NITRATE TRANSPORT IN THE UNSATURATED ZONE BELOW AGRICULTURAL FIELDS

Suzanna L. Moore

57 Pages August 2005

Nitrate is necessary for agricultural productivity, but can cause considerable problems if released into the environment. This study investigated the movement of nitrate below agricultural fields in different soil types.

APPROVED:

Date	Eric W. Peterson, Chair
Date	Elizabeth M. King
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Each year in Illinois, billions of pounds of nitrogen fertilizers are applied to agricultural fields. Although fertilizer application is necessary to sustain and maximize agricultural production, much of this nitrogen is released into the environment as nitrate. The purpose of this study was to quantify vertical transport rates of nitrate below agricultural fields, specifically looking at transport rates: 1) associated with normal opposed to wet soil conditions; 2) below soybean compared to corn fields; 3) based on soil grain size; and 4) based on organic matter content of the soil. Samples were collected at the Illinois State University Research Farm during the summer and fall 2004 from three fields, two of which were planted with corn and one with soybean, representing three different soil types.

Most nitrate movement in the study area occurred during normal conditions, rather than after heavy precipitation events. The soils where corn was growing had lower nitrate concentrations than the soils growing soybeans. Within the coarser grained soils, the nitrate transport rate was slower. The results also demonstrated that soils high in organic matter content have lower nitrate concentrations than soils with lower organic matter content.

Based on the results of the study, a large amount of nitrate is utilized by plants at the beginning of the growing season. Once plants reach a certain growth stage, nitrate is utilized at a slower rate. As the plants expire they begin to decompose releasing nitrogen into the soil. The conversion of the nitrogen to nitrate correlates to elevated nitrate concentrations measured at the end of the growing season.

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CONTENTS

		Page
ACKNOWL	LEDGEMENTS	i
CONTENTS	S	ii
TABLES		iv
FIGURES		v
CHAPTER		
I.	INTRODUCTION	1
	Statement of the Problem Nitrogen Cycle Significance Study Area	1 3 5 7
	Glacial History Soils Site History	8 9 11
	Hypotheses	12
II.	METHODOLOGY	14
	Methods	14
III.	RESULTS	19
	Soil Properties	19
	Bulk density Moisture Content Organic Matter	20 21 23

	Grain Size	24
	Porosity	26
	Hydraulic Conductivity	27
	Climate	28
	Nitrate Content	30
	Flanagan Unit	31
	Drummer Unit	33
	Saybrook Unit	34
IV.	DISCUSSION	35
	Overview of Results	35
	Trends	38
	Movement During Normal Condition	39
	Crop Type	42
	Soil Type	43
	Organic Matter	46
V.	CONCLUSIONS	48
REFERENCE	ES	51
APPENDIX:	Nitrate Concentrations	54

TABLES

Table		Page
1.	Soil properties of the study area.	11
2.	Sampling Schedule; including maximum sample depth and number of samples collected.	19
3.	Average moisture content for each sampling location based on depth.	21
4.	Average organic matter content at each sampling interval.	23
5.	Average grain size composition for each soil unit.	26
6.	Average porosity at each sampling interval.	26
7.	Nitrate ranges for the Flanagan Unit.	32
8.	Nitrate ranges for the Drummer Unit.	33
9.	Nitrate ranges for the Saybrook Unit.	34

FIGURES

Figures		Page
1.	Nitrogen Cycle.	4
2.	Rates of nitrogen accumulation in crops.	6
3.	Site location of ISU Farm.	8
4.	Soil map and sample location within study area.	10
5.	Calculated dry bulk densities for the soils at the study area.	21
6.	Moisture content for each sampling location at the study area.	22
7.	Average soil organic matter content at each sampling location.	24
8.	Cumulative grain size distribution for each soil type.	25
9.	Average porosity for each sampling interval, at each location.	27
10.	Hydraulic conductivity determined for each sampling location interval.	28
11.	Precipitation data for the study area, showing monthly precipitation for 2004.	29
12.	Analytical error data.	31
13.	Nitrate concentrations for each sampling day from the Flanagan Unit.	32
14.	Nitrate concentrations for each sampling day from the Drummer Unit.	33

15.	Nitrate concentrations for each sampling day from the Saybrook Unit.	34
16.	Nitrate profile within the unsaturated zone underlying a corn field.	36

CHAPTER I

INTRODUCTION

Statement of the Problem

Agricultural productivity is dependent upon the addition of nitrogen fertilizers. Without nitrogen, plants cannot produce essential proteins, resulting in stunted growth and decreased crop yields (Saull, 1990). While there is little disagreement that sustaining and maximizing agricultural production requires nitrogen application, a large percentage of the nitrogen remains in the environment since not all of the applied nitrogen fertilizer is utilized by the plants. Studies have shown that typically only half of nitrogen fertilizer applied to crops is taken up by plants as nitrate (Soffe, 2003). Soils have the ability to store a limited amount of nutrients for use in future years, but excess nutrients are leached out or carried away as erosion of materials occurs (Troeh and Thompson, 1993). The amount of nutrients that is removed from the system due to leaching or erosion is dependent upon many factors including soil type and rainfall.

Leaching of nitrate perturbs the natural nitrogen cycle and can cause a number of problems including contamination of drinking water supplies, which in turn can lead to health problems. One familiar health problem associated with high nitrate levels in drinking water is methemoglobinemia, or blue-baby syndrome. Blue-baby syndrome is a blood disorder, commonly affecting infants and elderly, in which bacteria convert nitrate

(NO₃⁻) to nitrite (NO₂⁻). Hemoglobin in the blood will then preferentially absorb the NO₂⁻ instead of oxygen, depriving the body of vital oxygen and possibly causing respiratory failure (Saull, 1990). Evidence from animal experiments has also indicated that nitrogen compounds are carcinogenic. These data are the basis for the U.S. Environmental Protection Agency drinking water standard for nitrate as nitrogen (NO₃⁻ - N) being 10 mg/L.

On a local and regional level, NO₃⁻ in drinking water is a concern in central Illinois, an agricultural area where the majority of the land surface is fertilized and tilled. According to the Illinois Department of Agriculture, more than 28 million acres, or nearly 80%, of the state's land is covered by farms (Illinois Department of Agriculture, 2004). In 2002, approximately 1.7 billion pounds of nitrogen fertilizer were applied to corn fields in Illinois (United States Department of Agriculture, 2004). Consequently, NO₃⁻ concentrations in surface water reservoirs for municipalities, i.e. the city of Bloomington, occasionally exceed the drinking water standard (Illinois State Water Survey, 2001). This project looks at the rate of NO₃⁻ movement below agricultural fields. The rate at which NO₃⁻ moves vertically will determine how much NO₃⁻ will be available for plant utilization. The portion of unused NO₃⁻ can continue moving vertically through the soil profile until the water table is reached. Determining the rate of movement will be useful in predicting the amount of NO₃⁻ that will move through soils below agricultural fields.

Nitrogen Cycle

Nitrogen composes the largest portion of the Earth's atmosphere and is essential to all living organisms. Nitrogen occurs in different oxidation states (Figure 1), with shifts between these states typically occurring in soils (Paul and Clark, 1989). Most nitrogen in our environment occurs as atmospheric nitrogen (N_2) , but this form is unable to be used by many plants and animals. The nitrogen is converted to usable forms through a process known as nitrogen fixation. Nitrogen is fixed by one of two ways: 1) by lightning in the air, or 2) by nitrogen-fixing bacteria. Nitrogen fixing by lightning is rare. The lightening form of fixation occurs in the atmosphere, and the fixed nitrogen is carried to the surface with precipitation. Bacteria can fix nitrogen through symbiotic or nonsymbiotic fixation. Free-living nitrogen-fixing bacteria in soils will convert N₂ to organic nitrogen (Manahan, 1984). Through a multiple-step process known as ammonification, organic N is converted to ammonium (NH₄⁺), which in turn is converted to NO₃⁻ by a process known as nitrification. More commonly, nitrogen is fixed by bacteria associated with leguminous plants. Leguminous plants, such as soybeans, contain bacteria in their roots that are capable of converting N₂ to usable forms, such as NH₄⁺ or NO₃⁻, by nitrogen fixation through a symbiotic relationship (Myrold, 1998).

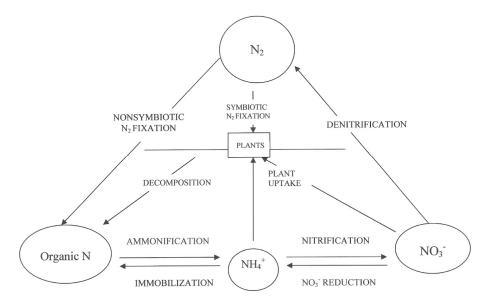


Figure 1: Nitrogen cycle.

Once nitrogen is in the form of NO₃⁻, it will either be used by plants or will eventually make its way into water supplies through leaching. The portion of the NO₃⁻ used by plants, such as corn, will be released back into the environment as the organic material decomposes. Unused portions of NO₃⁻ may also undergo denitrification, which occurs as NO₃⁻ is reduced to nitrous oxide (N₂O) or N₂. Denitrification occurs when N₂O or N₂ are volatilized from soils that are saturated with water only part of the time. There are many steps involved in the denitrification process, but once the steps are complete the N₂ can be returned to the atmosphere, thus completing the nitrogen cycle (Myrold, 1998).

Significance

In agricultural fields, pulses of NO₃⁻ moving through the unsaturated zone have been linked to specific fertilizer application events (Peterson et al., 2002). Currently, there are two primary mechanisms to explain NO₃⁻ movement through the unsaturated zone; relatively slow movement through the soil matrix or more rapid movement through macropores, such as animal burrows, root channels, and wormholes (Iqbal and Krothe, 1995; Quisenberry and Phillips, 1976). Flow through the soil matrix is generally thought of as piston flow and can be characterized by Darcy's Law. Transport through macropores is most significant during precipitation events and can contribute five times as much NO₃⁻ to ground water recharge as matrix flow (Aley, 1977). Because of the high flow velocity of the waters through the macropores (Quisenberry and Phillips1976; Wild and Babiker, 1976), diffusion of NO₃⁻ into and out of the soil matrix is limited; hence, displacement of NO₃⁻ in the soil matrix should be minimal during precipitation events.

