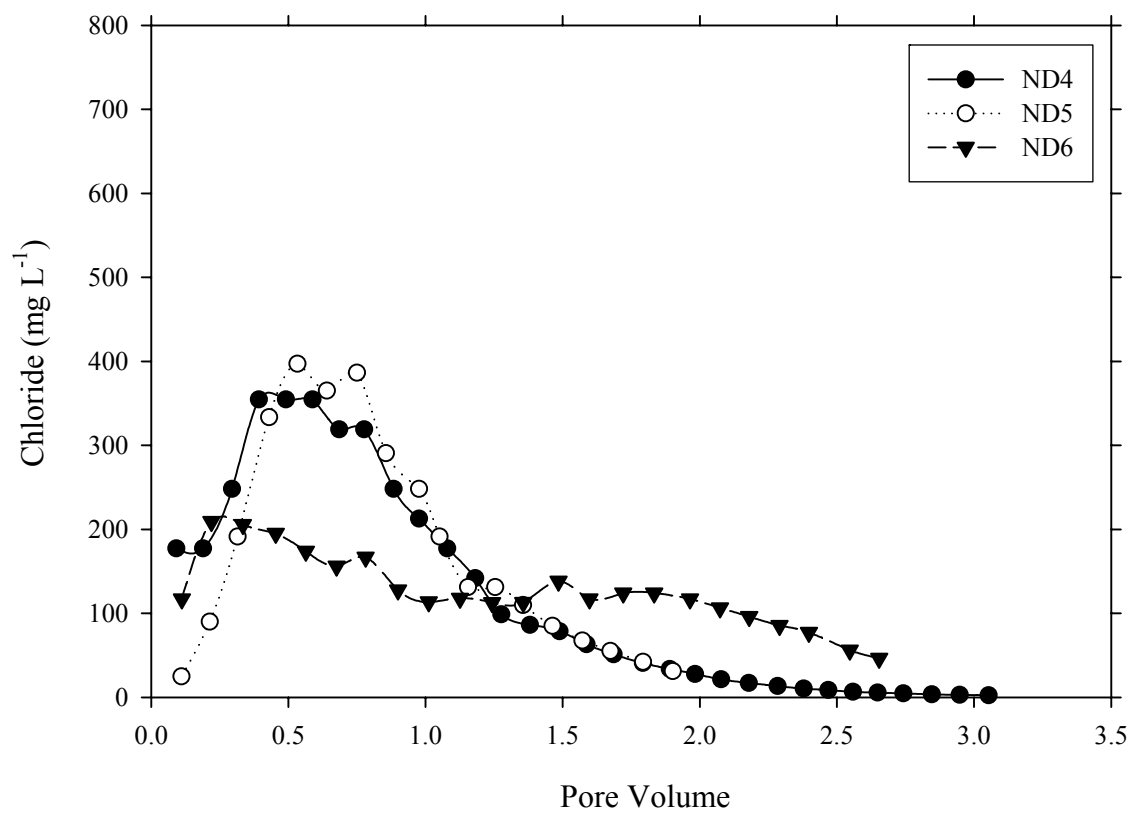


Figure 15. Ammonium-N breakthrough curves in Norfolk depositional within row intact soil cores.

