

**TRANSPORT AND LOSS OF AGRICULTURALLY-DERIVED  
NITROGEN THROUGH THE VADOSE ZONE AND SHALLOW  
AQUIFER IN SUSSEX COUNTY, DELAWARE**

by

Claudia Shuman

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science in Marine Studies

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## **ABSTRACT**

Southern Delaware's Inland Bays – Rehoboth, Indian River, and Little Assawoman – are subjected to high nitrogen loads, contributing to the Bays' eutrophic conditions. These nitrogen loads are in large part derived from agricultural land use. Southern Delaware's surficial sediments are generally sandy and highly permeable, meaning that leaching of agricultural fertilizers – specifically nitrogen as nitrate – beyond the root zone of crops and into the underlying shallow aquifer is a regional problem. Groundwater discharge accounts for approximately 80% of all freshwater flowing into the Bays. Understanding the transport and loss of nitrate through the aquifer is therefore important in constraining and managing overall nitrogen fluxes to the Bays.

For my thesis, I collected groundwater during multiple field samplings to measure nitrogen (as nitrate and ammonium) and evaluate potential nitrogen loss within the vadose zone (down to 1.65 m), shallow aquifer (down to 6 m), and deep aquifer (down to 18 m) beneath an agricultural field adjacent to the Indian River estuary – the primary tributary to Indian River Bay. Shallow groundwater was assumed to contain nitrogen derived from the agricultural field directly above, while deeper, older groundwater was assumed to contain nitrogen derived from

similar agricultural sources elsewhere in the watershed. Dissolved oxygen, nitrogen gas, and isotopic signatures of nitrogen and oxygen in nitrate were analyzed as a means of assessing denitrification as a potential pathway of nitrogen loss.

Ammonium concentrations throughout the vadose zone, shallow, and deep aquifer were generally very low ( $< 7 \mu\text{M}$ ) compared to nitrate concentrations ( $>200 \mu\text{M}$ ). Data analysis was therefore focused on variations in nitrate. Based on a comparison of nitrate concentrations, no apparent nitrogen loss was observed with groundwater flow through the vadose zone and shallow aquifer. At the deepest sampling point in the aquifer however, nitrate concentrations were significantly lower, suggesting some nitrogen loss at that depth.

Conditions within the vadose zone and shallow aquifer were consistently too oxic ( $> 1 \text{ mg/L}$ ) to allow denitrification. As expected, nitrogen gas concentrations showed no evidence of excess nitrogen gas produced via denitrification. Furthermore, isotopic data did not show evidence of the typical isotopic enrichment resulting from denitrification. In the deep aquifer however, dissolved oxygen generally decreased with depth, at points reaching a minimum below  $1 \text{ mg/L}$ . Isotopic data suggested some degree of denitrification in the deep aquifer, with samples showing evidence of isotopic enrichment associated with denitrification.

Overall, my data showed no evidence of nitrogen loss via denitrification in the vadose zone and shallow aquifer. However, some apparent loss of nitrogen occurred within the deep aquifer. This apparent loss was likely related to more favorable denitrifying conditions, potentially occurring in anoxic pockets associated with subsurface heterogeneity along the groundwater flow path. The data suggest that at this site, all fertilizer-derived nitrate leached beyond the root zone of crops ultimately makes its way through the shallow aquifer and into Indian River via groundwater discharge. This emphasizes the need for more controlled fertilizer management on agricultural land lying adjacent to surface water bodies, especially within a region highly susceptible to groundwater contamination.

## Chapter 1

### INTRODUCTION AND LITERATURE REVIEW

#### 1.1 Introduction

Anthropogenic nitrogen (N) loads have significantly accelerated the process of eutrophication in fresh, estuarine, and marine water bodies (Anderson et al. 2002; Ryther and Dunstan 1971; Howarth and Marino 2006). Eutrophic water bodies are characterized by algal blooms, potentially including toxic algal species. The decay of algal biomass can lead to a reduction in dissolved oxygen, negatively impacting aquatic ecosystems and the humans that depend on them as a resource for food, water, and recreation (Anderson et al. 2002). Southern Delaware's Inland Bays are among many estuaries heavily impacted by anthropogenic N loads along the eastern coast of the United States (Kasper and Strohmeier 2007; Volk et al. 2007; EPA 2007). N derived from agricultural land use is the principal contributor to water quality impairment of the Bays (Hamilton et al. 1993; Ator et al. 2011; Clune and Denver 2012). Worldwide, approximately 75% of anthropogenic N is created through artificial N fixation via the Haber-Bosch process and through the cultivation of certain crops capable of biological

nitrogen fixation. These two processes produce N that is used to increase food production on agricultural lands (Galloway et al. 2003).

The coastal plain sediments of southern Delaware are generally sandy, unconsolidated, and very permeable. The region's groundwater is therefore highly susceptible to N contamination via aquifer recharge through agricultural soils (Kasper and Strohmeier 2007). Excessive N as nitrate ( $\text{NO}_3^-$ ) has been measured in groundwater throughout the Inland Bays watershed (Andres 1991a, 1991b; Denver 1989, 1993; Ritter and Chirnside 1982, 1984; Robertson 1977, 1979; Kasper and Strohmeier 2007). Groundwater is a significant vector for N loading both to stream base flow and as direct discharge to the Bays (Clune and Denver 2012; Andres 1987). Agriculturally-derived, groundwater-driven N loading therefore warrants further study to better understand and manage overall N loads originating from agricultural land use.

A simple nitrogen loading model (NLM) was developed by Valiela et al. (1997, 2000) to account for N loads and losses on a watershed scale for the Cape Cod region in Massachusetts. This model approximates N loads originating from different sources including atmospheric deposition, fertilizer use, and wastewater; it also approximates N losses throughout the watershed. Specifically, the model approximates an 84% loss of N derived from fertilizer use on agricultural land other than cranberry bogs (the primary form of agriculture in the region). This

model was applied to watersheds across the Delmarva (Giordano et al. 2011). Results from that work showed good agreement, generally, but the model tended to over-predict or under-predict loads in the smallest and largest watersheds, respectively. More regionally-specific data on losses of N during groundwater travel are needed to improve application of the NLM to the heavily agricultural Delmarva region.

This thesis assesses N in groundwater flowing through the vadose zone, shallow aquifer, and deep aquifer beneath an agricultural field, prior to discharging into Indian River – the primary tributary to Indian River Bay. One of Delaware’s three Inland Bays, Indian River is considered eutrophic in large part due to N over-enrichment derived from agriculture, which comprises 37% of land use within the watershed (Kasper and Strohmeier 2007). The purpose of my research was to measure and compare agriculturally-derived N concentrations in groundwater collected from the vadose zone, shallow, and deep aquifer to determine if N loss occurred with groundwater flow. Dissolved oxygen (DO), nitrogen gas (N<sub>2</sub>), and isotopic signatures of N and O in NO<sub>3</sub><sup>-</sup> were analyzed to determine if denitrification was a potential means of N loss within the vadose zone and aquifer.

## **1.2 Local Hydrogeology**

### **1.2.1 The Columbia Aquifer**

The Columbia Aquifer is present throughout most of Delaware, save for the northernmost piedmont region of the state (Johnston 1973). It occurs in largely unconsolidated, permeable sediments ranging in age from Miocene to Holocene. In addition to supporting domestic, public, agricultural, and industrial water demands, the aquifer is the primary contributor to stream base flow within the Indian River Bay watershed. The Scotts Corners Formation, a Pleistocene component of the Columbia Aquifer, outcrops along Indian River (Andres and Klingbeil 2006). The Scotts Corners is heterogeneous, composed of varying proportions of light-gray to yellowish-brown, course to fine-grained sands, pebbles, and rare, discontinuous lenses of clays and silts (Delaware Geological Survey <<http://www.dgs.udel.edu/delaware-geology/unit/scotts-corners-formation>>). It ranges in thickness from 0 to 5 meters and is underlain by the Lynch Heights or Beaverdam Formation (Andres and Klingbeil 2006). The top of the water table, marking the start of saturated conditions, occurs within 3 to 6 meters of the land surface along the northern shore of Indian River (Martin and Andres 2008), where this study took place.



### 1.2.2 Aquifer Flow

Constraining the flow rate of groundwater through an aquifer is necessary to estimate the residence time of groundwater from recharge to discharge. Unlike river channels, which have an average residence time on the order of weeks, groundwater residence times can range into the 10's, 100's, and 1000's of years (Freeze and Cherry 1979). The residence time of groundwater at my project site was an important factor controlling N transport from the field to Indian River.

The rate of flow ( $v$ ) through a saturated medium, as through an aquifer, is characterized by the hydraulic conductivity ( $K$ ), hydraulic gradient ( $i$ ), and the porosity ( $n$ ) of the medium (Freeze and Cherry 1979; Andres 1987). Hydraulic conductivity is a constant specific to the permeability of the sediment. The hydraulic gradient is a pressure gradient with two components – elevation head and pressure head. Porosity is given as a percentage expressing the void space between sediment grains through which fluid can flow (Freeze and Cherry 1979). The flow rate of groundwater is related to the hydraulic conductivity, hydraulic gradient, and porosity of sediments by the following equation:

$$v = K \times i / n$$

**Equation 1.**

### 1.2.3 Vadose Zone Flow

Less straightforward than aquifer flow, moisture flow through the vadose zone was another factor controlling N transport through this system. The vadose zone is defined as the unsaturated, vertical expanse from the land surface down to the water table. The water table is the surface on which the fluid pressure in the pores of a porous medium is exactly atmospheric, and the pressure head zero. Below the water table, under saturated conditions, a positive pressure head exists; above the water table in the vadose zone, a negative pressure head exists. Water is bound to soil particles by surface tension, sometimes referred to as tension head or suction head. Unsaturated flow is dependent upon the hydraulic conductivity and porosity of soil, as well as the degree of subsurface heterogeneity (Freeze and Cherry 1979). Flow through the vadose zone can be uniform or non-uniform. Non-uniform flow – accelerated in some areas relative to others – is a product of heterogeneity within the subsurface. Accelerated flow can expedite the vertical distribution of soluble contaminants (Hendrickx and Flury 2001).