Most nitrogen compounds in soil, including NO₃⁻, are water soluble and therefore will move through soils with the ground water (Saull, 1990). Coarser grained materials have larger pores and less ability to retain water. Sandy soils may contain 5-10% available water, while silty soils may contain as much as 20% available water. Because of this, water will move more quickly through coarser grained soils (Soffe, 2003), which in turn leads to a higher rate of NO₃⁻ movement.

All living organisms require nitrogen for survival. According to Troeh and Thompson (1993), plants will absorb nitrogen whenever they are actively growing, but not always at the same rate. Maximum levels of nitrogen are absorbed when agricultural

crops are young, and uptake will decrease as plants age (Figure 2). Plants also have the ability to absorb extra nitrogen and store it for later use if needed.

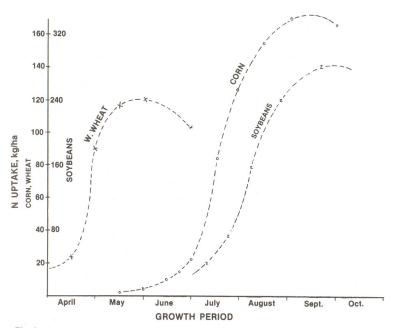


Figure 2: Rates of nitrogen uptake in crops (Olson and Kurtz, 1982).

Rhizobia, legume bacteria, form nodules on the roots of leguminous plants, including soybeans, where nitrogen fixation occurs (Troeh and Thompson, 1993). The nitrogen that is fixed by the bacteria will be utilized by the plant during its growth period, often times in exchange of applying fertilizer. The amount of nitrogen fixed by Rhizobia will decrease when nitrogen is readily available in the soil, but will not go to zero. A low estimate of the amount for nitrogen fixed each year by soybeans is 60 kg/ha, but the fixation potential is nearly twice as high under favorable conditions, such as those when NO₃⁻ is not readily available in the soil for plant use. On average, soybeans remove

approximately 144 kg/ha of nitrogen from the soil they are being grown on each year (Troeh and Thompson, 1993). It is possible for there to be excess amounts of nitrogen in the soil during seasons when soybean crops are grown.

Unlike soybeans, corn crops cannot utilize atmospheric nitrogen. Corn needs nitrogen compounds from the soil or fertilizer applications in order to maximize growth. Because of this, much of the NO₃⁻ initially in the soil or applied as fertilizer will be depleted from within the root zone during the growing season. Corn uptake of nitrogen ranges from 35 kg/ha to 170 kg/ha (Olson and Kurtz, 1982). Nitrate below the root system of corn will not be utilized.

As a by-product of the agricultural activity, there is a high amount of residual organic material left within the fields, i.e. corn stalks, soybean plants, etc., that contributes to higher organic carbon and nitrogen content. High organic carbon content in the soil may result in high biological activity that produces reducing conditions which promote the removal of NO₃⁻ through denitrification (Alexander, 1977).

Study Area

The study area for this thesis project is located at the Illinois State University

Research Farm, near Lexington, McLean County, Illinois (Figure 3). The Lexington

Farm serves as a tool for Illinois State University (ISU) agricultural students to gain

knowledge and hands-on farming experience, including crop and live-stock farming, that

otherwise might not be possible. The farm is also used for experimental crop plots for

seed companies growing either soybeans or corn.



Figure 3: Site location of ISU Farm.

Glacial History

The ISU Farm is situated on the El Paso Moraine which is part of the Wedron Group. The Wedron Group, divided into four formations, formed during the Wisconsin Glacial Episode, beginning approximately 20,000 years ago and ending 10,000 years ago. The Yorkville Member represents sub-glacial and ice-marginal facies of multiple offlapping glacigenic sequences, consisting mainly of till with less subaqueous debris flow and lacustrine sediment

The study area is composed of soils formed from the Yorkville Member which is one of three members belonging to the Lemont Formation. The Yorkville Member was deposited approximately 17,700 to 16,200 years ago during the Livingston Phase of the Michigan Subepisode. This member has been described as a calcareous, grey, fine textured diamicton, at times containing lenses of gravel, sand, silt, and clay (Hansel and Johnson, 1996).

Soils are produced as Earth processes act on geologic materials that have been weathered in situ or eroded and deposited. There are many factors that will influence soil characteristics including 1) the mineralogy of the parent material, 2) climate at which the soil was formed, 3) biological activity in and on the soil, 4) topography, and 5) amount of time that soil-forming processes have acted on the parent material. Parent materials of soils in McLean County, Illinois are most commonly associated with glaciers. The soils in this study originated from loess. Loess is wind-deposited sediment, consisting of uniform, calcareous, silt-sized particles. Initially, glacial materials were deposited as sediments in rivers full of meltwaters. As rivers dry up, these materials were left behind and exposed to winds moving through. The loess was picked up and transported many miles, then deposited over other glacial materials throughout McLean County (United States Department of Agriculture, 1998).

The soils at the Lexington Farm are predominantly silty loams overlying loamy glacial deposits. There are thirteen mapped soil units belonging to Parr–Lisbon–Drummer association over the area of the farm (Figure 4). This study focuses on soils of the Saybrook, Drummer, and Flanagan Units.

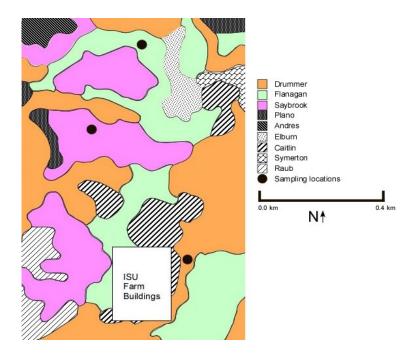


Figure 4: Soil map and sample location within study area.

The Saybrook Unit is a moderately permeable silt loam, with moderate organic matter content (Table 1). This unit typically occupies uplands, till plains, and moraines, with its parent material being loess 50 to 102 cm thick and the underlying loamy glacial till (United States Department of Agriculture, 1998). During the study period, the soils of the Saybrook Unit were used for soybean cultivation.

The Drummer Unit is a silty clay loam that forms uplands, till plains, terraces, and outwash plains. This soil is moderately permeable with high organic matter content (Table 1). The parent materials of the Drummer Unit are loess approximately 100 to 150 cm thick and the underlying loamy outwash (United States Department of Agriculture, 1998). During the study, corn was grown on the field site representing the Drummer Unit.

The Flanagan Unit is a silty loam typically forming uplands and till plains, with a high organic matter content. The permeability of the Flanagan varies from moderately permeable in the upper part to moderately low in the underlying material (Table 1). The parent materials of the Flanagan Unit are loess 100 to 150 cm thick and the underlying loamy glacial till (United States Department of Agriculture, 1998). As with the Drummer Unit, corn was grown on the site representing the Flanagan Unit.

Table 1: Soil properties of the study area (from United State Department of Agriculture, 1998 – converted to metric).

			Organic Content	Crop Type
Soil Unit	Depth (cm)	Permeability (m/s)	(%)	Sampled
Saybrook	0-20.3	$4.2 \times 10^{-6} - 1.4 \times 10^{-5}$	3-4	Soybean
	20.3-73.7	$4.2 \times 10^{-6} - 1.4 \times 10^{-5}$		
	73.7-152.4	$1.4 \times 10^{-6} - 4.2 \times 10^{-6}$		
Drummer	0-33.02	$4.2 \times 10^{-6} - 1.4 \times 10^{-5}$	5-7	Corn
	33.02-104.1	$4.2 \times 10^{-6} - 1.4 \times 10^{-5}$		
	104.1-119.4	$4.2 \times 10^{-6} - 1.4 \times 10^{-5}$		
	119.4-152.4	$4.2 \times 10^{-6} - 1.4 \times 10^{-5}$		
Flanagan	0-38.1	$4.2 \times 10^{-6} - 1.4 \times 10^{-5}$	4-5	Corn
	38.1-119.4	$4.2 \times 10^{-6} - 1.4 \times 10^{-5}$		
	119.4-152.4	$1.4 \times 10^{-6} - 4.2 \times 10^{-6}$		

Site History

Until 1999, the present ISU Farm was owned and farmed by Farm Services (FS). ISU began farming the site, which is approximately 360 acres in size, in 2001. From this time on, ISU has continued growing crops such as corn, soybeans, and alfalfa and raising cows, swine, and sheep (Kalmer, 2005). Much of the history of the farm before ISU took ownership is unknown. During the time that FS operated the farm, 10 acres of land were

set aside each year for manure disposal. The most recent area where manure was disposed is believed to be the corn field where the Flanagan Unit is located. The most recent fertilizer application on the Flanagan and Saybrook Units was April 22, 2003, while the Drummer Unit had fertilizer applied April 23, 2003.

Hypotheses

Current data suggest that there is a complex relationship between fertilizer application rate and timing and NO₃⁻ concentrations in the unsaturated zone. These data imply that soil type may exert significant control on NO₃⁻ concentrations. The goal of this study was to conceptually understand and quantify the nitrogen transport processes occurring within the unsaturated zone beneath agricultural fields by testing four hypotheses:

Hypothesis 1: The majority of NO₃⁻ movement through the unsaturated zone occurs during normal conditions, not under wet conditions such as those after infiltration caused by rain events. Most NO₃⁻ movement through the soils observed during this study will be through the soil matrix under normal conditions, not through macropores after rain events.

Hypothesis 2: The rate of NO_3^- movement beneath corn fields will be slower than beneath soybean fields. Corn crops do not have the ability to convert N_2 to NO_3^- ; therefore corn will be more likely to use available NO_3^- . In contrast, soybeans can convert N_2 to NO_3^- . Because of this there would be excess NO_3^- in the soil that would not be utilized by the soybean crops. The excess portion of the NO_3^- would be capable of

moving through the soil.

Hypothesis 3: The rate of NO₃⁻ movement in silty soils will be slower than in sandy soils. Silty soils have the ability to retain more water, therefore more NO₃⁻, due to the smaller grained materials and smaller pores. Water moves more quickly through coarser grained material, which will also increase the rate of movement of NO₃⁻ through these materials.

Hypothesis 4: The lowest NO₃⁻ concentrations in the unsaturated zone will be in soils with high organic matter content. Soils that are high in organic matter may result in high biological activity leading to reducing conditions. Reducing conditions promote removal of NO₃⁻ through denitrification.