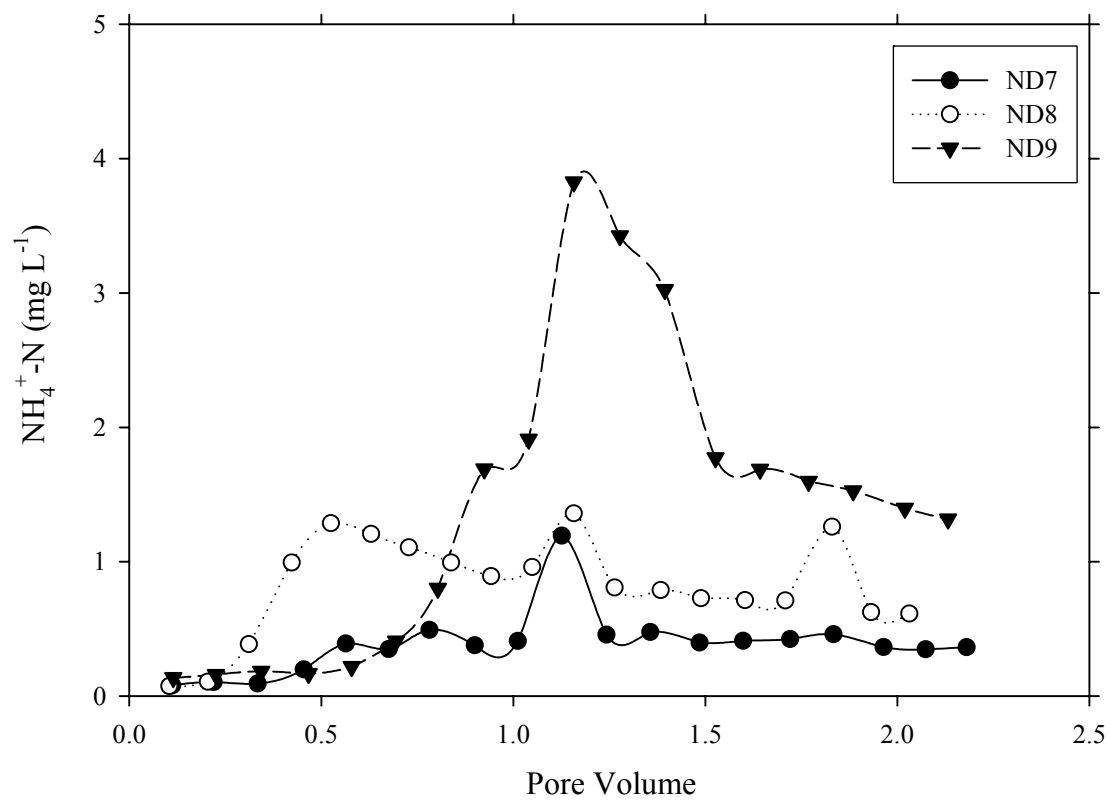


Figure 16. Chloride breakthrough curves in Norfolk depositional within row intact soil cores.

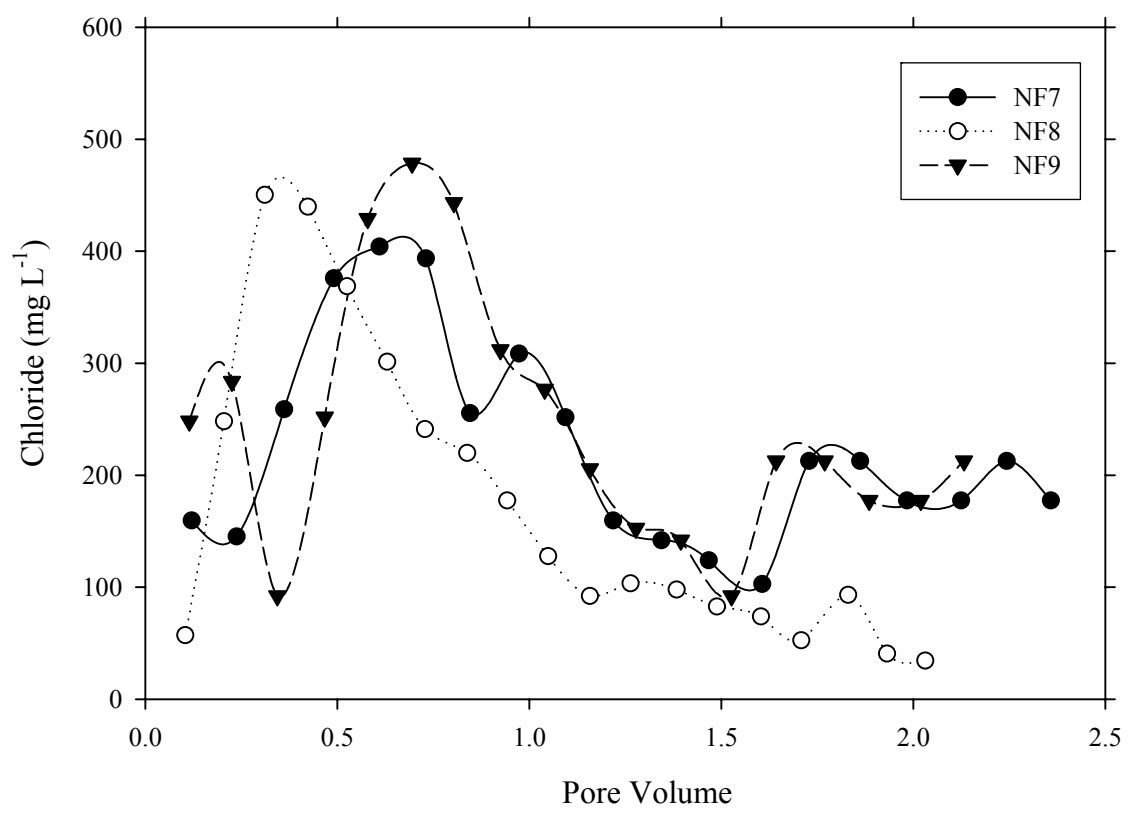


Figure 17. Ammonium-N breakthrough curves in Bonifay topsoil packed soil cores.