In the largely sandy sediments of southern Delaware, such as exist at my project site, 2.54 cm of rain can transport  $\text{NO}_3^-$  15-20 cm down through the subsurface (University of Delaware Cooperative Extension 2008). Temporal fluctuations in  $\text{NO}_3^-$  concentrations within the vadose zone and shallow aquifer are primarily due to variability associated with precipitation and seasonal plant

growth, most notably crop cultivation (Costa et al. 2002). Evapotranspiration typically balances precipitation during the summer months (Andres 2004). On Delmarva, in areas of good groundwater recharge potential (Kasper and Strohmeier 2007) such as my project site, aquifer recharge is estimated between 30 and 60 cm/year (Dunkle et al. 1993).

### **1.3 Nitrogen Cycling**

#### **1.3.1 Forms of Nitrogen**

The most common form of N is nitrogen gas ( $N_2$ ), an unreactive species making up more than 99% of N in the environment.  $N_2$ , however, cannot be assimilated by more than 99% of organisms. To be assimilated by most organisms, it must first be converted into forms of reactive N including ammonia ( $NH_3$ ), ammonium ( $NH_4^+$ ), nitrous oxide ( $N_2O$ ), nitrate ( $NO_3^-$ ), and organic compounds including urea, amines, proteins, and nucleic acids. The initial conversion process, known as N fixation, is carried out by a unique set of microbes. The availability of reactive N is essential in crop cultivation, which is aided by the application of N fertilizer synthetically-fixed via the Haber-Bosch process (Galloway et al. 2003; Smil 1999).

Nitrate is the most abundant and mobile form of N associated with agricultural land use, readily leached through the subsurface and incorporated into

aquifer recharge (Ator and Denver 2012; Böhlke and Denver 1995; Tesoriero et al. 2004). The geochemical conditions within an aquifer dictate whether  $\text{NO}_3^-$  persists or is lost, largely via the process of denitrification. Denitrification, the reduction of  $\text{NO}_3^-$  to  $\text{N}_2$ , is facilitated by the microbial oxidation of organic matter in the absence of dissolved oxygen. A reservoir of N typically exists in agricultural soils as organic matter derived from crop residue. This organic N, once re-mineralized to  $\text{NH}_4^+$ , can be oxidized to  $\text{NO}_3^-$  in groundwater. The readiness with which  $\text{NO}_3^-$  leaches into groundwater is dependent upon soil composition, the timing of fertilizer application, and tilling and irrigation practices (International Plant Nutrition Institute 2013).

### 1.3.2 Stable Isotopes of Nitrate

The isotopic ratios of N and O in  $\text{NO}_3^-$  can be used as a tracer to indicate sources and processing of N in groundwater (Böhlke et al. 2009; Hastings et al. 2013; Kendall et al. 2007). Isotopic signatures refer to the ratios of  $^{15}\text{N}$  to  $^{14}\text{N}$  and  $^{18}\text{O}$  to  $^{16}\text{O}$  in  $\text{NO}_3^-$  derived from a specific source. N and O isotopic ratios are reported relative to atmospheric  $\text{N}_2$  and Vienna Standard Mean Ocean Water, respectively. Ratios are written in parts per thousand (‰) as  $\delta$  (delta)  $^{15}\text{N}$  and  $\delta^{18}\text{O}$  (Kaushal et al. 2011).  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  vary predictably with  $\text{NO}_3^-$  derived from different sources, such that isotopic signatures provide a tool for determining the source of  $\text{NO}_3^-$  (Böhlke et al. 2009; Kendall 1998). **Equation 2** below, in

which  $R$  represents either the ratio of  $^{15}\text{N}$  to  $^{14}\text{N}$  or  $^{18}\text{O}$  to  $^{16}\text{O}$ , defines isotopic ratios relative to these standards. Because lighter isotopes are generally more reactive than heavier ones, the biologically-facilitated conversion of  $\text{NO}_3^-$  to different chemical forms almost always results in a deficit of  $^{15}\text{N}$  and  $^{18}\text{O}$  in the products and an enrichment of  $^{15}\text{N}$  and  $^{18}\text{O}$  in the remaining  $\text{NO}_3^-$  (Kendall 1998).

$$\delta(\text{‰}) = \{[(R)_{\text{sample}} - (R)_{\text{standard}}] / (R)_{\text{standard}}\} \times 1000 \quad \textbf{Equation 2.}$$

Biological processes involving N include fixation, assimilation, mineralization, nitrification, and denitrification (Klump and Martens 1983; Seitzinger et al. 1991; Kendall et al. 2007). Nitrogen fixation produces organic matter with an N isotope ratio similar to atmospheric  $\text{N}_2$ . Assimilation – the uptake of reactive N compounds by organisms – typically results in a negligible N isotope fractionation relative to distinguishing N sources (Kendall et al. 2007). The conversion of organic matter into  $\text{NH}_4^+$ , referred to as mineralization, also produces a negligible N fractionation – on the order of  $\pm 1\text{‰}$  (Hoch et al. 1994; Kendall et al. 2007). Nitrification however, involves several oxidative steps, beginning with  $\text{NH}_4^+$  and ultimately producing  $\text{NO}_3^-$  and an N isotopic enrichment of the substrate between -12 and -29‰. The rate of nitrification is dependent upon the quantity of  $\text{NH}_4^+$  available; this varies in an agricultural

setting with the application of  $\text{NH}_4^+$ -containing fertilizers. With an ample pool of  $\text{NH}_4^+$  available, the rate of nitrification following fertilizer application is initially high, but declines as the pool is depleted. The rate at which nitrification occurs drives the degree of fractionation, thereby producing different degrees of N fractionation throughout the entire process (Kendall et al. 2007). Denitrification involves multiple reductive steps in the conversion of  $\text{NO}_3^-$  to  $\text{N}_2$ ; this typically results in an increase in the  $\delta^{15}\text{N}$  value of residual  $\text{NO}_3^-$  between 5 and 40 ‰ (Kendall 1998).

The  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of  $\text{NO}_3^-$  in groundwater can be used as indicators of the  $\text{NO}_3^-$  source (Böhlke et al. 2009; Hastings et al. 2013; Kendall et al. 2007). Synthetic fertilizer, manure, and soil  $\text{NO}_3^-$  have isotopic signatures that distinguish them from one another.  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of  $\text{NO}_3^-$  derived from  $\text{NH}_4^+$  fertilizer for instance, range from approximately -5 to 5‰ and -8 to 15‰, respectively. Soil and manure  $\delta^{15}\text{N}$  values range from about 2 to 15‰ and 15 to 35‰, respectively. These unique signatures are the result of biological and chemical processes from which they are derived.

In this study, isotopic signatures were used to determine  $\text{NO}_3^-$  source and the presence or absence of denitrification in the vadose zone and aquifer. As denitrification occurs, the residual  $\text{NO}_3^-$  in a groundwater becomes enriched in both  $^{15}\text{N}$  and  $^{18}\text{O}$  (Chang et al. 2003; Kendall 1998). This enrichment results in a

predictable increase in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values at a ratio of either 2:1 or 1:1. While a 1:1 increase has been observed as a result of denitrification in laboratory settings, a 2:1 increase has been shown to be characteristic of many groundwaters (Sigman et al. 2005; Granger 2006; Kendall 2007). Fractionation factors determined in controlled laboratory studies are indicative of the process of denitrification, only, whereas in groundwater, denitrification might only be one of several processes contributing to N loss. Other means of N attenuation might include processes such as  $\text{NO}_3^-$  assimilation by bacteria, oxygen exchange between  $\text{NO}_3^-$  and water, and aerobic denitrification, resulting in isotopic signatures that reflect more than one process (Granger 2006; Kendall 2007).

#### **1.4 Nitrate in Groundwater**

Southern Delaware has a long tradition of agricultural land use impacting groundwater quality (Robertson 1980; Ritter and Chirnside 1982, 1984; Kasper and Strohmeier 2007). The first comprehensive groundwater quality survey with a focus on  $\text{NO}_3^-$  was conducted in Sussex County between 1976 and 1977 (Robertson 1980). Robertson correlated agricultural land use with elevated  $\text{NO}_3^-$  concentrations in groundwater samples collected throughout the county. The mean  $\text{NO}_3^-$  concentration he measured in shallow groundwater within agriculturally-impacted recharge areas was 514  $\mu\text{M}$ , comparable to concentrations measured during my project; this value substantially exceeds the 27  $\mu\text{M}$

concentration representing un-impacted groundwater (Hamilton et al. 1993; Kasper and Strohmeier 2007). Furthermore, concentrations exceeded the Environmental Protection Agency's (EPA) drinking water standard of 714  $\mu\text{M}$  (10 mg/L) in approximately 83% of Robertson's samples collected from the shallow aquifer just north of Indian River, an area encompassing my project location.

Robertson (1980) further observed a decrease in  $\text{NO}_3^-$  concentrations with depth in the aquifer. Flow paths within the Columbia Aquifer range from 30 meters to 5 kilometers, with groundwater dated back to recharge as early as 1940 (Dunkle et al. 1993). Robertson's (1980) observation of decreasing  $\text{NO}_3^-$  with depth likely reflects older groundwater with inherently less  $\text{NO}_3^-$  (a result of land use changes through time) and or different geochemical conditions within the deep aquifer that promote the loss of  $\text{NO}_3^-$ .

In a more recent study conducted specifically within the Indian River Bay watershed,  $\text{NO}_3^-$  concentrations were found to exceed the EPA drinking water standard in 32% of samples collected. Excessive concentrations were measured at aquifer depths ranging from 6 to 24 meters below the land surface, with no apparent trend through depth (Kasper and Strohmeier 2007). Between these two studies, it is apparent that  $\text{NO}_3^-$  contamination in the Columbia Aquifer has been a problem since the late 1970's. Robertson's observation of decreasing  $\text{NO}_3^-$



concentrations with depth in the aquifer suggest that older groundwater at that time of sampling was less impacted by anthropogenic N loads than shallower, younger groundwater. Kasper and Strohmeier's study however, suggests that presently, both deep and shallow groundwater has been affected by agricultural  $\text{NO}_3^-$  loads.