CHAPTER II

METHODOLOGY

Methods

In order to determine the rate at which NO₃⁻ is moving through the unsaturated zone, soil samples were collected below corn and soybean fields located on a set of soils developed on glacial terrain. Each sample was then analyzed for numerous soil properties.

Soil cores were collected monthly from three plots, at multiple locations in each plot for statistical testing. Selection of sampling locations was based on site accessibility and soil type. Each sampling plot needed to be composed of a different soil unit. Another requirement was that at least two crop types were sampled. At each sampling location, three cores were extracted and described to the local depth of the water table (approximately 1.5 m) and sub-sampled every 0.15 m. Each core was collected by one of two different processes. From 0 to 0.30 m, samples were collected using a split spoon auger. Below 0.30 m, samples were first collected using a 2.54 cm soil probe, and then bulk samples were collected using a hand auger. Each sample was wrapped in foil, labeled and placed in a cooler until returning to the lab.

Samples that were used to determine physical properties of the soil were immediately weighed then placed in an oven to dry. Physical properties that were

measured or calculated included gravimetric moisture content, organic matter content, bulk density, grain size, porosity, and hydraulic conductivity. Bulk samples were frozen immediately after returning to the lab for preservation until NO₃⁻ extraction and analysis could be performed.

Gravitational moisture content was determined for each sample in order to relate precipitation during the study to the amount of water in the soil. Organic matter content was measured in each sample, and averaged for each sampling site. The amount of organic matter at each site was used to determine the interaction between NO₃⁻ concentrations and organic matter in soils. Bulk density of the soil samples were calculated as a way of determining porosity for each sample. Grain size, porosity, and hydraulic conductivity of the soils at the study area were measured and calculated in order to determine the expected rate of water movement through each of the soil profiles.

Moisture content was determined by weighing a wet sample to determine its mass (m_s) . The sample was then oven-dried at a temperature of 105° C for 24 hours to remove all the moisture. The oven-dried sample was re-weighed to determine the mass of the dry sample (m_d) . The mass of the water (m_w) in the sample is the difference between the wet sample mass and the dry sample mass. Moisture content (θ) , as defined by Marshall et al. (1996), is the ratio of the mass of the water divided by the mass of the dry sample:

$$\theta = \frac{m_w}{m_d} = \frac{(m_s - m_d)}{m_d} \tag{1}$$

Organic content was determined by first weighing each dry sample (m_d), then placing it in a muffle furnace at 500° C for two hours after which time the sample was

reweighed (m_f). Heating the sample to high temperatures causes the organic carbon in the soil to be oxidized and driven off as CO₂. This results in a change in mass

$$m_c = m_d - m_f \tag{2}$$

and allows for calculation of the organic content (m_c) of the sample as: (Schulte and Hopkins, 1996).

$$OC\% = \frac{m_c}{m_d} \tag{3}$$

Bulk densities were determined by drying a known volume (v) of the soil sample and weighing it to determine the dry mass (m_d) . Using the inside diameter (2r) of the split spoon or the soil probe and the known length (1) of the core, the volume of core is calculated using the formula:

$$v = \pi r^2 l \tag{4}$$

The bulk density (ρ_b) is the mass of the dry sample divided by the volume of the dry sample (Marshall et al., 1996):

$$\rho_b = \frac{m_d}{v} \tag{5}$$

Once the bulk density was calculated, it was used to determine to porosity (n) of the soil matrix using the relationship:

$$n = 1 - \frac{\rho_b}{\rho_s} \tag{6}$$

where ρ_s is the material density. The average density of material is 2.65 g/cm³ (typical of most soils).

Grain size was determined by sieve analysis for the coarse fraction, ranging from silt- to medium sand-sized materials, and by the use of a hydrometer for the finer fraction, clay-sized materials. The main focus of the grain size analysis was the mass fraction of sands, silts, and clays, and not the overall distribution of each grain size. This allowed wet sieving to be completed on the selected samples using 1Φ , 2Φ , 3Φ , and 4Φ to measure the amounts of coarse materials in the samples.

The finer materials in the soils at the study area were analyzed using the hydrometer method (Bowles, 1992). Approximately 60 g of sediment from the bulk samples collected at the field site were weighed out. The 60 g sample was placed into a beaker and 125 mL of Calgon[®] solution (made by mixing 4 g Calgon[®] powder, a dispersion agent, and 1 L tap water) was added and the sample was allowed to soak in the solution for at least an hour. The Calgon® was used to separate the clay materials by breaking the bonds created by the charges on the clay. After soaking, the sample and Calgon[®] solution were emptied into a stainless-steel malt mixer, taking care that all sediment particles were removed from the beaker, and enough tap water was added to bring the mixer container to $\frac{2}{3}$ full. The sediment solution was then agitated for at least 2 minutes, or until all lumps of sediment were destroyed, all of the sediment was suspended in the solution, and the solution was smooth. The sediment suspension was emptied into a 1000 mL sedimentation cylinder and enough tap water was added to equal 1000 mL. Temperature and hydrometer readings were recorded from a control sedimentation cylinder containing 125 mL of Calgon® solution and enough tap water to equal 1000 mL. Hydrometer measurements were recorded at approximately two, four, eight, sixteen and

thirty minutes of elapsed time and again at one, two, four, eight, sixteen, twenty-four, and thirty-two hours elapsed time.

Saturated hydraulic conductivity (K) is the rate at which water can move through a permeable material (Fetter, 2001). For the soils, K, in m/s, was determined using the Campbell (1985) equation:

$$K = Ce^{(-6.9m_c - 3.7m_s)} (7)$$

where m_c is the mass fraction of clay, m_s is the mass fraction of silt, and C is an equilibrium constant, with a value of -4×10^{-3} kg·s/m³. The mass fractions of the silt and clay materials were derived from the grain-size analysis.

To determine NO₃⁻ concentrations in the soil, the NO₃⁻ was extracted from within the sediment following the method used by Mulvaney (1996). Ten grams of oven-dried sediment was placed in a glass container. The NO₃⁻ was extracted from the soil by adding 100 mL of 0.01 M solution of potassium chloride (KCl) to the sediment. The sediment and solution mixture were shaken for 60 minutes then allowed to settle. Five mL of the solution were withdrawn from the container, filtered, and analyzed using an ion chromatograph.

CHAPTER III

RESULTS

Soil Properties

Samples were collected during the summer and fall of 2004 (Table 2). Each of the samples collected was analyzed to determine soil properties including bulk density, gravimetric moisture content, organic matter content, porosity, hydraulic conductivity, and grain size. The soils examined in the study were the Drummer, Flanagan, and Saybrook Units, which are predominantly silty loams overlying loamy glacial deposits. The soils range from poorly to moderately well drained, with moderate to moderately slow permeability (United States Department of Agriculture, 1998).

Table 2: Sampling schedule; including maximum sample depth and number of samples collected.

Date	Flanagan Unit	Drummer Unit	Saybrook Unit
6/14/2004	150 cm; 8 samples	135 cm; 8 samples	
6/21/2004			150 cm; 10 samples
6/28/2004	150 cm; 10 samples	150 cm; 10 samples	
7/6/2004	150 cm; 10 samples	150 cm; 10 samples	
7/26/2004	150 cm; 10 samples		150 cm; 10 samples
8/9/2004		150 cm; 10 samples	150 cm; 10 samples
8/31/2004	150 cm; 10 samples	150 cm; 10 samples	150 cm; 10 samples
9/28/2004	150 cm; 10 samples	150 cm; 10 samples	150 cm; 10 samples
10/26/2004	150 cm; 10 samples		
11/15/2004	150 cm; 9 samples	150 cm; 10 samples	150 cm; 10 samples

Bulk Density

Bulk density was measured for each sample collected over the course of the study period. As can be observed in Figure 5, the dry bulk density of the soil at each sampling site increased with depth. The soils from the Flanagan Unit were determined to have dry bulk densities ranging from 1.31 g/cm³ to 1.90 g/cm³, which were similar to the 1.2 g/cm³ to 1.7 g/cm³ values reported by United States Department of Agriculture (1998). Dry bulk densities for the Drummer Unit range from 1.28 g/cm³ to 1.69 g/cm³. These values were within the values reported by the United States Department of Agriculture (1998), which range from 1.10 g/cm³ to 1.70 g/cm³. For the Saybrook Unit the dry bulk density ranged from 1.31 g/cm³ to 1.71 g/cm³ (Figure 5). Overall, these values were consistent with those reported by the United States Department of Agriculture (1998), which ranged from 1.10 g/cm³ to 1.70 g/cm³.

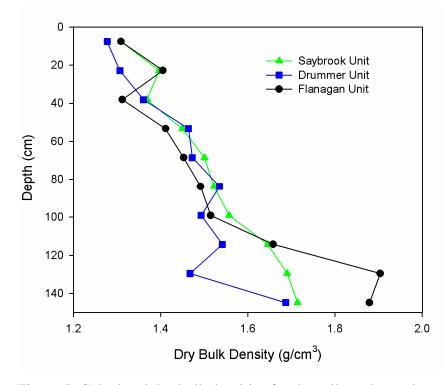


Figure 5: Calculated dry bulk densities for the soils at the study area.

Moisture Content

Using samples collected at the study area, moisture content was calculated for each site. At all three of the sample locations, over each sample interval, the moisture content ranged from 17% to 30% (Table 3, Figure 6).

Table 3: Average moisture content for each sampling location based on depth.

		1 &				
	Flanagan Unit		Drummer Unit		Saybrook Unit	
Depth	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
(cm)	(%)	(%)	(%)	(%)	(%)	(%)
0-30	18	27	19	29	21	28
30-76	20	30	19	27	23	30
76-150	19	27	21	30	17	30

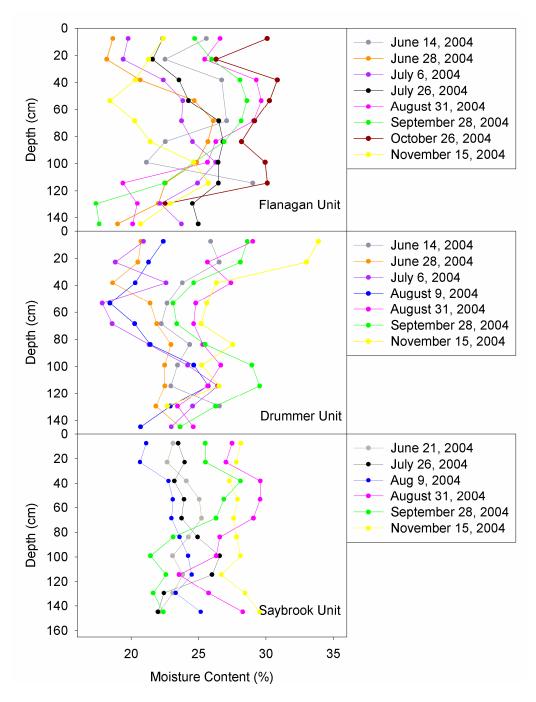


Figure 6: Moisture content for each sampling location at the study area. Moisture content was determined each day samples were collected, at each sampling interval.