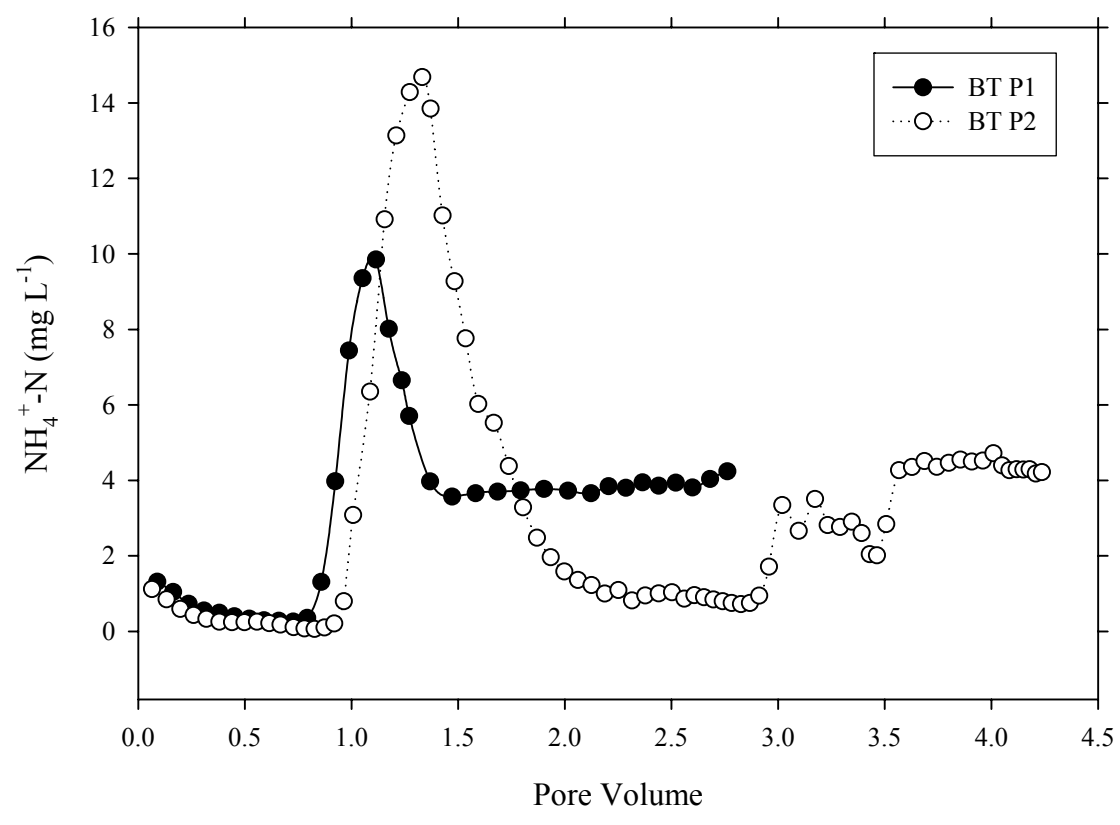


Figure 18. Chloride breakthrough curves in Bonifay topsoil packed soil cores.