### **1.5 Project Objectives**

My thesis examines agriculturally-derived N (as  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) within vadose zone, shallow, and deep aquifer groundwater below an agricultural field in southern Delaware. The goal of my research was to determine if N loss occurred with groundwater flow through the vadose zone, shallow, and deep aquifer, prior to discharge into Indian River. I measured DO,  $\text{N}_2$ , and  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  in samples to determine if denitrification was a potential pathway for N loss within the vadose zone, shallow, and deep aquifer. The three objectives of this work were to:

1. Compare N concentrations in groundwater collected from vadose zone, shallow aquifer, and deep aquifer beneath the field to determine if N is lost with groundwater flow, prior to discharge into Indian River.
2. Determine if denitrification is a potential means of N loss within the vadose zone and shallow aquifer.

3. Determine if denitrification is a potential means of N loss within the deep aquifer.

## Chapter 2

### **METHODS**

#### **2.1 Site Description**

My project site is within the Indian River Bay watershed in Sussex County, Delaware on a piece of agricultural land separated from the northern shore of Indian River by a narrow, forested buffer (**Figure 1**). Approximately 37% of land within the watershed is dedicated to agriculture, specifically corn and soybean production for use as chicken feed (Kasper and Strohmeier 2007). The crop field at my site undergoes a 2-year crop rotation between soybeans, winter wheat, corn, and wheat, all of which are un-irrigated. Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) fertilizer is applied to the corn crop at the time of planting and again at its peak in growth. At the start of my study in October, 2012, soybeans were in the ground. The crop was harvested in mid-fall, followed by the planting of winter wheat in mid-winter. The majority of soybean plant material was left in the field, following harvest. Winter wheat was removed using an herbicide in late-March, followed by the planting of corn in mid-April. Fertilizer was applied to the corn crop at the time of planting and again in mid-June. Corn had been harvested by the conclusion of my study in November, 2013.

## 2.2 Field Methods

Twelve groundwater sampling tips were inserted into the shallow aquifer at depths between 4 and 6 meters. Six tips were placed below the field, and six below the near-shore, above the tidal zone (**Figure 2**). Sampling tips consisted of a length of Teflon tubing with a screened, metal tip allowing for the passage of groundwater, but not large particles. Following initial sampling in October 2012, 9 suction lysimeters were inserted into the vadose zone at depths of 30, 80, and 165 cm below the field surface (**Figure 2**). A multi-level well with 6 sampling points ranging from 2 to 18 meters was used to collect groundwater from the deep aquifer. Groundwater was collected from the sampling tips and multi-level well using peristaltic pumps, and from the lysimeters using hand pumps.

Groundwater was collected from the sampling tips in October 2012 and January, April, June, August, and November 2013. The sampling tips in the near-shore shallow aquifer were not sampled in June – only the field tips. The multi-level well was sampled in June and October, 2013. Lysimeters were sampled in January, April, June, August, and November 2013. Prior to collection, DO, salinity, temperature, and pH were measured in shallow and deep aquifer groundwater using a YSI Professional Plus instrument. Measured parameters were allowed to stabilize prior to collection, and samples with a salinity greater than 0.1 ppt were rejected. At the time of collection, samples taken from the tips and multi-level well were filtered through 0.45  $\mu\text{m}$  filters, and lysimeter samples

through 0.2  $\mu\text{m}$  filters. Samples were collected from the tips, multi-level well, and lysimeters for analysis of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{N}_2$ , and  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$ .

## 2.3 Laboratory Methods

Following collection, all samples, except for those for  $\text{N}_2$ , were frozen.  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  concentrations were analyzed using a SEAL AutoAnalyzer. I report only concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  because  $\text{PO}_4^{3-}$  concentrations were uniformly low and showed little variation throughout all samples. Samples for  $\text{N}_2$  were collected into gas-tight exetainers, then stored under water at 40° F, to minimize changes in dissolved gases prior to analysis.  $\text{N}_2$  concentrations were analyzed as a direct indicator of denitrification. Because atmospheric  $\text{N}_2$  incorporated at recharge makes up most of that present in groundwater, comparison of measured concentrations to an inert, atmospheric gas such as argon (Ar), is necessary in order to differentiate between atmospheric  $\text{N}_2$  and  $\text{N}_2$  derived from denitrification. Membrane inlet mass spectrometry (MIMS) was used to measure and compare  $\text{N}_2$  and Ar gas concentrations in samples, to discriminate between atmospheric  $\text{N}_2$  and  $\text{N}_2$  derived from denitrification (Young et al. 2013).

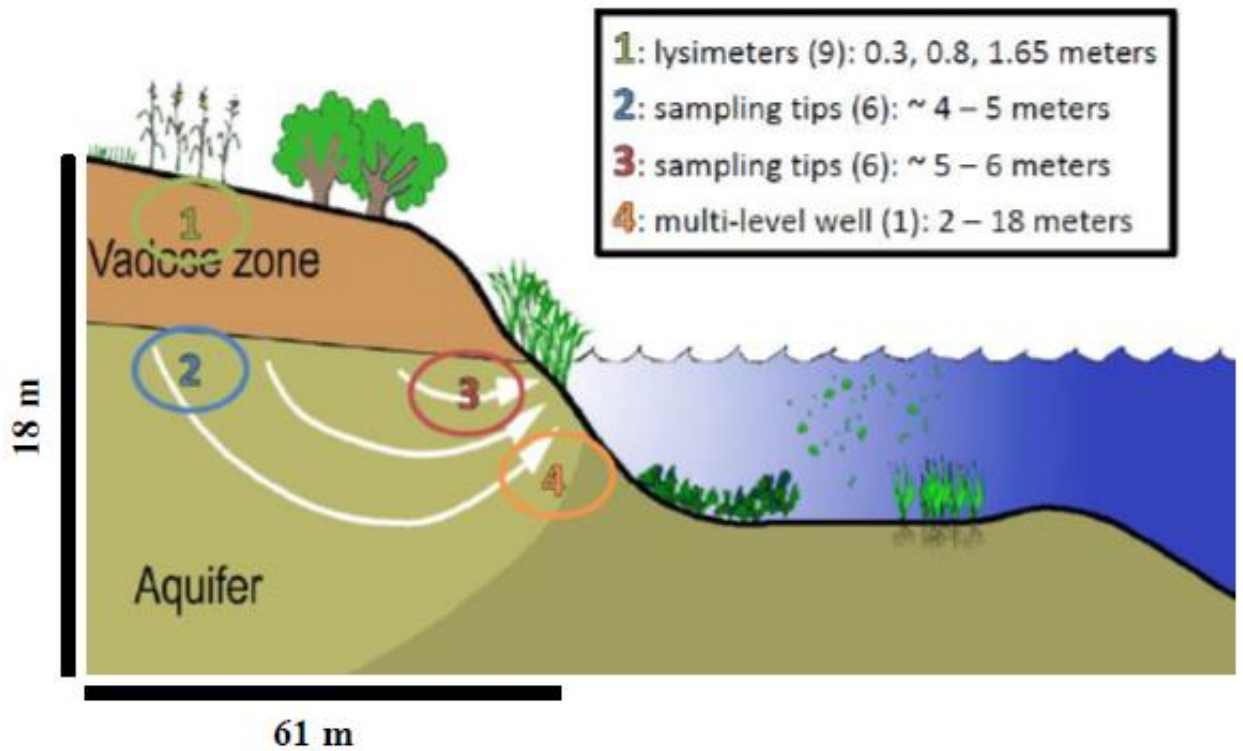
Samples were further analyzed for  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  using the microbial denitrifier method (Sigman et al. 2001; Casciotti et al. 2002). Briefly, groundwater samples were injected into gas-tight vials containing denitrifying bacteria (*Pseudomonas aureofaciens*), which converted all  $\text{NO}_3^-$  present into

nitrous oxide ( $\text{N}_2\text{O}$ ). Samples were then analyzed for N and O isotopes of  $\text{N}_2\text{O}$  at the UC Davis Stable Isotope Facility. Measured  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values were corrected for isotopic fractionation associated with the entire analytical process using IAEA and USGS international reference standards.

For this thesis, data from January, June, October, and November, 2013 were selected as representative of trends observed throughout the study period. Lysimeters, field tips, and near-shore tips were sampled during January, June, and November. The multi-level well was sampled in June and October. Data from the October and November samplings is displayed on the same plots in discussed in the text as Oct-Nov samples because these samplings occurred back to back. ANOVAs (using a significant  $p$  value of 0.05) were performed on all data sets to determine if there was a significant difference in  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , DO, and  $\text{N}_2$  concentrations between vadose zone, shallow aquifer, and deep aquifer samples. ANOVAs were also performed on lysimeter samples to better understand any variation in vadose zone N associated with changes in crop cover between samplings.



**Figure 1. The project site, located along the north shore of Indian River in Sussex County, Delaware.**



**Figure 2.** A schematic of sampling sites and methods including lysimeters (9) in the vadose zone below crop field, sampling tips (6) in the shallow aquifer below the field, sampling tips (6) in the shallow aquifer below the shoreline, and a multi-level well reaching into the deep aquifer below Indian River (Valiela and Bowen 2002).



## Chapter 3

### RESULTS

#### 3.1 Shallow Aquifer Sampling

##### 3.1.1 Nitrate

During January, mean  $\text{NO}_3^-$  concentrations increased significantly ( $p < 0.05$ ) from the vadose zone to the shallow aquifer below the field (**Figure 3a and Table 1**). Concentrations did not vary significantly between the vadose zone and shallow aquifer during June and Oct-Nov (**Figure 3b, 3c and Table 1**). Overall, the data indicate no loss of  $\text{NO}_3^-$  with groundwater flow through the vadose zone.

Crop cover changed between samplings at my project site. However, correlation of  $\text{NO}_3^-$  concentrations in vadose zone and shallow aquifer groundwater with specific crops may not be possible due to the time delay associated with vertical movement of  $\text{NO}_3^-$  from fertilizer application. That is,  $\text{NO}_3^-$  concentrations measured in shallow aquifer may have resulted from fertilization of different crop cover relative to that which was in place at the time of sampling.  $\text{NO}_3^-$  concentrations measured in vadose zone groundwater samples were compared between all samplings (**Figure 4c**); no significant difference was determined, despite variations in crop cover. This strengthens the argument that

any variation or lack thereof observed between  $\text{NO}_3^-$  concentrations in vadose zone and shallow aquifer samples was not simply a result of changing crop cover.