Organic matter content was measured for each sample collected (Table 4, Figure 7). The measured organic matter content decreases overall with depth at each of the sampling sites. Near the ground surface there is more variation in the measured organic matter content at each site, but becomes less variable with depth. The Flanagan Unit has a moderate organic matter content of approximately 5% near the surface and decreases to 1.5 to 3.5% at depths of 35 cm to 145 cm. The Drummer Unit has high organic matter content, ranging from 7 – 7.5%, from the surface to approximately 35 cm below the surface and decreases to low to moderate levels ranging from 1.5 to 5% at depths of 35 cm to 145 cm. The Saybrook Unit has a moderately high amount of organic matter near the surface, ranging from approximately 5 - 6%, which decreases to a low to moderate amount, approximately 2 – 4%, below 35 cm.

Table 4: Average organic matter content at each sampling interval.

Flanagan Unit		Drummer Unit		Sayb	Saybrook Unit	
	Average		Average		Average	
Average	Organic	Average	Organic	Average	Organic	
Depth	Matter	Depth	Matter	Depth	Matter	
(cm)	Content (%)	(cm)	Content (%)	(cm)	Content (%)	
7.6	5.2	7.6	7.4	7.6	5.9	
22.9	4.9	22.9	7.2	22.9	5.6	
38.1	3.5	38.1	4.7	38.1	4.0	
53.3	3.3	53.3	3.2	53.3	3.2	
68.6	2.6	68.6	3.0	68.6	2.6	
83.8	2.3	83.8	2.8	83.8	2.1	
99.1	2.0	99.1	2.5	99.1	2.4	
114.3	1.5	114.3	2.2	114.3	2.0	
129.5	1.4	129.5	1.6	129.5	1.9	
144.8	1.4	144.8	1.4	144.8	1.8	

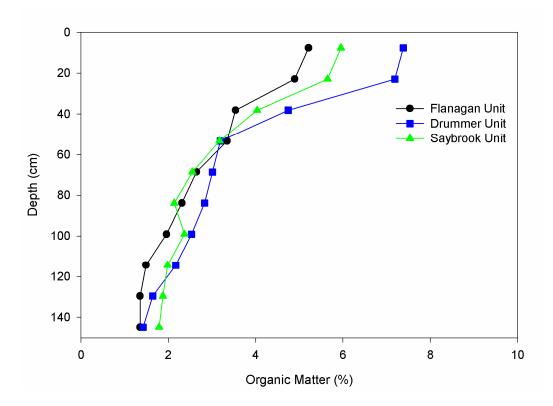


Figure 7: Average soil organic matter content at each sampling location.

Grain Size

Grain size was determined for representative cores from each sampling location (Figure 8). Based on grain size analysis, overall average soil compositions were determined (Table 5). At each of the three sites there are grain size trends that can be seen as depth increases. Near the surface of the Flanagan and Saybrook Units, the material tends to be mainly silt-sized grains. Near the surface in the Drummer Unit, sand-size particles compose the largest fraction of the materials. From approximately 30 to 80 cm deep in all the units, the clay fraction of the soil increases. Below 80 cm in all the units,

the portion of clay-sized materials decreases drastically, and the amount of sand-sized particles increases.

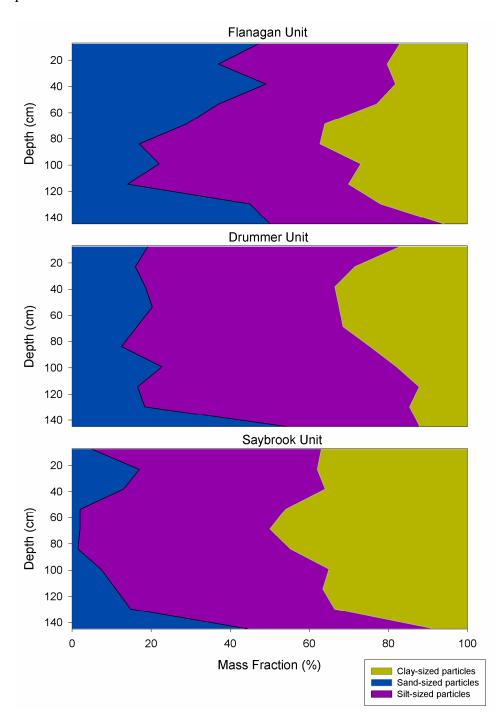


Figure 8: Cumulative grain size distribution for each soil type.

Table 5: Average grain size composition for each soil unit.

	Flanagan	Saybrook	Drummer
_	Unit	Unit	Unit
Particle			
Size	Per	rcent Composit	ion
Sand	35	12	22
Silt	41	52	56
Clay	24	36	22

Porosity

Porosity values calculated for samples collected from the Flanagan Unit ranged from 12% to 64%. Porosity values calculated for the Drummer Unit range from 32% to 65%. Based on the samples collected, calculated porosity values for the Saybrook Unit ranged from 29% to 51% (Table 6, Figure 9). As can be observed from Figure 9, the porosity decreases with depth at each sampling site.

Table 6: Average porosity at each sampling interval.

Flanagan Unit		Drumm	Drummer Unit		Saybrook Unit	
Average Depth (cm)	Average Porosity (%)	Average Depth (cm)	Average Porosity (%)	Average Depth (cm)	Average Porosity (%)	
7.6	51	7.6	52	7.6	50	
22.9	47	22.9	50	22.9	47	
38.1	50	38.1	49	38.1	48	
53.3	47	53.3	45	53.3	45	
68.6	45	68.6	44	68.6	43	
83.8	50	83.8	42	83.8	43	
99.1	48	99.1	44	99.1	41	
114.3	37	114.3	42	114.3	38	
129.5	28	129.5	45	129.5	37	
144.8	29	144.8	36	144.8	36	

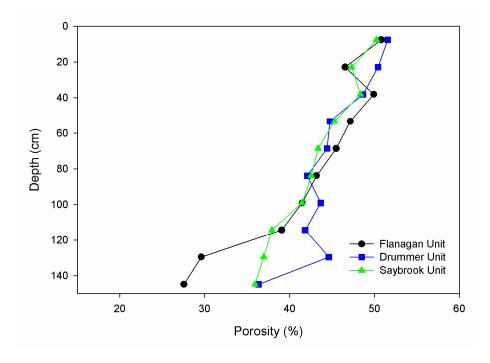


Figure 9: Average porosity for each sampling interval, at each location.

Hydraulic Conductivity

Hydraulic conductivity values determined for the Flanagan Unit range from 2.9 x 10^{-4} to 6.5 x 10^{-4} m/s. Hydraulic conductivity for the Drummer Unit range from 3.9 x 10^{-5} to 3.25 x 10^{-4} m/s. Based on calculations, the Saybrook Unit has hydraulic conductivities ranging from 1.8 x 10^{-5} to 4.25 x 10^{-4} m/s (Figure 10).

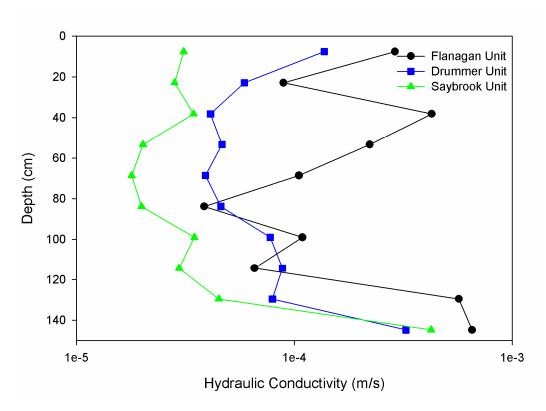


Figure 10: Hydraulic conductivity determined for each sampling location interval.

Climate

The average climate in Illinois is temperate, with a large degree of variation between seasons. Based on historical climate data from 1971 to 2000, the average minimum temperatures in Normal, Illinois range from approximately -10.2° C in January to 18.2° C in July. Average maximum temperatures range from -0.56° C in January to 29.8° C in July, with mean temperatures ranging from -5.3° C in January to 24° C in July (Midwestern Regional Climate Center, 2005). During the period from 1971 to 2000 annual mean precipitation in Normal, Illinois was 95.1 cm. The months with the highest

mean precipitation are May (11.5 cm), June (9.9 cm), July (10.03 cm) and August (9.7 cm) (Midwestern Regional Climate Center, 2005).

During the study period (June – November 2004), precipitation data were collected at the ISU Farm using a tipping bucket rain gauge (Figure 11). Based on rainfall data collected on-site, the average monthly precipitation at the study area was 7.53 cm. The highest monthly precipitation, 13.97 cm, occurred in August 2004 and the lowest precipitation recorded was 3.43 cm in October 2004.

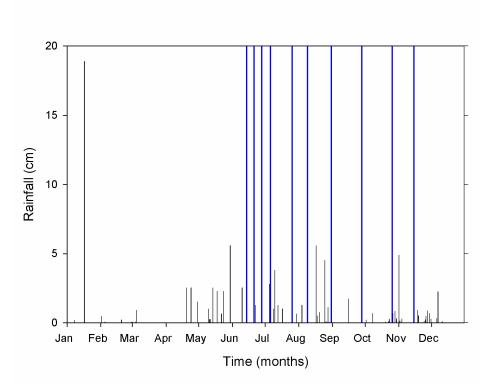


Figure 11: Precipitation data for the study area, showing monthly precipitation for 2004. Blue lines represent sampling days.