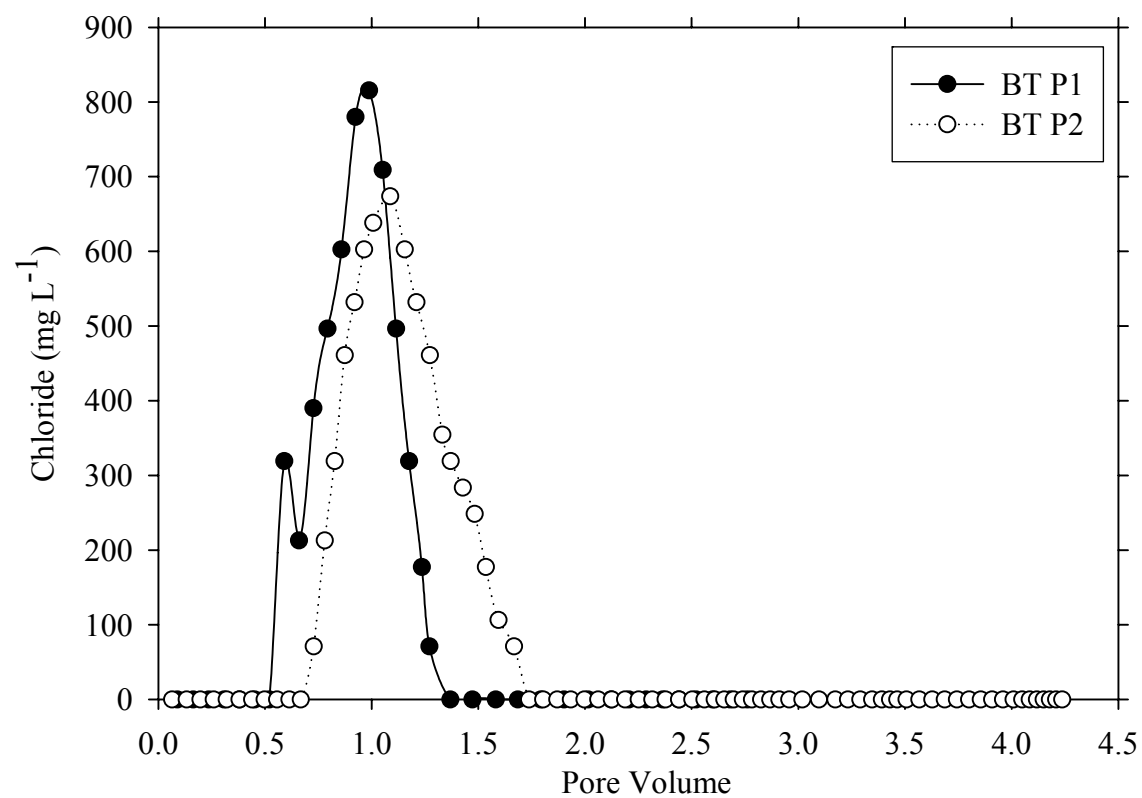


Figure 19. Ammonium-N breakthrough curves in Bonifay subsoil packed soil cores.