January samples showed a further significant ( $p < 0.05$ ) increase in  $\text{NO}_3^-$  concentrations with shallow groundwater flow from below the field to the near-shore (**Figure 3a and Table 1**). Oct-Nov samples showed no significant difference in shallow aquifer  $\text{NO}_3^-$  concentrations from the field to the near-shore (**Figure 3c and Table 1**). These data indicate no loss of  $\text{NO}_3^-$  with flow through the shallow aquifer. Overall, the data show no loss of  $\text{NO}_3^-$  with groundwater flow through the vadose zone and shallow aquifer.

### 3.1.2 Ammonium

Overall,  $\text{NH}_4^+$  concentrations were much lower than  $\text{NO}_3^-$  concentrations throughout the vadose zone and shallow aquifer (**Table 1**). No significant difference was observed between  $\text{NH}_4^+$  concentrations in the vadose zone and shallow aquifer below the field during January, June, and Oct-Nov (**Figure 5 and Table 1**). Furthermore, concentrations did not vary significantly with flow through the shallow aquifer (**Figure 5 and Table 1**). These data suggest that not only does  $\text{NH}_4^+$  constitute a very small fraction of N moving through the system, but that it does not vary significantly as groundwater moves through the vadose zone and shallow aquifer.

However,  $\text{NH}_4^+$  concentrations in the vadose zone did appear to be more tightly correlated with changes in crop cover than  $\text{NO}_3^-$ , varying significantly ( $p < 0.05$ ) between Oct-Nov, April, and June (**Figure 4b**). This indicates that changes in crop cover likely play a role in dictating  $\text{NH}_4^+$  in vadose zone groundwater.

### 3.1.3 Dissolved Oxygen and Nitrogen Gas

Dissolved oxygen was measured in the shallow aquifer, but not the vadose zone; conditions in the vadose zone were assumed to be highly oxic based on the sandy, unconsolidated nature of the substrate (Kasper and Strohmeier 2007). For the January, June, and Oct-Nov samplings, DO in the shallow aquifer did not vary significantly from below the field to the near-shore. Conditions were consistently oxic, over 7 mg/L in all shallow aquifer samples (**Figure 6 and Table 1**).

Nitrogen gas concentrations were analyzed in shallow aquifer samples collected in January and Oct-Nov. Samples that showed evidence of degassing during collection were not reported. Groundwater in the shallow aquifer had no excess  $\text{N}_2$  beyond atmospheric concentrations (**Figure 7a**).

### 3.1.4 Nitrate Isotopes

Isotopic signatures indicated agricultural land use as the source of  $\text{NO}_3^-$  to the vadose zone and shallow aquifer.  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values (**Figure 8**) fell within the ranges of  $\text{NO}_3^-$  derived from  $\text{NH}_4^+$  fertilizer and  $\text{NO}_3^-$  in natural soils (**Figure**

9) (Böhlke et al. 2009; Kendall 1998). This suggests that groundwater sampled from the shallow aquifer was likely recharged through the agricultural field at the project site. Furthermore, isotopic signatures in shallow groundwater showed no evidence of the isotopic enrichment characteristic of denitrification. Vadose zone samples showed no significant variation in  $\delta^{15}\text{N}$  values between samplings, indicating a consistent, fertilizer source of  $\text{NO}_3^-$  to the vadose zone (**Figure 4a**).

### 3.2 Deep Aquifer Sampling

Nitrate concentrations in samples collected from the multi-level well varied little with depth, save for the deepest sample taken at 18 meters. During both June and Oct-Nov, the  $\text{NO}_3^-$  concentration in the deep groundwater was lower than all other samples collected from the well (**Figure 3b, 3c and Table 1**). Ammonium concentrations measured in the deep aquifer in June and Oct-Nov were not significantly different from concentrations in the shallow aquifer (**Figure 5b, 5c and Table 1**). As in the shallow aquifer, overall  $\text{NH}_4^+$  concentrations were much lower than  $\text{NO}_3^-$  concentrations, indicating that  $\text{NH}_4^+$  plays a relatively insignificant role in N cycling within the deep aquifer.

Dissolved oxygen concentrations reached a minimum below 1 mg/L in two multi-level well samples – one collected at the deepest sampling point in the aquifer (**Figure 6b, 6c**). There was no clear relationship between DO concentrations and  $\text{NO}_3^-$  concentrations in the deep aquifer (**Figure 11**) except in

the deepest sample, which had the lowest DO and  $\text{NO}_3^-$  concentrations.  $\text{N}_2$  concentrations of deep aquifer samples were measured only in samples collected in Oct-Nov. All samples but the deepest showed no evidence of excess  $\text{N}_2$ . Although the  $\text{N}_2$  concentration in this deep sample was inconsistent between replicates, it showed potential evidence of excess  $\text{N}_2$  related to denitrification (**Figure 7b**). Isotopic signatures indicated that denitrification had likely occurred in the deeper groundwater, with an increase in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  (**Figure 9**). While the majority of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values appeared to correspond to denitrification occurring at a 2:1 ratio, the deepest aquifer sample fell closer to the 1:1 line of denitrification (**Figure 9**). Despite the apparent increase in  $\delta^{15}\text{N}$  values, there was no clear relationship with  $\text{NO}_3^-$  concentrations (**Figure 10**). However, it is worth noting that the deepest sample, yielding the lowest  $\text{NO}_3^-$  concentration, also showed the highest  $\delta^{15}\text{N}$  value and one of the higher  $\delta^{18}\text{O}$  values.

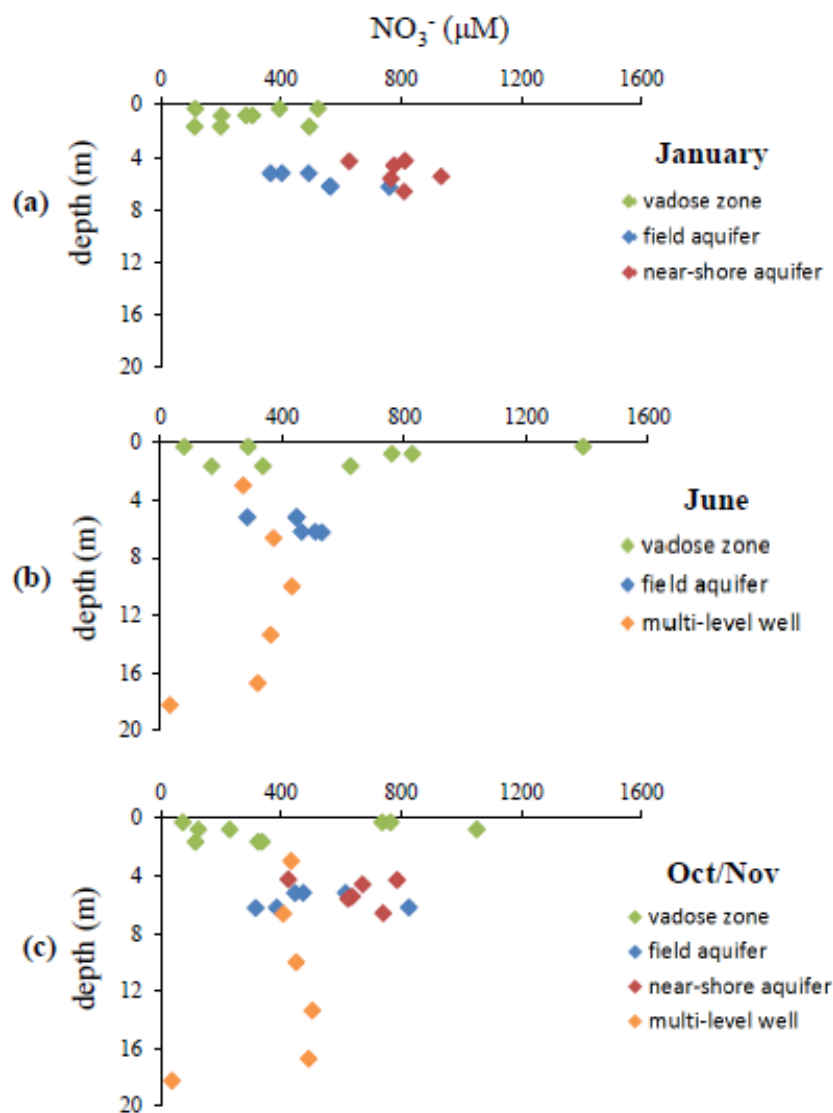
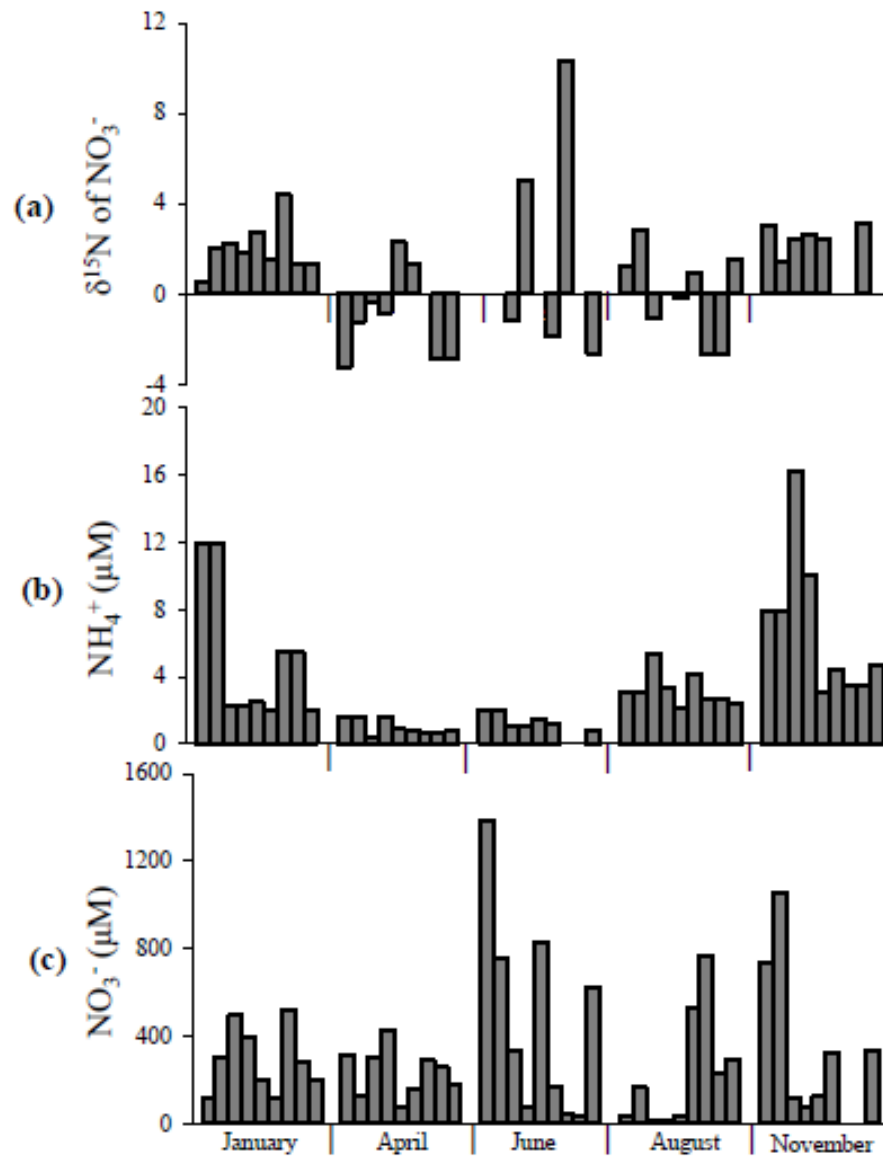