Nitrate Content

Over the duration of the study NO_3^- contents in the soil varied at each sampling location, and most commonly with depth as well. The range of the NO_3^- at the Flanagan Unit was $1.76 \times 10^{-4} \text{ kg NO}_3^-$ /kg soil to $1.49 \times 10^{-2} \text{ kg NO}_3^-$ /kg soil; at the Drummer Unit NO_3^- levels ranged from below detection limits (BDL) to $2.86 \times 10^{-3} \text{ kg NO}_3^-$ /kg soil; and samples collected form the Saybrook Unit had NO_3^- contents ranging from $5.39 \times 10^{-5} \text{ kg NO}_3^-$ /kg soil to $2.36 \times 10^{-3} \text{ kg NO}_3^-$ /kg soil.

Nitrate concentrations for each sample were measured using an ion chromatograph. The ion chromatograph measured NO_3^- concentrations in mg/L which were converted to kg NO_3^- /kg soil. For NO_3^- concentrations ≤ 2 mg/L the analytical error was 8.7%, for concentrations ≥ 2 mg/L the analytical error was 5%. Through conversion, the analytical error for all samples was approximately one order of magnitude lower than the actual measured NO_3^- concentration. The error between replicate samples was within the same order of magnitude as the actual measured NO_3^- concentration (Figure 12).

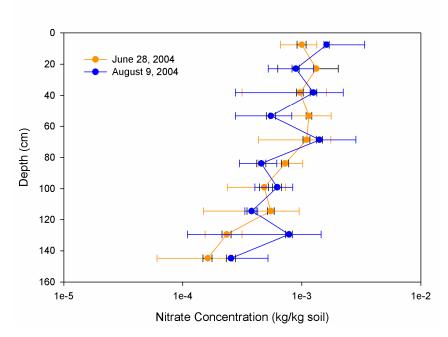


Figure 12: Analytical error data. Orange lines indicate samples collected June 28, 2004, shown with replicate sample errors. Blue lines indicate samples collected August 9, 2004, shown with replicate sample errors. For both sample dates, the black error bars represent analytical error.

Flanagan Unit

Over the course of the study, samples from the Flanagan Unit were collected eight times. Nitrate contents from this sample location ranged from $1.76 \times 10^{-4} \text{ kg NO}_3$ -/kg soil to $1.49 \times 10^{-2} \text{ kg NO}_3$ -/kg soil (Table 7, Figure 13).

Table 7: Nitrate ranges for the Flanagan Unit.

Date	Minimum (kg NO ₃ -/kg soil)	Maximum (kg NO ₃ -/kg soil)
June 14, 2004	9.41 x 10 ⁻⁴	9.09 x 10 ⁻³
June 28, 2004	1.76 x 10 ⁻⁴	1.06×10^{-2}
July 6, 2004	9.90×10^{-4}	1.09×10^{-2}
July 26, 2004	3.04×10^{-4}	1.55×10^{-3}
August 31, 2004	6.97×10^{-4}	1.49×10^{-2}
September 28, 2004	6.96×10^{-4}	2.02×10^{-3}
October 26, 2004	7.62×10^{-4}	1.36×10^{-3}
November 15, 2004	5.12 x 10 ⁻⁴	1.33 x 10 ⁻³

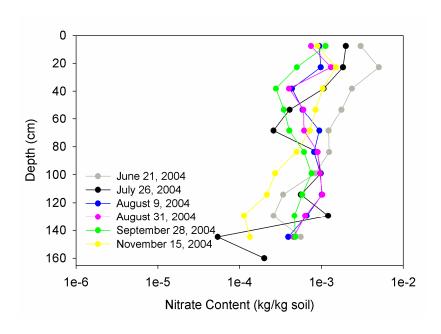


Figure 13: Nitrate concentrations for each sampling day from the Flanagan Unit.

Drummer Unit

Soil samples from the Drummer Unit were collected seven times during the time that this study was conducted. Nitrate contents from this sample location ranged from BDL to $2.03 \times 10^{-4} \text{ kg NO}_3\text{-/kg}$ soil (Table 8, Figure 14).

Table 8: Nitrate ranges by sampling date for the Drummer Unit.

Date	Minimum (kg NO ₃ -/kg soil)	Maximum (kg NO ₃ -/kg soil)
June 14, 2004	3.23 x 10 ⁻⁴	9.76 x 10 ⁻⁴
June 28, 2004	1.62×10^{-4}	1.32×10^{-3}
July 6, 2004	2.03×10^{-4}	2.86×10^{-3}
August 9, 2004	2.54×10^{-4}	1.62×10^{-3}
August 31, 2004	1.54×10^{-4}	1.03×10^{-3}
September 28, 2004	BDL	2.30×10^{-3}
November 15, 2004	BDL	1.65×10^{-3}

BDL = below detection limits

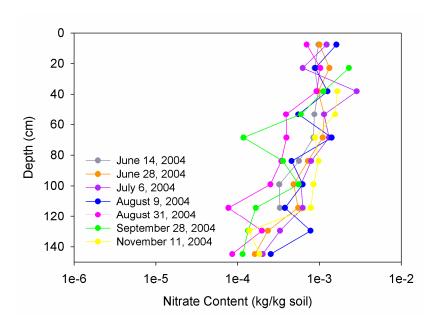


Figure 14: Nitrate concentrations for each sampling day from the Drummer Unit.

Saybrook Unit

Samples were collected from the Saybrook Unit six times over the course of this project. On average, NO_3^- contents from this sample location ranged from 5.39 x 10^{-5} kg NO_3^- /kg soil to 2.36×10^{-3} kg NO_3^- /kg soil (Table 9, Figure 15).

Table 9: Nitrate ranges by sampling date for the Saybrook Unit.

Date	Minimum (kg NO ₃ -/kg soil)	Maximum (kg NO ₃ -/kg soil)
June 21, 2004	2.60 x 10 ⁻⁴	5.03 x 10 ⁻³
July 26, 2004	5.39×10^{-5}	1.99×10^{-3}
August 9, 2004	3.93×10^{-4}	1.01×10^{-3}
August 31, 2004	4.02×10^{-4}	1.31×10^{-3}
September 28, 2004	2.78×10^{-4}	1.12×10^{-3}
November 15, 2004	1.13 x 10 ⁻⁴	1.50 x 10 ⁻³

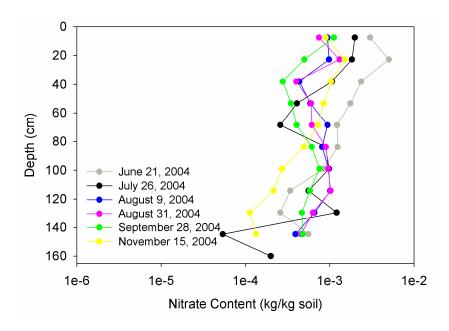


Figure 15: Nitrate concentrations for each sampling day from the Saybrook Unit.

CHAPTER IV

DISCUSSION

Overview of Results

Based on data collected at each of the sampling locations, NO₃⁻ was detected in the soil not only near the surface, but also at depths below plant root zones. This deeper NO₃⁻ can be attributed to residual NO₃⁻ from previous growing seasons. It might also be possible for this NO₃⁻ to be the product of fertilizer applied at the end of the previous growing season. NO₃⁻ applied at the end of the previous growing season would have the ability to make its way through the system following rain or snowmelt events due to the fact there would no longer be crop cover.

An initial assumption of this investigation was that NO₃⁻ concentrations would form "bulges" in the soil profile that could be followed vertically over the course of the study. Initial samples from the Drummer Unit collected and analyzed during June 2004 showed distinct NO₃⁻ "bulges" within the unsaturated zone at the study area (Figure 16). The changes in depth with time of the NO₃⁻ bulges at the study area were monitored over the course of the project similar to the work of Alberts and Spomer (1985), Peterson et al. (2002) and Bobier et al. (1993). Using these data, the downward transport rate of NO₃⁻ in soil was quantified by determining the difference in depth between observed peaks of NO₃⁻ bulges on different sampling days.

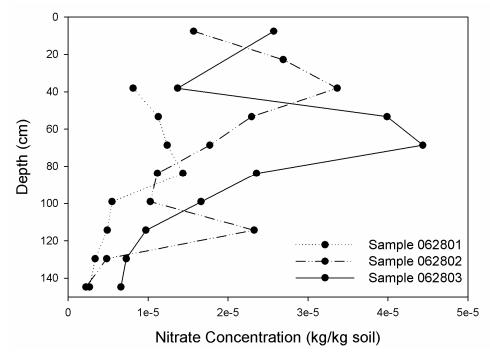


Figure 16: Nitrate profile within the unsaturated zone underlying a corn field. Drummer Unit, June 28, 2004.

Monitoring the change in NO₃⁻ levels over time allowed for the rate of vertical movement to be calculated. The transport rates were calculated using the most easily observed bulges. The calculated transport rate for the Flanagan Unit is approximately 0.59 cm/day (215.4 cm/year). The transport rates for the Drummer Unit range from 0.54 cm/day (197.1 cm/year) to 0.69 cm/day (251.9 cm/year). The calculated transport rates for the Saybrook Unit range from 2.8 cm/day (1022.0 cm/year) to 3.1 cm/day (1131.5 cm/year). Transport rates were calculated once for the Flanagan Unit, and twice for the Drummer Unit and the Saybrook Unit. A second transport rate for the Flanagan Unit was not calculated because there were no other distinguishable bulges to use for the calculation. Based on these calculated transport rates, any applied NO₃⁻ will move

through the unsaturated zone to the water table within one year.

When compared to studies by Alberts and Spomer (1985) and Bobier et al. (1993), vertical transport rates of the NO₃ in the soils at the study area are very high. Alberts and Spomer (1985) studied four corn-cropped sites in non-irrigated loess material at a study area in western Iowa. Samples were collected in 1975, with NO₃-N concentrations detected at 4 m below the surface. When samples were collected again nine years later, NO₃-N concentrations had moved vertically to depths of 10.7 m, which resulted in a vertical transport rate of 74 cm/year. A study by Bobier et al. (1993) measured NO₃ transport rates in the unsaturated zone below eight irrigated corn-cropped plots. The material at this study area was silt loam underlain by loess. Samples were collected in 1985 and 1990. Based on corresponding bulges between the sampling events, the NO₃ had moved vertically 381cm over a five year period, resulting in a vertical movement rate of 76 cm/year. Peterson et al. (2002) were unable to calculate an exact vertical transport rate because the timing of fertilizer application was unknown, but an approximate rate of 60 - 65 cm/year was determined based on observed NO₃ bulges. Although the transport rates were lower than those calculated for this work, the three previous studies measured NO₃-N concentrations similar to those measured during this study at the ISU Farm ($\sim 10^{-4}$ kg/kg).