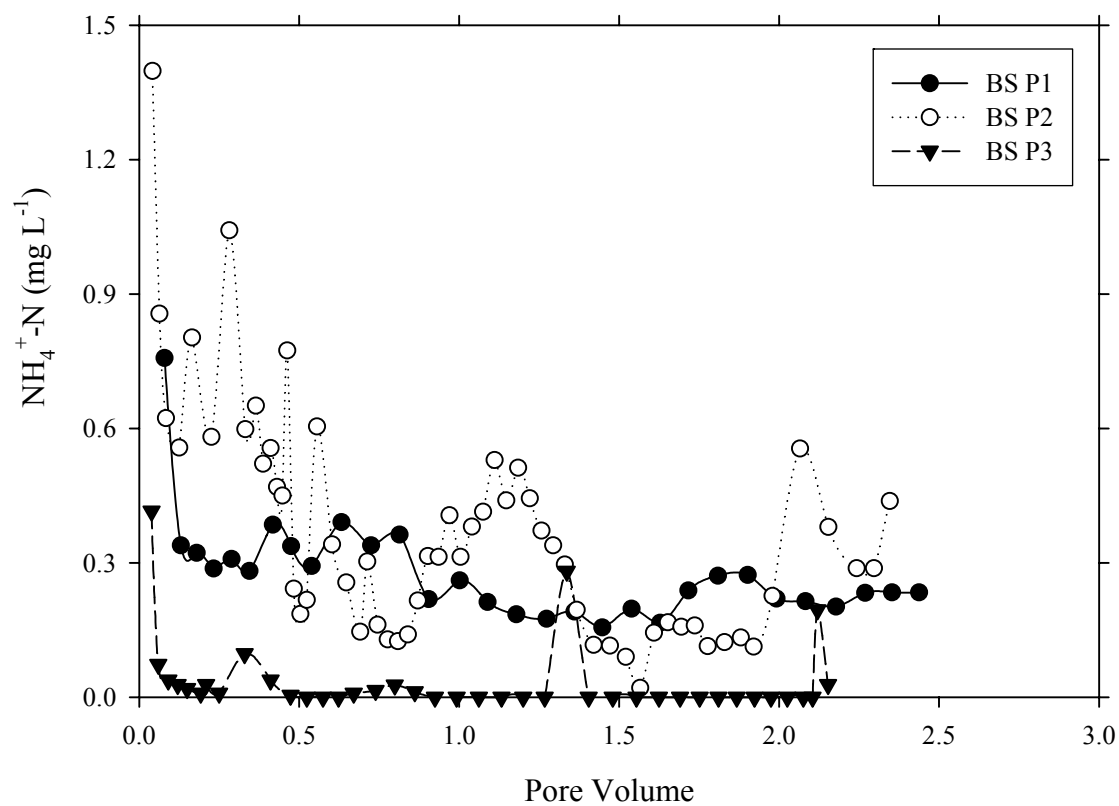


Figure 20. Chloride breakthrough curves in Bonifay subsoil packed soil cores.

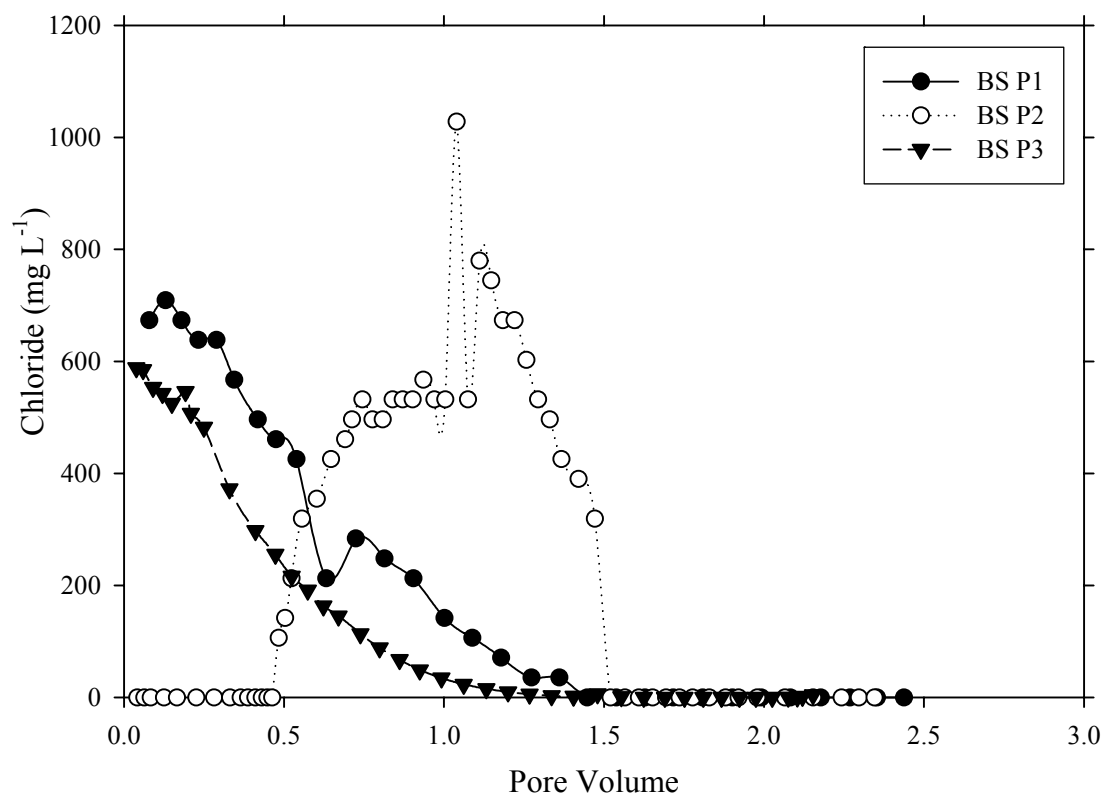


Figure 21. Ammonium-N breakthrough curves in Norfolk packed soil core.