Figure 3.  $\text{NO}_3^-$  concentrations measured in vadose zone, shallow aquifer, and deep aquifer samples during January (a), June (b), and October/November (c).



**Figure 4.**  $\delta^{15}\text{N}$ - $\text{NO}_3^-$  values (a),  $\text{NH}_4^+$  concentrations (b), and  $\text{NO}_3^-$  concentrations (c) measured in vadose zone samples during January, April, June, August, and November.

**Table 1. Mean (+ or – standard deviation) nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), and dissolved oxygen (DO) concentrations in the vadose zone, shallow aquifer, and deep aquifer during January, June, and October/November.**

	$\text{NO}_3^-$ ( $\mu\text{M}$ )	$\text{NH}_4^+$ ( $\mu\text{M}$ )	DO (mg/L)
<i>January</i>			
vadose zone	293 $\pm$ 51	3.42 $\pm$ 0.61	no data
field aquifer	525 $\pm$ 58	5.50 $\pm$ 0.68	7.55 $\pm$ 0.16
shore aquifer	788 $\pm$ 40	6.03 $\pm$ 0.27	7.85 $\pm$ 0.35
<i>June</i>			
vadose zone	559 $\pm$ 153	1.07 $\pm$ 0.08	no data
field aquifer	447 $\pm$ 35	1.14 $\pm$ 0.22	7.74 $\pm$ 0.24
multi-level well	299 $\pm$ 58	2.16 $\pm$ 0.72	3.08 $\pm$ 0.97
<i>October/November</i>			
vadose zone	418 $\pm$ 116	5.51 $\pm$ 0.91	no data
field aquifer	511 $\pm$ 75	3.04 $\pm$ 0.44	8.35 $\pm$ 0.36
shore aquifer	648 $\pm$ 51	3.20 $\pm$ 0.36	8.14 $\pm$ 0.24
multi-level well	388 $\pm$ 72	2.27 $\pm$ 0.38	4.23 $\pm$ 1.07



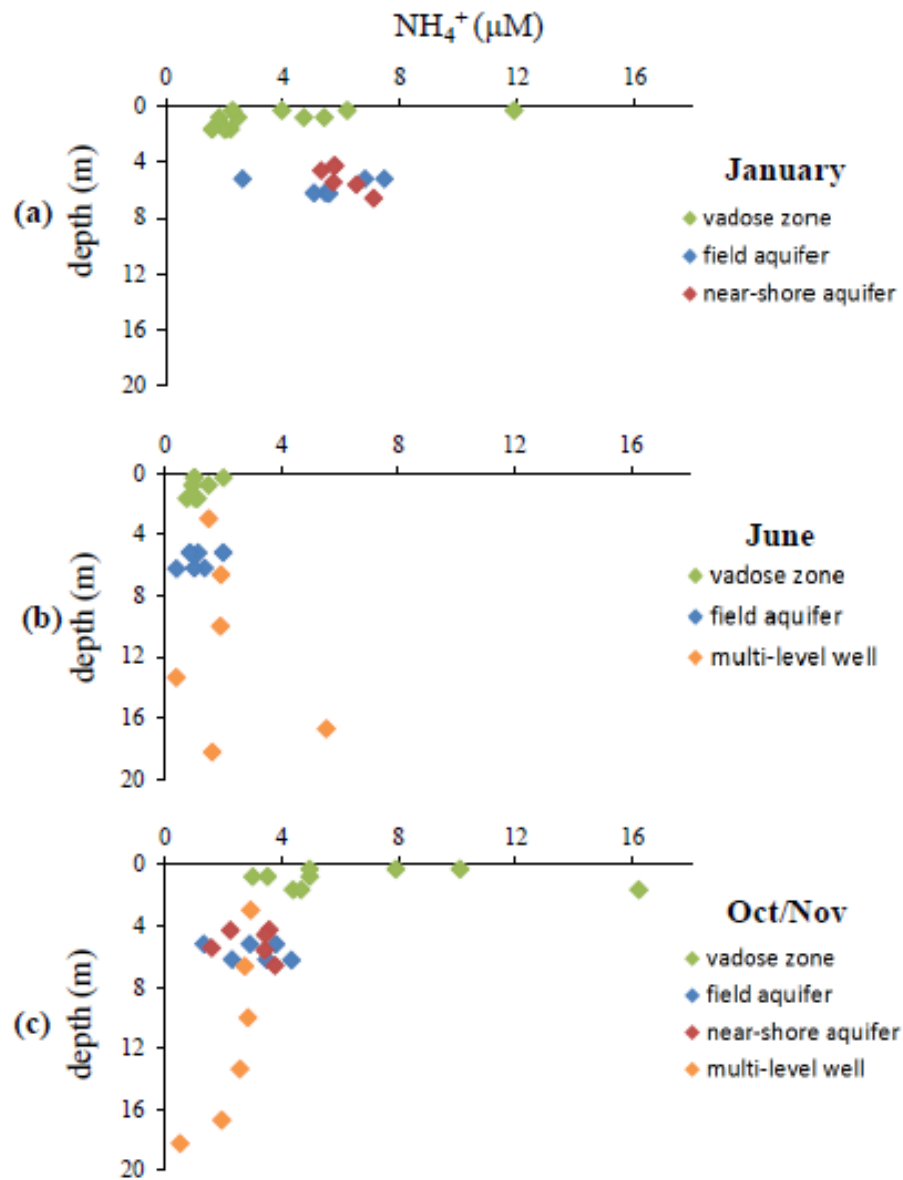


Figure 5.  $\text{NH}_4^+$  concentrations measured in vadose zone, shallow aquifer, and deep aquifer samples during January (a), June (b), and October/November (c).