After comparing the results of the current study to previous work, it was determined that most likely the NO₃⁻ bulge patterns observed at the study area are not good indicators of NO₃⁻ movement through the soil profile. This was determined by the fact that at the study area there were not very many distinguishable NO₃⁻ bulges, and also

by the high NO₃⁻ transport rates that were calculated based on these bulges. In comparison with transport rates from similar studies, the transport rates at this study area are drastically high. Presumably, the NO₃⁻ bulges observed in the soil profile at the study area are linked to previous years fertilizer applications or from the decomposition of plants. It is also very unlikely that if NO₃⁻ is moving through the system at a rate of 197.1 cm/year to 1131.5 cm/year, that there would have been any NO₃⁻ detectable since there has been no N-fertilizer applied to the area since April 2003. Based on this information, it is very likely that most NO₃⁻ in the soil systems at the study area is being utilized by plant uptake.

Trends

One overall trend that can be observed at each of the sampled sites is that a large portion of the NO₃⁻ in the system appears to be utilized at the beginning of the growing season by plant uptake. On June 28, 2004, near the beginning of the sampling season, NO₃⁻ levels collected from the top 38 cm of the soil profile averaged 8.32 x 10⁻³ kg NO₃⁻/kg soil in the Flanagan Unit. In the top 23 cm of the Drummer Unit average NO₃⁻ levels were 1.16 x 10⁻³ kg NO₃⁻/kg soil. On June 21, 2004, NO₃⁻ levels collected from the top 38 cm averaged 3.47 x 10⁻³ kg NO₃⁻/kg soil in the Saybrook Unit. When samples were collected from depths near the surface at these sites again 9 days later, average NO₃⁻ levels decreased. At the Flanagan Unit, NO₃⁻ levels averaged 7.41 x 10⁻³ kg NO₃⁻/kg soil and at the Drummer Unit NO₃⁻ levels averaged 9.25 x 10⁻⁴ kg NO₃⁻/kg soil on July 6, 2004. Similarly, on July 26, 2004 samples collected from the Saybrook Unit had average

 NO_3^- levels of 1.63 x 10^{-3} kg NO_3^- /kg soil.

Another common trend that was observed during this study was increased NO₃⁻ concentrations near the end of the growing season. Once plants reach a certain stage during growth, the plants will begin breaking down and NO₃⁻ will no longer be utilized. This trend could be seen in samples collected beginning in September 2004, to depths of 40 cm. The trend of increased NO₃⁻ concentrations could be related to this period when plant decomposition begins.

Movement During Normal vs. Wet Conditions

In order to determine if the NO₃⁻ was moving vertically through the soil during normal conditions or after rain events, cores were collected subsequent to significant recharge events and analyzed following the same procedures described previously. Concentrations of NO₃⁻ at specified depths were compared to the previous sampling to quantify movement rates associated with the recharge events. The influence of frequency, duration, and intensity of the recharge events were analyzed to determine whether there is a certain size storm that initiates subsurface movement.

Over the course of this study there was significant rainfall, totaling approximately 45.2 cm, with monthly average rainfall of 7.5 cm. Although it rained significantly throughout this investigation, there were no large recharge events to measure or compare with movement during normal conditions. During months that had high total rainfall, most precipitation occurred as small amounts of rain over multiple days. Because of this it was not possible to determine whether the majority of NO₃⁻ movement through the

unsaturated zone occurs as movement during normal conditions or under wet conditions, such as those after infiltration caused by rain events.

Although there was significant rain to sustain the crops during the study period, the crop cover prevented some of the rain from reaching the ground surface on areas where fields were planted. This was apparent in the dry surface and large mud-cracks that were visible at the sampling locations, even after significant rain events. According to Ward and Dorsey (1995), soil surface conditions will control infiltration. Plants or crops serve as ground cover, which will absorb the energy from falling precipitation, thus allowing water to infiltrate more slowly instead of puddling on the soil. After rain events, the ground was not visibly wet which indicates that the water had time to slowly percolate into the unsaturated zone.

The plants created an umbrella that does not allow falling precipitation to come into direct contact with the ground surface, but rather absorbs the energy of the rain and allows the rain to run down the plant stalks to the surface. Given that precipitation only reached the ground after first coming into contact with plants, macropores play a very small role in the movement of NO₃⁻. If large amounts of precipitation were to move through the macropores most likely only NO₃⁻ at the surface or interface of these macropores would be available for transport, which is related to the fact that most NO₃⁻ is bound in the soil matrix and during flow through macropores will remain there because water is flowing rapidly through macropores and not the soil matrix.

If precipitation is unable to penetrate the ground surface, there is less water in the system to transport NO₃⁻ through the unsaturated zone. At the beginning of the sampling

for this project, the soil moisture contents at each site ranged from approximately 21% to 29%. Throughout the course of the investigation, these values varied depending on rainfall events. For instance, during the month of July approximately 11 cm of precipitation fell. On June 28, 2004 at the Flanagan site the moisture content ranged from 18% to 26%. At this same location on July 26, 2004 moisture content ranged from 22% to 27%. During the month of August there was significant rainfall at the study area, with approximately 14 cm of precipitation. At the Flanagan site on August 31, 2005 the moisture content ranged from 20% to 30%. The soil moisture contents in the Flanagan Unit remained close to these values through the end of the investigation. Even though there were higher than average amounts of rainfall during July and August there were still visible soil cracks and dry soils at the surface at the sampling locations. The fluctuations in moisture content could also be observed at the Drummer and Saybrook Units depending on precipitation. The ground surface at each of these sites was also dry with soil cracks visible.

Over the course of the study (June – November 2004), there was a total of 45.2 cm of precipitation measured at the study area. Annual mean precipitation at the study area is 95.1 cm (Midwestern Regional Climate Center, 2005). The amount of annual precipitation at the study area is high in comparison with the areas studied by Alberts and Spomer (1985) and Bobier (1993), which are approximately 75.1 cm and 66 cm respectively. The increase in vertical transport rate at the study area could be partially attributed to the higher amount in precipitation, but this alone cannot account for the order of magnitude difference in transport rates.

Crop Type

Based on one of the primary hypotheses, the NO₃⁻ concentrations would be greater in soils below corn fields, than below soybean fields. Soybeans have the ability to "make" NO₃⁻ that can be utilized by the plant; therefore it is often not necessary to apply as much fertilizer to soils that will be planted with soybean crops. Corn relies on residual NO₃⁻ in the soil or on the application of fertilizer in order to have enough NO₃⁻ during the growing period.

In order to determine if crop type affected NO₃⁻ concentrations in the soils below, data from one corn field and one soybean field were compared. The corn crop chosen was growing on the Drummer Unit and the soybean crop was growing on the Saybrook Unit. These two soil units were chosen because of their similar grain size distribution. The Saybrook Unit contains 12% sand, 52% silt, and 36% clay-sized particles. The Drummer Unit is composed of 22% sand, 56% silt, and 22% clay-sized particles on average. Although there are differences in the sand and clay-sized fractions of the soils, they are the most similar of the soils sampled at the study area.

On average, the Drummer Unit having the corn crop had lower NO₃⁻ levels than the Saybrook Unit, with concentrations ranging from BDL to 2.86 x 10⁻³ kg NO₃⁻/kg soil, while samples collected form the Saybrook Unit had NO₃⁻ concentrations ranging from 5.39 x 10⁻⁵ kg NO₃⁻/kg soil to 2.36 x 10⁻³ kg NO₃⁻/kg soil. Each year at the study area, corn is grown on the Drummer Unit. This could possibly lead to the depletion of the soil nutrients, explaining the lower NO₃⁻ concentrations in the Drummer Unit. The Saybrook

Unit is rotated between corn and soybean crops. During growing seasons when soybeans are planted, it is possible that not all of the NO₃⁻ in the system is utilized, which would lead to residual NO₃⁻ in the soil. This could explain the higher NO₃⁻ concentrations in this soil unit. Nitrate concentrations at the Drummer Unit are more consistent in the top 53 cm of the soil profile while the NO₃⁻ concentrations in the Saybrook Unit vary more from 0 to 53 cm. The difference in NO₃⁻ concentrations in the top 53 cm of the soil profile could also be linked to the fact that soybeans can make their own NO₃⁻.

Soil Type

Grain size analyses determined that the Flanagan Unit is the sandiest soil at the study area, containing 41% silt, 35% sand, and 24% clay-sized particles. The Drummer Unit is composed of the highest amount of silt in comparison with the other soils sampled at the study area. The Drummer Unit contains 56% silt, 22% sand, and 22% clay-sized particles on average. The Saybrook Unit has only slightly less silt, but is more clay-rich than the Drummer Unit, with an overall composition of 52% silt, 12% sand, and 36% clay-sized particles. As can be noted from these data, the sand composition of the Saybrook Unit is considerably lower than the other two sampled units. The hydraulic conductivity for the Flanagan Unit ranges from 2.9 x 10⁻⁴ to 6.5 x 10⁻⁴ m/s; the Drummer Unit ranges from 3.9 x 10⁻⁵ to 3.25 x 10⁻⁴ m/s; and the Saybrook Unit has hydraulic conductivities ranging from 1.8 x 10⁻⁵ to 4.25 x 10⁻⁴ m/s.

Derived from one of the original hypotheses, the NO₃⁻ concentrations below silty soils will be higher than below sandy soils. This would be due to the fact that the rate at

which water is able to move through a system is dependent on grain size. As water moves through the soil profile, the NO₃⁻ will be transported with it, therefore decreasing the amount of NO₃⁻ in the system. If the system is composed of coarser grained materials, water, along with NO₃⁻, will move through the system more quickly. In a system composed of finer grained materials, water will be retained longer, giving the NO₃⁻ more time to be utilized by plants or microorganisms.

On average, the Flanagan Unit has the highest NO₃⁻ concentrations and the Drummer Unit has the lowest levels of NO₃⁻ over the course of the study. Both of these sites were planted with corn during the 2003 and 2004 growing seasons, therefore the crop type in this case can not be linked to the difference in NO₃⁻ levels at the two sites.