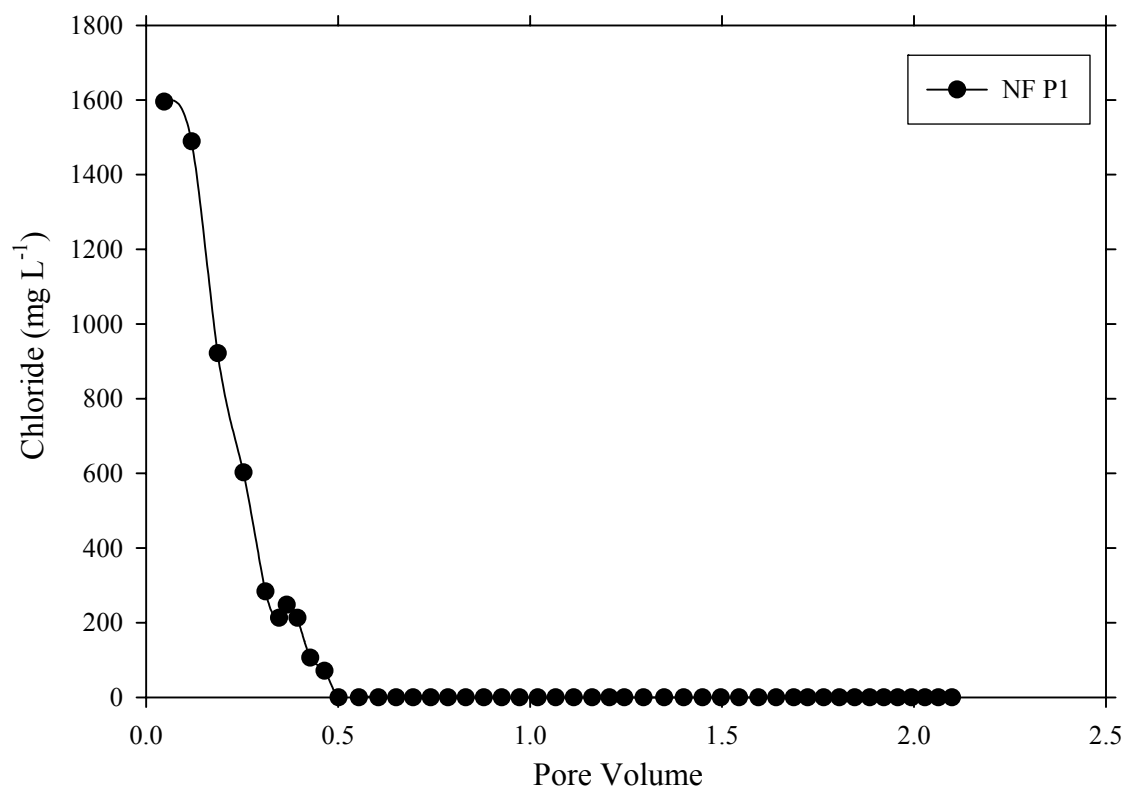


Figure 22. Chloride breakthrough curve in Norfolk packed soil core.