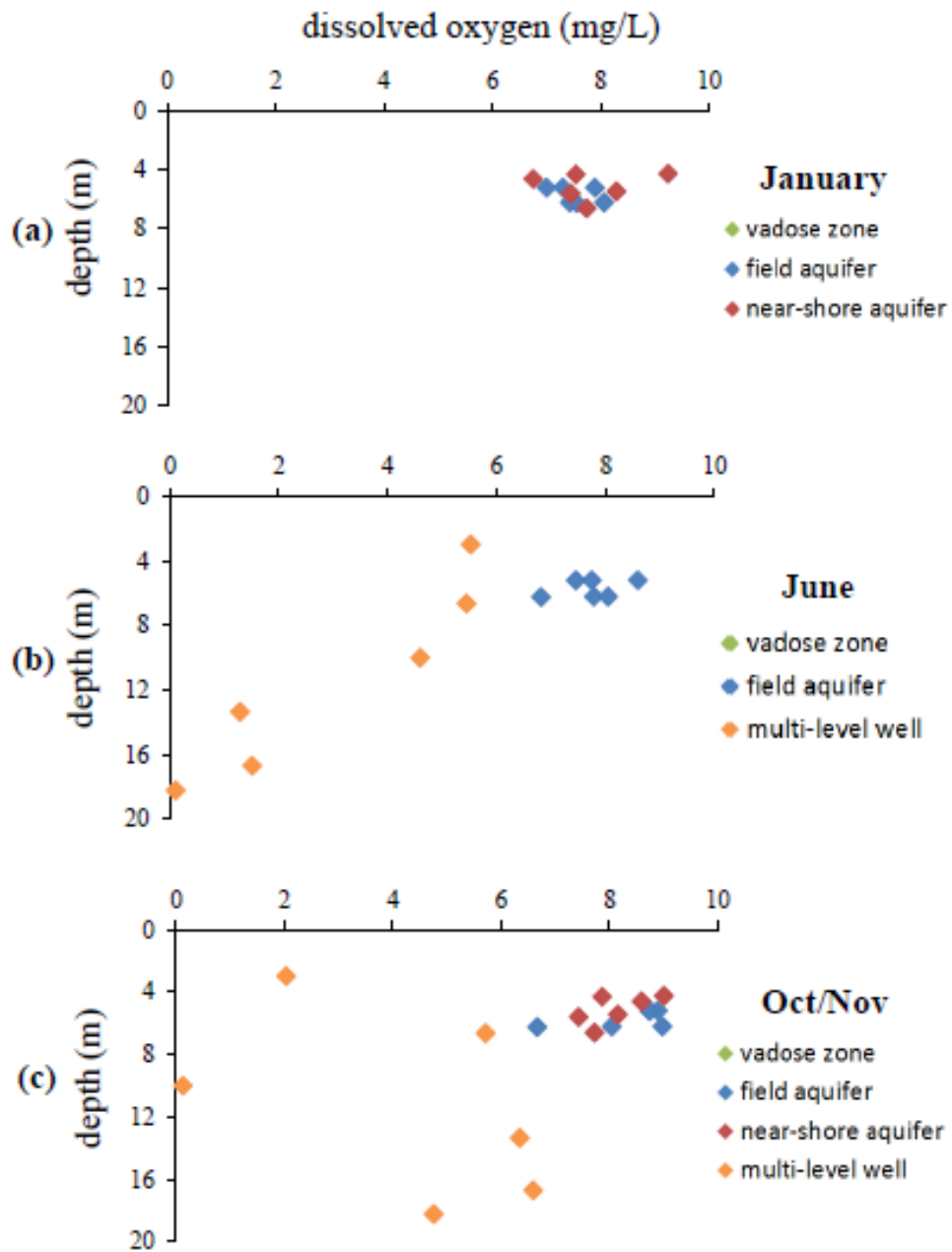
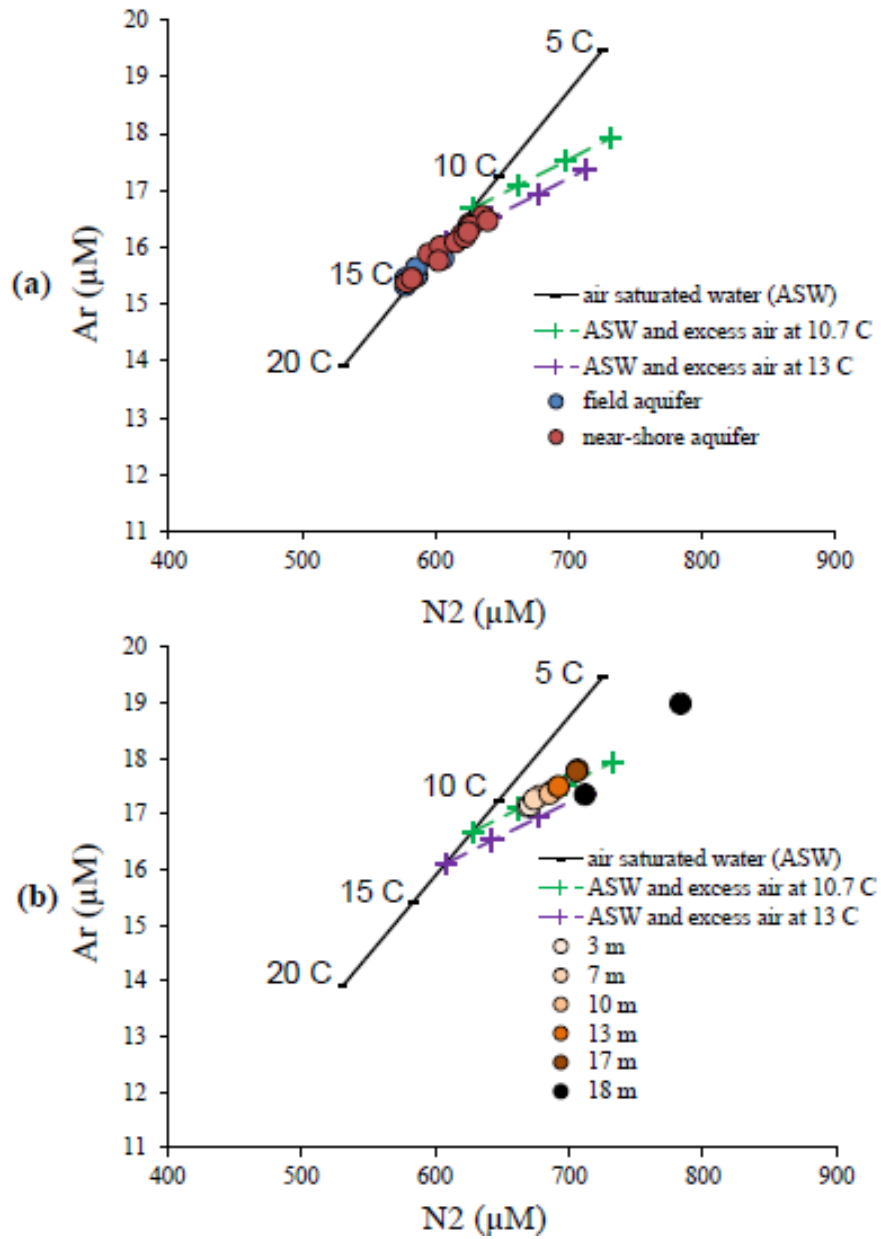


Figure 6. Dissolved oxygen concentrations measured in shallow aquifer and deep aquifer samples during January (a), June (b), and October/November (c).



**Figure 7. Argon concentrations versus N<sub>2</sub> concentrations, of vadose zone and shallow aquifer samples during January and November (a) and deep aquifer samples in October (b). The dashed lines indicate expected N<sub>2</sub> gas concentrations in fresh groundwater at 10.7 and 13.0 °C recharge temperatures, and up to 4 cc/L excess air.**

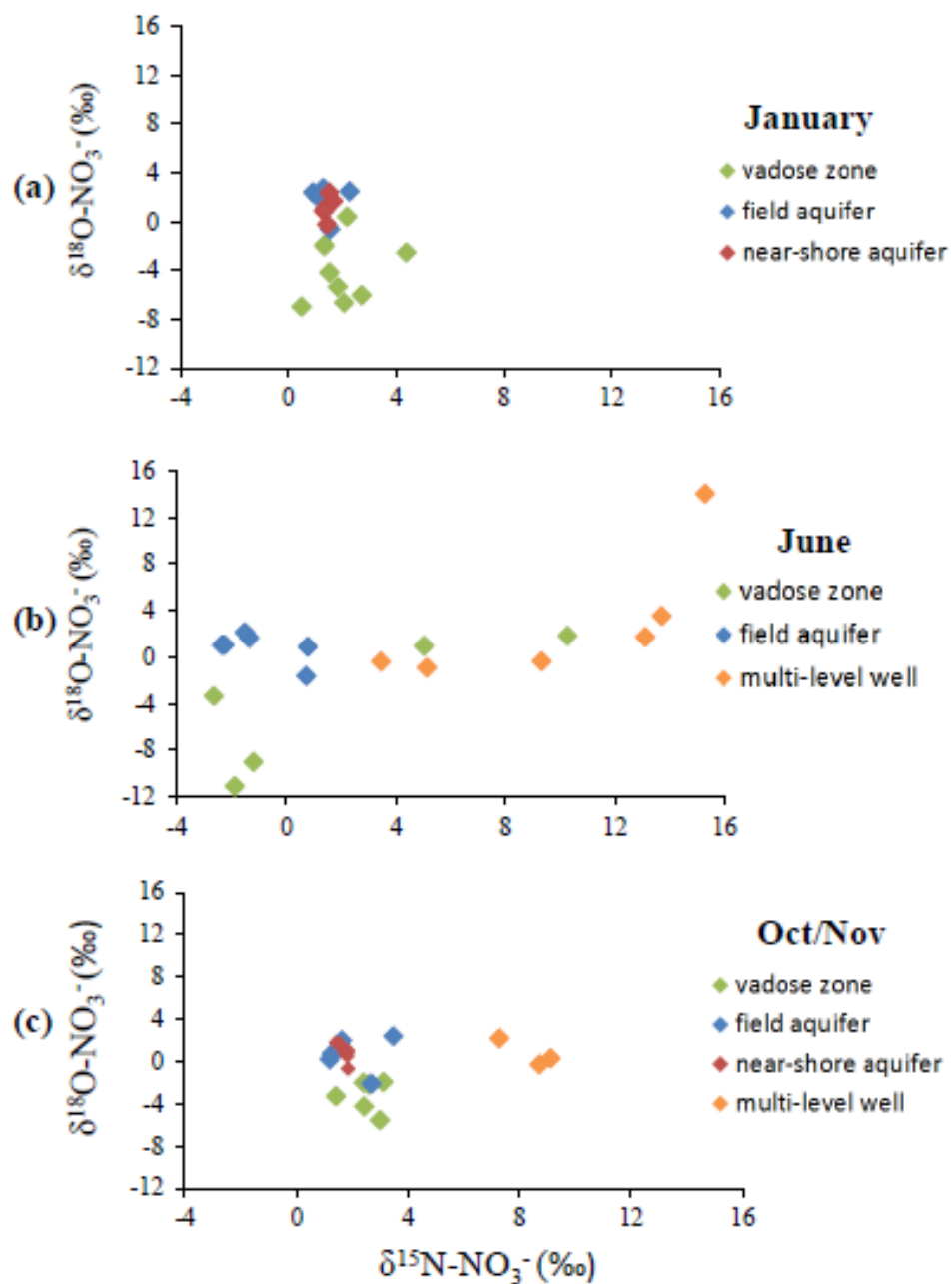
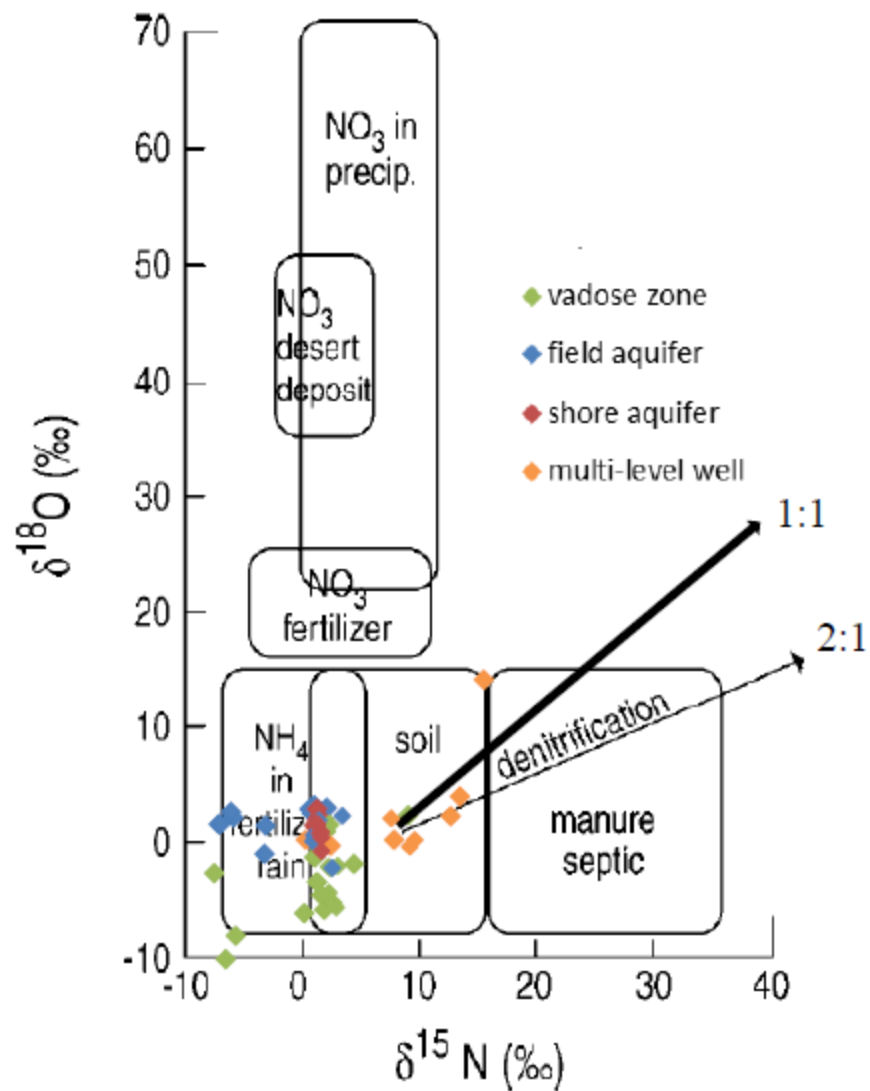
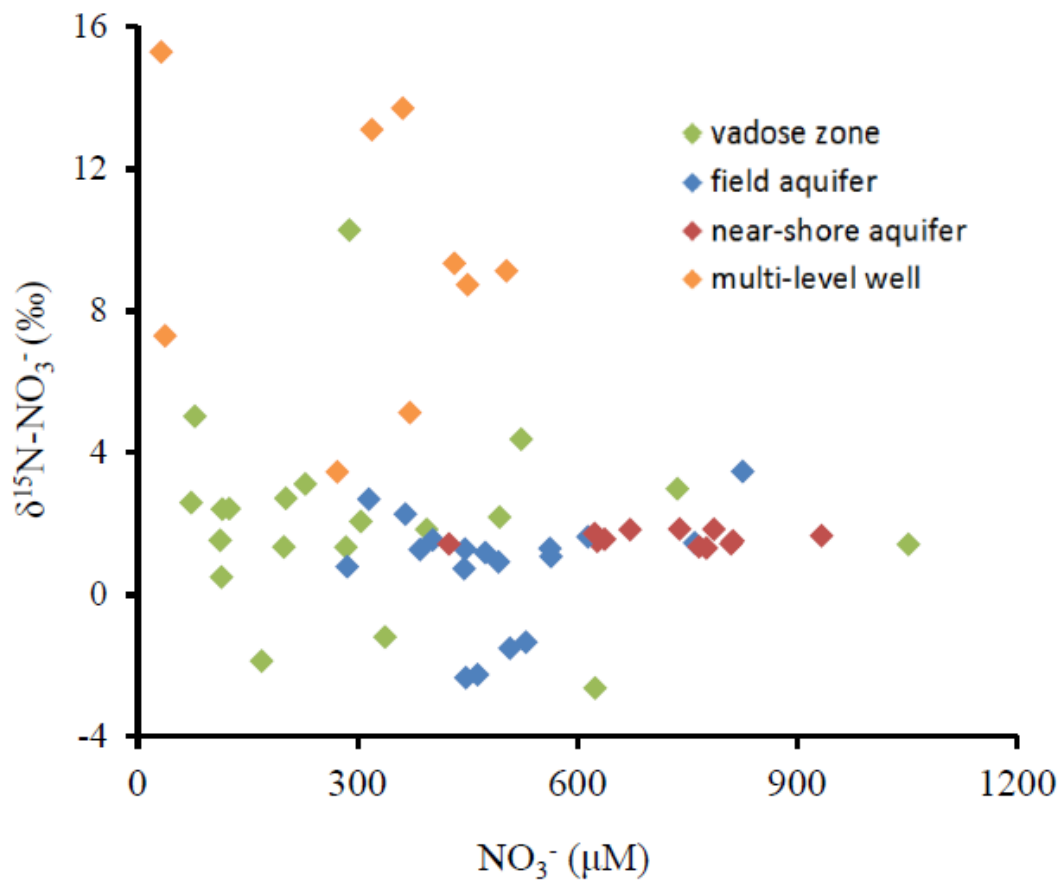