One possible explanation for the higher NO₃⁻ concentrations at the Flanagan Unit could be that there was more NO₃⁻ in the system before the growing season began. This could be explained by the fact that this site had been used as a storage site for animal waste previous to the time that ISU took ownership of the farm. Often times, NO₃⁻ levels in the soils are not tested before fertilizer applications, which can lead to an excess of NO₃⁻ in the system. It is also possible for NO₃⁻ to remain in soil for prolonged periods; for example, according to Gormly and Spalding (1979) NO₃⁻ continued leaching out of a feedlot 10 years after it was abandoned.

The rate at which water and NO_3^- are moving through each soil profile can be supported by the hydraulic conductivity values calculated for each site. Hydraulic conductivity values determined for the Flanagan Unit range from 2.9×10^{-4} to 6.5×10^{-4} m/s, which is the highest measured rate at the study area. Based on this hydraulic

conductivity, the water is moving through the system as would be expected in a soil composed of mainly silt- to sand-sized particles.

In the Drummer Unit, the overall silty grain size could make it more difficult for water and NO₃⁻ to move down through the system, which could lead to less NO₃⁻ at depth. If NO₃⁻ is not moving through the system, there will be more available NO₃⁻ for plant uptake. In the Drummer Unit, the overall silty grain size could also make it more difficult for water and NO₃⁻ to enter the system initially. Because the grains are so small and tightly fitted, water infiltration into the soil is more difficult. Fertilizers are applied at the surface and depend on water to become part of the soil system. If water is unable to infiltrate the soil, the NO₃⁻ will also remain at the surface which will lead to more NO₃⁻ being lost to runoff at this site. The Drummer Unit has a lower hydraulic conductivity than the Flanagan Unit, ranging from 3.9 x 10⁻⁵ to 3.25 x 10⁻⁴ m/s. This would indicate that water and NO₃⁻ entering the system move at slower rates, therefore allowing the NO₃⁻ more time to be used by plant uptake or microbial denitrification.

The soils studied during this investigation are very similar in grain size and parent materials to those studied by Alberts and Spomer (1985) and Bobier et al. (1993).

Because of this, differences in vertical transport rates between the sites cannot be attributed to differences in grain size.

Organic Matter

Soil organic matter is concentrated near the surface due to the fact that this is the area where most plant roots occur (Troeh and Thompson, 1993), and then the concentrations decrease with depth. This holds true with the samples collected at the study area over the course of this project.

On average, the Drummer Unit at the ISU Farm, which was planted with corn during the sampling of this project, has the highest percent of organic matter based on the soils studied during this investigation.

At shallow depths corresponding with root zones, the lowest average NO_3^- levels measured were from the Drummer Unit, which had an average measured NO_3^- concentration of 3.32×10^{-3} kg NO_3^- /kg soil.

As hypothesized, that the lowest NO₃⁻ contents were measured in soils with high organic matter content. The hypothesis was based on the assumption that high organic content may result in high biological activity that produces reducing conditions.

Reducing conditions promote removal of NO₃⁻ through denitrification. The rate of denitrification is faster in soils with high organic matter content than in soils low in carbon. Denitrification also occurs more quickly in environments that are depleted in oxygen (O₂) because in oxygen depleted systems, bacteria and microorganisms will consume NO₃⁻ and carbon (C) from organic matter as food sources (Alexander, 1977). The soils at the study area are described as being mottled below 23 cm (United States Department of Agriculture, 1998). Mottling in the soil profile results from oxidizing and reducing conditions in soils that are fully saturated part of the time, and indicates the

potential for denitrifying conditions. During the collection of soil sampling, some mottling was noted at depths near the water table.

The hydraulic conductivity of the Drummer Unit is low in comparison with the other sites samples during this project, ranging from 3.9×10^{-5} to 3.25×10^{-4} m/s. This tends to support the theory that there is NO_3^- being consumed at or near the surface by plants, microorganisms, and bacteria since it would be slow to move through the system with water considering the hydraulic conductivity for this site.

CHAPTER V

CONCLUSIONS

The goal of this study was to conceptually understand and quantify the nitrogen transport processes occurring within the unsaturated zone below agricultural fields. This thesis study was prompted by the amount of nitrogen fertilizers applied to agricultural fields throughout the state of Illinois, and the possible outcome if too much NO₃⁻ reaches ground water supplies.

From June 2004 to November 2004, samples were collected on ten days from three sampling locations to depths of approximately 145 cm below the ground surface. Based on the samples collected and analyzed, vertical transport rates are determined for each soil type. The calculated transport rate for the Flanagan Unit is 0.59 cm/day (215.4 cm/year). The transport rates for the Drummer Unit range from 0.54 cm/day (197.1 cm/year) to 0.69 cm/day (251.9 cm/year). The calculated transport rates for the Saybrook Unit range from 2.8 cm/day (1022.0 cm/year) to 3.1 cm/day (1131.5 cm/year). There are many factors that contribute to the transport rates of the NO₃⁻ at each sampling location including hydraulic conductivity, moisture content, grain size, and porosity; which were all determined during sample analyses. Based on the results of similar studies, as well as the results of the soil properties for this study, it was determined that these transport rates are unrealistic.

Over the time that this investigation was conducted, there was significant rainfall, averaging approximately 7.5 cm per month. Despite the high monthly average rainfall, most precipitation occurred over many days as small amounts; therefore, there were no large recharge events to compare with normal recharge events. Due to the fact that there were no large recharge events, it was not possible to determine if most NO₃⁻ was moving during normal conditions or in response to large rainfall events. Under the rainfall conditions over the course of the study most NO₃⁻ moves through the soil profile as water moves through the soil matrix.

Soils below soybean and corn crops were studied during this project. Corn plants rely on the application of fertilizer for nutrients or residual NO₃⁻ in the soil in order to have enough NO₃⁻ during the growing season. Soybeans can transform N to NO₃⁻, with the help of bacteria, that can be utilized during the growing season. The Drummer Unit was cultivated with corn during the growing season that this study was conducted, while the Saybrook Unit was cultivated with soybeans. On average it was determined that the soil below the soybean crop had higher NO₃⁻ concentrations than the soil below the corn crop.

Based on grain size analyses of the soils at the study area, it was determined that NO₃⁻ movement occurred more slowly in coarser grained soils than in finer grained soils. The Flanagan Unit was the sandiest soil at the study site and was determined to have the fastest hydraulic conductivity and the highest NO₃⁻ concentrations. The Drummer Unit and Saybrook Unit, which are finer-grained than the Flanagan Unit, were determined to

have slower hydraulic conductivities and lower NO₃⁻ concentrations than the Flanagan Unit.

Based on the data collected during this investigation, it has been determined that soils with high organic matter contents will have lower NO₃⁻ concentrations than soils with low organic matter contents. Most soil organic matter is concentrated near the ground surface in the soil profile and decreases with depth, which was proved to be correct at each of the sampling locations at the study area. The Drummer Unit was determined to have the highest organic matter content followed by the Saybrook Unit, and the Flanagan Unit respectively. The Drummer Unit had the lowest average NO₃⁻ concentrations, while the Flanagan Unit had the highest NO₃⁻ concentrations.

The specific outcome of this project was to gain a greater understanding of how nitrogen is cycled relative to soil and crop type in an agricultural setting. In the long term, this knowledge could be applied towards decreasing the nitrogen load to ground water. It is recognized that this outcome will be part of a long term effort in that it will take years for changes in agricultural practices to be accepted by producers, and for those changes to have an impact on water quality.

REFERENCES

- Alberts, E.E. and Spomer, R.G., 1985. NO₃ N movement in deep loess soils. American Society of Agricultural Engineers Paper No. 85-2030. ASAE, St. Joseph, Michigan. 16pp.
- Alexander, M., 1977. *Introduction to Soil Microbiology*; 2nd Edition. Krieger Publishing Company: Malabar, Florida.
- Aley, T.J., 1977. A model for relating land use and groundwater quality in Southern Missouri. *Hydrologic Problems in Karst Regions*; Dilamarter, R. R., Csallany, S. C., Eds.; Western Kentucky Univ.: Bowling Green, Kentucky, p. 323-332.
- Bobier, M.W.; Frank, K.D.; and Spalding R.F., 1993. Nitrate-N movement in a fine-textured vadose zone. *Journal of Soil and Water Conservation*, vol. 48, no. 4, p. 350-354.
- Bowles, J.E., 1992. Engineering Properties of Soils and their Measurements; 4th Edition; Ch. 6. Irwin-McGraw Hill: Boston, Massachusetts.
- Campbell, G.S., 1985. Soil Physics with BASIC: transport models for soil-plant systems. Elsevier: New York.
- Fetter, C.W., 2001. Applied Hydrology, 4th Edition. Prentice Hall: Upper Saddler River, New Jersey. 598pp.
- Gormly, J.F. and Spalding, R.F., 1979. Sources and Concentrations of nitrate-nitrogen in Ground Water of the Central Platte Region, Nebraska. *Ground Water*, vol. 17, no. 3, p. 291-301.
- Hansel, A.K. and Johnson, W.H., 1996. Wedron and Mason Groups: Lithostratigraphic Reclassification of Deposits of the Wisconsin Episode, Lake Michigan Lobe Area. Department of Natural Resources, Illinois State Geological Survey, Bulletin 104.
- Illinois Department of Agriculture, Facts about Illinois Agriculture. http://www.agr.state.il.us/about/agfacts.html. August 24, 2004.

- Illinois State Water Survey "A Plan for Scientific Assessment of Water Supplies in Illinois," Illinois State Water Survey, 2001.
- Iqbal, M.Z.; Krothe, N.C., 1995. Infiltration mechanisms related to agricultural waste transport through the soil mantle to karst aquifers of southern Indiana. *Journal of Hydrology*, vol. *164*, p. 171-192.
- Kalmer, K., 2005. Personal communication, February 9, 2005. Illinois State University, Lexington, Illinois.
- Marshall, T.J.; Holmes, J.W.; and Rose C.W., 1996. Soil Physics, 3rd Edition. Cambridge University Press: New York.
- Manahan, S.E., 1984. Environmental Chemistry, 4th Edition. Willard Grant Press: Boston, Massachusetts. 612pp.
- Midwestern Regional Climate Center Climate of the Midwest, Climate Summaries for Normal, Illinois.

 http://sisyphus.sws.uiuc.edu/climate_midwest/mwclimate_data_summaries.htm.