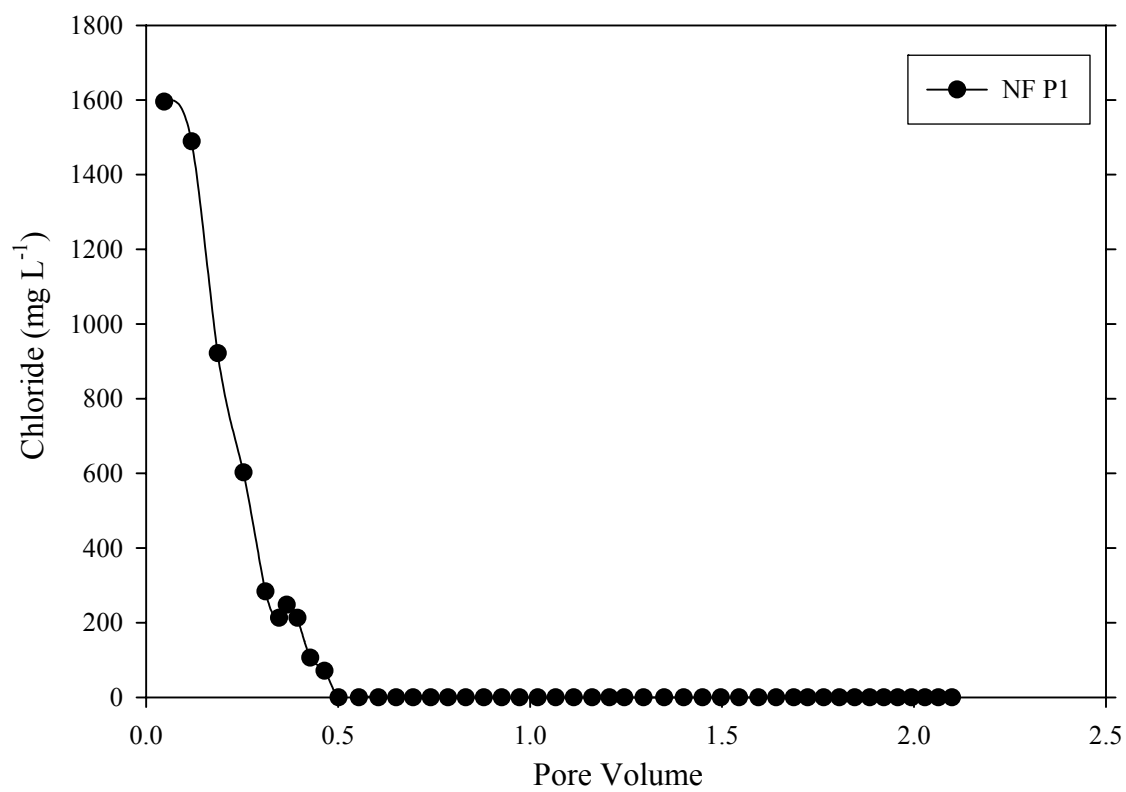


Figure 23. Ammonium-N breakthrough curves Norfolk depressional packed soil cores.

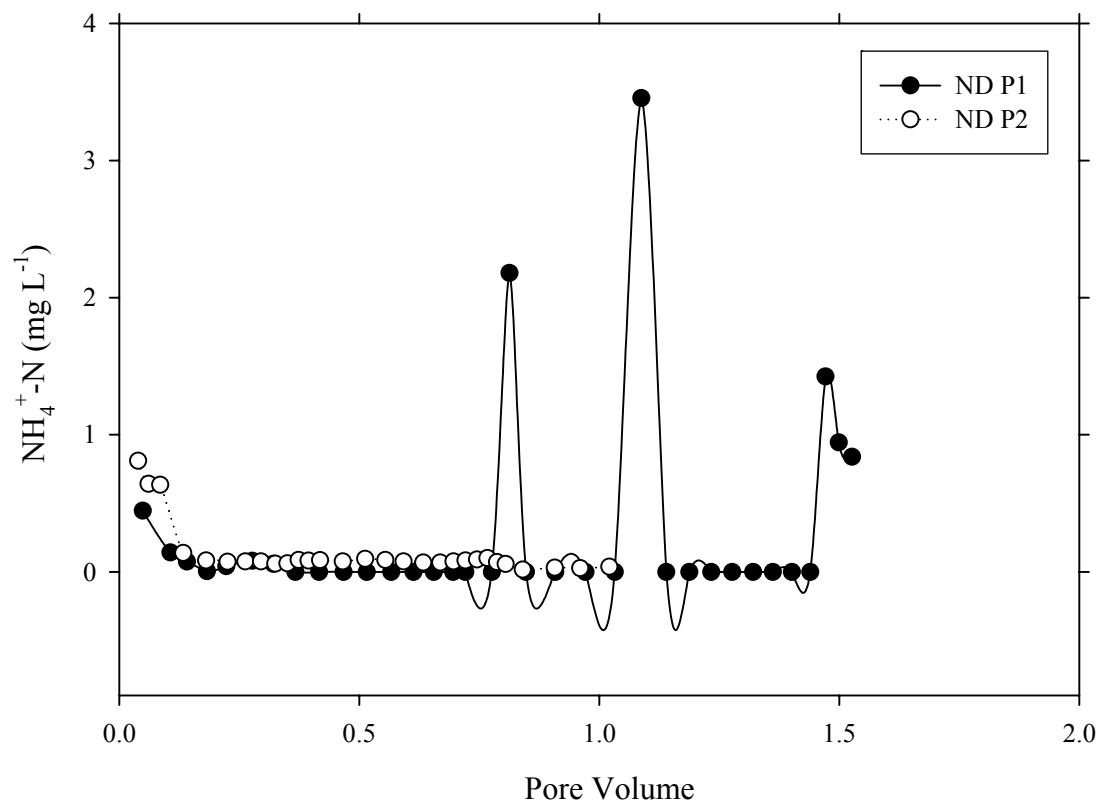


Figure 24. Chloride breakthrough curves in Norfolk depositional packed soil cores.