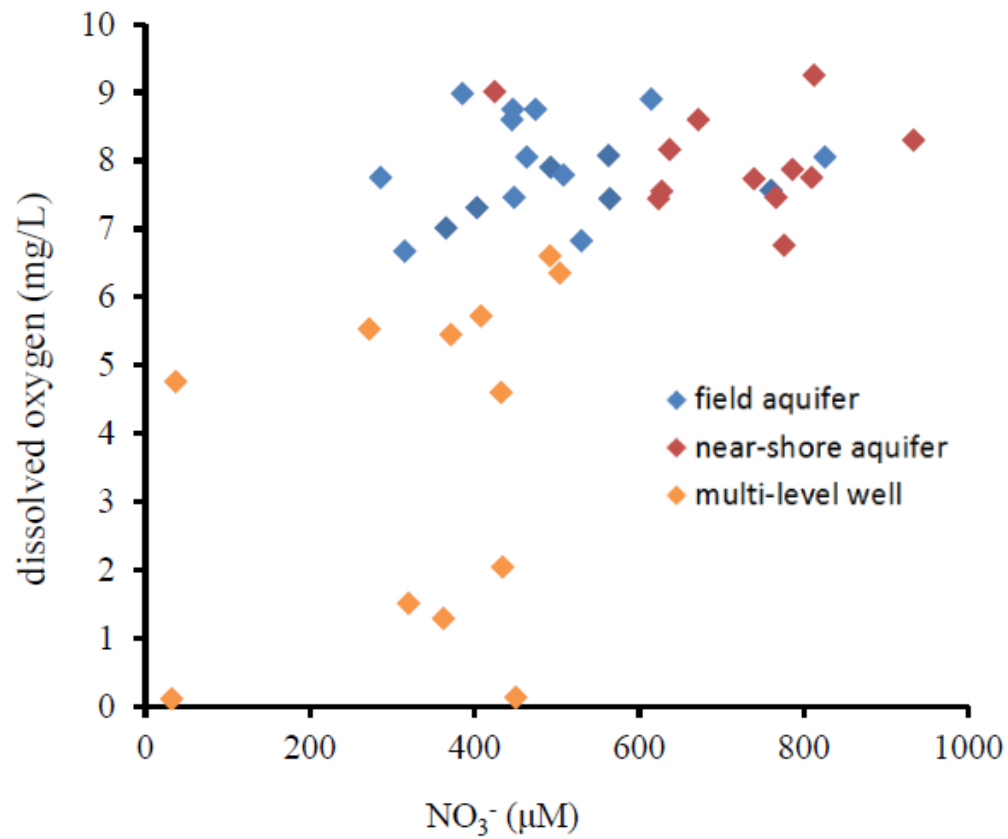
Figure 8.  $\delta^{18}\text{O}$  versus  $\delta^{15}\text{N}$  values of vadose zone, shallow aquifer, and deep aquifer samples during January (a), June (b), and October/November (c).



**Figure 9. Isotopic signatures of vadose zone, shallow aquifer, and deep aquifer samples (collected in January, June, and October/November).  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  ranges from Kendall (1998).**



**Figure 10.  $\delta^{15}\text{N-NO}_3^-$  values versus  $\text{NO}_3^-$  concentrations in vadose zone, shallow aquifer, and deep aquifer samples collected in January, June, and October/November.**



**Figure 11. Dissolved oxygen versus  $\text{NO}_3^-$  concentrations in shallow aquifer and deep aquifer samples collected in January, June, and October/November.**

## **Chapter 4**

### **DISCUSSION, CONCLUSIONS, AND APPLICATIONS**

#### **4.1 Groundwater Flow**

The rate of groundwater flow through the vadose zone and shallow aquifer are important factors controlling N transport in my system, and more generally in areas underlain by similar geology, as on the Delmarva, Long Island (NY), Cape Cod (MA), and elsewhere. In the sandy subsurface of southern Delaware, 2.54 cm of rain can transport  $\text{NO}_3^-$  15-20 cm down through the vadose zone (University of Delaware Cooperative Extension 2008). This rate ignores evapotranspiration, which is important during the summer growing season (Andres 2004). Variability associated with precipitation and seasonal plant growth results in the variable flow of moisture down through the vadose zone (Costa et al. 2002). Total aquifer recharge in southern Delaware is between 30 and 60 cm/year (Dunkle et al. 1993).

Significant leaching of  $\text{NO}_3^-$  beyond the root zone of crops takes place when rainfall exceeds 20 cm of rain over seven days (University of Delaware Cooperative Extension 2008). Rainfall during the week prior to each of my



samplings was below 13 cm (**Table 2**), meaning that significant  $\text{NO}_3^-$  leaching likely did not occur within the weeks before sampling.