 June 8, 2005.
- Mulvaney, R.L., 1996. "Nitrogen Inorganic Forms," *in* Methods of Soil Analysis Part 3. Chemical Methods, SSSA Book Series no. 5, Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., and Sumner, M.E. eds., Soil Science Society of America, Inc., Madison WI, p. 1123-1184.
- Myrold, D.D., 1998. "Transformations of Nitrogen." *Principles and Applications of Soil Microbiology*. Sylvia, D.M., Fuhrmann, J.J., Hartel, P.G., and Zuberer, D.A., eds. Prentice Hall: New Jersey, p 259 -294.
- Olson, R.A. and Kurtz, L.T., 1982. "Crop Nitrogen Requirements, Utilization, and Fertilization." *Nitrogen in Agricultural Soils*. F.J. Stevenson, ed. American Society of Agronomy, Inc., Madison, Wisconsin, p 567-604.
- Paul, E.A. and Clark, F.E, 1989. Soil Microbiology and Biochemistry. Academic Press: San Diego. 273pp.
- Peterson, E.W., Davis, R.K., Brahana, J.V., Orndorff, H.A., 2002. "Movement of nitrate through regolith covered karst terrane, northwest Arkansas." *Journal of Hydrology*, vol. 256, p. 35-47.
- Quisenberry, V.L., Phillips, R.E., 1976. Percolation of surface-applied water in the field. *Soil Science Society of America Journal*, vol. 40, p. 484-489.

- Saull, M., 1990. "Nitrates in Soil and Water." New Scientist, vol. 15, no. 37, p. 1-4.
- Schulte, E.E. and Hopkins, B.G., 1996, "Estimation of Soil Organic Matter by Weight Loss-On-Ignition," *in* Soil Organic Matter: Analysis and Interpretation SSSA Special Publication No. 46, Magdoff, F.R., Tabatabai, M.A., and Hanlon, E.A., eds., Soil Science Society of America, Inc., Madison WI, p. 21-31.
- Soffe, R.J., ed., 2003. The Agricultural Notebook, 29th Edition. Blackwell Publishing Company: Malden, Massachusetts. 744pp.
- Troeh, F.R., and Thompson, L.M. 1993. Soils and Soil Fertility, 5th Edition. Oxford University Press: New York, New York. 462pp.
- United States Department of Agriculture National Agricultural Statistics Service, 2004 Agricultural Statistics; fertilizers and pesticides. http://www.usda.gov/nass/pubs/agstats.htm. August 24, 2004.
- United States Department of Agriculture Natural Resources Conservation Service in cooperation with Illinois Agricultural experiment Station "Soil Survey of McLean County, Illinois," Government Printing Office, 1998.
- Ward, A.D. and Dorsey, J., 1995. "Infiltration and Soil Water Runoff." *Environmental Hydrology*. Andy D. Ward and William J. Elliot, eds. Lewis Publishers: New York, p 51 90.
- Wild, A.; Babiker, I.A. 1976. Journal of Soil Science. Vol. 27, p. 460-466.

APPENDIX NITRATE CONCENTRATIONS

Flanagan Unit
Nitrate Concentrations (kg NO₃-/kg soil)

Depth				
(cm)	06/14/04	06/28/04	07/06/04	07/26/07
8	9.09×10^{-3}	1.06 x 10 ⁻²	1.09×10^{-2}	3.04 x 10 ⁻⁴
23	2.64×10^{-3}	1.03×10^{-2}	1.03×10^{-2}	5.56×10^{-4}
38		4.09×10^{-3}	1.05×10^{-2}	7.63×10^{-4}
53	2.06×10^{-3}	1.67×10^{-3}	5.71×10^{-3}	7.29×10^{-4}
69	2.25×10^{-3}	1.03×10^{-3}	3.73×10^{-3}	1.35×10^{-3}
84		1.23×10^{-3}	6.32×10^{-3}	1.49×10^{-3}
99	9.41×10^{-4}	2.20×10^{-3}	5.29×10^{-3}	7.71×10^{-4}
114	1.23×10^{-3}	8.40×10^{-4}	2.00×10^{-3}	1.55×10^{-3}
130	3.18×10^{-3}	7.58×10^{-4}	1.19×10^{-3}	1.40×10^{-3}
145		1.76 x 10 ⁻⁴	9.90×10^{-4}	9.63 x 10 ⁻⁴

	Flanagan Unit			
		Nitrate Concentrat	ions (kg NO ₃ -/kg so	oil)
Depth				
(cm)	08/31/04	09/28/07	10/26/04	11/15/04
8	1.49×10^{-2}	1.62×10^{-3}	1.13×10^{-3}	
23	5.03×10^{-3}	6.96×10^{-4}	9.13×10^{-4}	1.25×10^{-3}
38	2.81×10^{-3}	1.49×10^{-3}	1.36×10^{-3}	1.22×10^{-3}
53	3.08×10^{-3}	1.71×10^{-3}	1.34×10^{-3}	8.99×10^{-4}
69	1.79×10^{-3}	8.44×10^{-4}	1.07×10^{-3}	1.22×10^{-3}
84	1.67×10^{-3}	1.96×10^{-3}	7.94×10^{-4}	1.28×10^{-3}
99	1.99×10^{-3}	2.02×10^{-3}	7.62×10^{-4}	1.19×10^{-3}
114	8.33×10^{-4}	1.44×10^{-3}	7.69×10^{-4}	1.33×10^{-3}
130	1.13×10^{-3}	1.30×10^{-3}	1.06×10^{-3}	6.59×10^{-4}
145	6.97 x 10 ⁻⁴	8.49 x 10 ⁻⁴		5.12 x 10 ⁻⁴

Drummer Unit
Nitrate Concentrations (kg NO₃-/kg soil)

Depth				
(cm)	06/14/04	06/28/04	07/06/04	08/09/04
8	9.76 x 10 ⁻⁴	9.98 x 10 ⁻⁴	1.23 x 10 ⁻³	1.62 x 10 ⁻³
23	8.74 x 10 ⁻⁴	1.32×10^{-3}	6.24×10^{-4}	8.89×10^{-4}
38	9.64 x 10 ⁻⁴	9.66×10^{-4}	2.86×10^{-3}	1.25×10^{-3}
53	8.67 x 10 ⁻⁴	1.15×10^{-3}	1.14×10^{-3}	5.50×10^{-4}
69	8.44 x 10 ⁻⁴	1.10×10^{-3}	1.31×10^{-3}	1.41×10^{-3}
84	5.63×10^{-4}	7.24×10^{-4}	7.93×10^{-4}	4.58×10^{-4}
99	3.23×10^{-4}	4.84×10^{-4}	5.95×10^{-4}	6.22×10^{-4}
114	3.28×10^{-4}	5.50×10^{-4}	6.26×10^{-4}	3.79×10^{-4}
130		2.34×10^{-4}	3.30×10^{-4}	7.81×10^{-4}
145		1.62×10^{-4}	2.03×10^{-4}	2.54×10^{-4}

Drummer Unit
Nitrate Concentrations (kg NO ₃ /kg soil)

Depth			
(cm)	08/31/04	09/28/04	11/15/04
8	6.99 x 10 ⁻⁴	BDL	BDL
23	1.03×10^{-3}	2.30×10^{-3}	BDL
38	9.22×10^{-4}	1.12×10^{-3}	1.65×10^{-3}
53	3.92×10^{-4}	5.94×10^{-4}	1.56×10^{-3}
69	3.95×10^{-4}	1.18×10^{-4}	8.85×10^{-4}
84	3.42×10^{-4}	3.59×10^{-4}	9.79×10^{-4}
99	2.52×10^{-4}	5.57×10^{-4}	8.47×10^{-4}
114	1.54 x 10 ⁻⁴	1.67×10^{-4}	7.87×10^{-4}
130	1.98 x 10 ⁻⁴	1.34×10^{-4}	1.38×10^{-4}
145	1.72 x 10 ⁻⁴	1.15×10^{-4}	1.85×10^{-4}

Saybrook Unit
Nitrate Concentrations (kg NO₃-/kg soil)

Depth			
(cm)	06/21/04	07/26/04	8/9/2004
8	3.02×10^{-3}	1.99 x 10 ⁻³	9.40×10^{-4}
23	5.03×10^{-3}	1.83×10^{-3}	9.82×10^{-4}
38	2.36×10^{-3}	1.07×10^{-3}	4.36×10^{-4}
53	1.76×10^{-3}	4.09×10^{-4}	5.89×10^{-4}
69	1.23×10^{-3}	2.59×10^{-4}	9.42×10^{-4}
84	1.24×10^{-3}	8.92×10^{-4}	8.14×10^{-4}
99	8.45×10^{-4}	9.85×10^{-4}	9.73×10^{-4}
114	3.40×10^{-4}	5.60×10^{-4}	1.01×10^{-3}
130	2.60×10^{-4}	1.21×10^{-3}	6.62×10^{-4}
145	5.61×10^{-4}	5.39×10^{-5}	3.93×10^{-4}
160		2.00 x 10 ⁻⁴	

Saybrook Unit
Nitrate Concentrations (kg NO₃-/kg soil)

	Milrale Co	ncentrations (kg N	$(O_3/\text{kg soii})$
Depth		_	_
(cm)	08/31/04	09/28/07	11/15/04
8	7.47 x 10 ⁻⁴	1.12×10^{-3}	8.97 x 10 ⁻⁴
23	1.31×10^{-3}	5.01 x 10 ⁻⁴	1.50×10^{-3}
38	4.02×10^{-4}	2.78×10^{-4}	1.04×10^{-3}
53	6.03×10^{-4}	3.47×10^{-4}	8.47×10^{-4}
69	6.14×10^{-4}	4.06×10^{-4}	7.21×10^{-4}
84	9.00×10^{-4}	6.13×10^{-4}	4.95×10^{-4}
99	9.61 x 10 ⁻⁴	7.55×10^{-4}	2.72×10^{-4}
114	1.02×10^{-3}	5.83×10^{-4}	2.16×10^{-4}
130	6.34×10^{-4}	4.69×10^{-4}	1.13×10^{-4}
145	4.57×10^{-4}	4.79×10^{-4}	1.34×10^{-4}