The rate of groundwater flow through the aquifer was constrained using **Equation 1**. I used a value of 38 m/day for hydraulic conductivity (K) and a value of 0.0015 for the hydraulic gradient (i), as determined by Andres (1987) for subsurface sediments along the north shore of Indian River. I used porosity (n) values of 0.25 and 0.70 (Freeze and Cherry 1979) to bound the maximum and minimum possible flow rates through the heterogeneous subsurface. These values represent the porosity of a gravel substrate (0.25) and of a clay substrate (0.70) (Freeze and Cherry 1979). The groundwater flow rate through the shallow aquifer was bound as follows:

Upper bound:  $v = 38 \text{ m/day} * 0.0015 / .25 = 0.23 \text{ m/day} = 83 \text{ m/year}$

Lower bound:  $v = 38 \text{ m/day} * 0.0015 / .7 = 0.08 \text{ m/day} = 30 \text{ m/year}$

The lateral distance from the shallow aquifer below the field to the shallow aquifer below the near-shore is approximately 61 meters – recharge to discharge. Applying the flow rates calculated above along this distance, the shallow aquifer residence time of groundwater recharged through the field is bound as follows:

Upper bound:  $61 \text{ m} / 30 \text{ m/year} = 2 \text{ years}$

Lower bound:  $61 \text{ m} / 83 \text{ m/year} = 0.7 \text{ year}$

Based on these calculations,  $\text{NO}_3^-$  recharged with groundwater through the field travels 0.7 to 2 years through the shallow aquifer before discharging into Indian River. This has important repercussions for understanding lag times associated with changes in agricultural practices and land-use, and also for the potential for losses.

## **4.2 Shallow Aquifer Sampling**

### **4.2.1 Nitrate**

Based on a comparison of  $\text{NO}_3^-$  concentrations in groundwater from the vadose zone and shallow aquifer, it is apparent that no  $\text{NO}_3^-$  loss occurred with groundwater flow through the vadose zone and shallow aquifer (**Figure 3, Table 1**). A lack of significant variation in  $\text{NO}_3^-$  concentrations measured in the vadose zone between samplings (**Figure 4c**) suggests a consistent presence of excess  $\text{NO}_3^-$  within the vadose zone, independent of crop cover.

The effective root zone of a crop is half of its maximum rooting depth – the depth through which the majority of roots active in moisture and nutrient uptake are located. The effective rooting depth of soybeans, winter wheat, corn, and wheat is approximately 61 cm (University of Delaware Cooperative

Extension 2007). Vadose zone samples were drawn from within the effective rooting depth (30 cm), within the maximum rooting depth (80 cm) and below the maximum rooting depth (165 cm). Collectively, it is therefore probable that vadose zone  $\text{NO}_3^-$  concentrations were impacted by crop uptake, despite the lack of significant variation in  $\text{NO}_3^-$  concentrations observed between samplings. Because crops or cover crops were always in the ground at my site, it can be assumed that a substantial reservoir of N existed not only in the dissolved, inorganic forms measured, but also as organic matter associated with the crops.

Although  $\text{NO}_3^-$  concentrations did not consistently vary significantly through the shallow aquifer, it is possible that concentrations were impacted by the convergence and mixing of multiple groundwater flow paths, especially close to the point of groundwater discharge into Indian River. The deeper the position groundwater occupies within the aquifer, the older it is (Böhlke 2002). Land use is ever-changing, whether that change is between land use types or within a single land use type (for example, changing agricultural practices involving crop rotation, tilling, irrigation, and fertilizer use) (Galloway et al. 2003). Converging groundwater flow paths might result in the mixing of  $\text{NO}_3^-$  concentrations derived from differing types of agricultural land use.

Overall, my data did not indicate  $\text{NO}_3^-$  loss with flow through the vadose zone and shallow aquifer. This implies that there is no means of significant  $\text{NO}_3^-$

removal within the vadose zone and shallow aquifer. It appears that at this site, and likely at sites with similar geologic settings, all fertilizer- $\text{NO}_3^-$  leached beyond the root zone of crops eventually makes its way into Indian River.

#### **4.2.2 Ammonium**

Ammonium concentrations were much lower than  $\text{NO}_3^-$  concentrations throughout the vadose zone and shallow aquifer during all samplings (**Figure 5 and Table 1**), indicating that  $\text{NH}_4^+$  likely makes up a minor fraction of the N load discharging into Indian River with shallow groundwater. As in comparable studies (Kasper and Strohmeier 2007; Denver et al. 2004),  $\text{NH}_4^+$  concentrations from this study were on the lower end of the  $< 56 \mu\text{M}$  typical of Delmarva groundwater. This is likely due in part to the ease with which  $\text{NH}_4^+$  is assimilated by microbes, and in part to the tendency of  $\text{NH}_4^+$  to bind to soil particles, minimizing transport (Wang and Alva 2000).

#### **4.2.3 Denitrification**

One of the dominant mechanisms for N loss from groundwater is attenuation via microbially-mediated denitrification (Kaushal et al. 2011). Denitrifying bacteria require an environment with  $< 1 \text{ mg/L}$  of DO to carry out the process (Kasper and Strohmeier 2007). Mean DO concentrations exceeded  $7 \text{ mg/L}$  in all shallow groundwater samples (**Figure 6 and Table 1**), likely

precluding the process of denitrification in the shallow aquifer. The absence of excess  $N_2$  in all samples (**Figure 7**) further suggested a lack of significant denitrification. This is consistent with the  $NO_3^-$  data, showing no loss of  $NO_3^-$  with flow through the vadose zone and shallow aquifer.

Isotopic signatures further supported a lack of denitrification and  $NO_3^-$  loss throughout the vadose zone and shallow aquifer (**Figure 8, 9**). A comparison with literature values showed that our samples were characteristic of  $NO_3^-$  derived from  $NH_4^+$  in fertilizer and soil  $NO_3^-$  (**Figure 9**) (Chang et al. 2002; Kendall 1998; Böhlke et al. 2009), un-impacted by denitrification, which produces a characteristic increase in both  $\delta^{15}N$  and  $\delta^{18}O$  values (Kendall 1998). Isotopic signatures were consistent through time in the vadose zone and shallow aquifer, indicating both that the primary source of  $NO_3^-$  to the shallow aquifer was agricultural and that denitrification was negligible throughout the system.

#### **4.3 Deep Aquifer Sampling**

The deepest point sampled in the aquifer yielded a much lower  $NO_3^-$  concentration than concentrations measured in the shallow aquifer (**Figure 3b, 3c**). Dissolved oxygen was measured below the 1 mg/L threshold (Denver 2004; Kasper and Strohmeier 2007) representing hospitable denitrifying conditions within a couple of samples collected from the multi-level well – one of them taken from the deepest sampling point (**Figure 6b, 6c and Table 1**). Unlike in the

shallow aquifer, the deep aquifer appears to be more conducive – albeit patchily – to denitrification. However, there was no consistent relationship between  $\text{NO}_3^-$  and DO concentrations within the deep aquifer (**Figure 11**). This lack of consistency might have to do with availability of organic matter to fuel denitrification (Kendall 2007), and subsequent  $\text{NO}_3^-$  loss to  $\text{N}_2$ . If organic matter is distributed unevenly in the heterogeneous subsurface, then even if DO conditions are conducive to denitrification, sufficient organic matter might not be available to fuel the process.

Apart from the deepest sample, nitrogen gas concentrations in deep aquifer samples showed no evidence of excess  $\text{N}_2$  produced through denitrification (**Figure 7b**). Even then, the replicates of this sample were inconsistent, with one yielding excess  $\text{N}_2$  and the other not. This discrepancy could have been caused by sample handling and subsequent degassing during collection or storage. To clarify the possibility of denitrification at this site, additional samples should be collected and analyzed for  $\text{N}_2$  gas.

A comparison of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values with literature values (Kendall 1998) further suggested that denitrification is likely occurring within the deep aquifer (**Figure 9**). Isotopic signatures showed the increases in both  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ , characteristic of denitrification. However, there is not a clear consensus on the exact ratio of increasing  $\delta^{15}\text{N}$  to  $\delta^{18}\text{O}$  values associated with denitrification.

Both 2:1 and 1:1 ratios have been observed. While most samples collected from the deep aquifer fall close to the 2:1 denitrification line (Kaushal et al. 2011), one point (the deepest sample) does depart from the others, aligning more closely with the 1:1 line (**Figure 9**). This discrepancy might be due to the isotopic influence of multiple processes resulting in  $\text{NO}_3^-$  attenuation. Laboratory studies of denitrification have found a 1:1 increase in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  (Sigman et al. 2005; Granger 2006; Kendall 2007). However, in groundwater, other  $\text{NO}_3^-$ -attenuating processes including  $\text{NO}_3^-$  assimilation by bacteria, oxygen exchange between  $\text{NO}_3^-$  and water, and aerobic denitrification might alter this signal of denitrification, producing a  $\delta^{15}\text{N}$ - $\delta^{18}\text{O}$  ratio that differs from the standard 2:1 or 1:1 ratio (Granger 2006; Kendall 2007).

It is also important to note that although isotopic signatures were indicative of denitrification in the deep aquifer, they did not necessarily correspond to low  $\text{NO}_3^-$  concentrations (**Figure 10**). It is possible that incomplete denitrification caused some increase in isotopic values, but did not deplete  $\text{NO}_3^-$  in groundwater. To better understand this possibility, I estimated the fraction of  $\text{NO}_3^-$  that was denitrified in the deepest aquifer sample using a version of the Rayleigh fractionation equation (Green et al. 2010). The deepest sample showed the clearest evidence of denitrification, with a  $\text{NO}_3^-$  concentration of 32.5  $\mu\text{M}$ , a DO concentration of 0.1 mg/L, an  $\text{N}_2$  concentration suggestive of denitrification,

and an isotopic signature showing clear evidence of denitrification. To calculate the fraction of  $\text{NO}_3^-$  lost to denitrification, the following equation was applied:

$$\delta^{15}\text{N}[\text{NO}_3^-]_p = (1 + \delta^{15}\text{N}[\text{NO}_3^-]_{p,0})(f_{\text{N},p})^\epsilon - 1 \quad \text{Equation 3.}$$

In **Equation 3**,  $\delta^{15}\text{N}[\text{NO}_3^-]_p$  refers to the isotopic composition of N in  $\text{NO}_3^-$  within the sample,  $\delta^{15}\text{N}[\text{NO}_3^-]_{p,0}$  the isotopic composition of N in  $\text{NO}_3^-$  at the time of groundwater recharge,  $\epsilon$  the isotopic fractionation factor associated with denitrification, and  $f_{\text{N},p}$  the fraction of remaining (not denitrified)  $\text{NO}_3^-$  in the sample (Green et al. 2010). The value for  $\delta^{15}\text{N}[\text{NO}_3^-]_p$  in the deepest sample was 15‰,  $\delta^{15}\text{N}[\text{NO}_3^-]_{p,0}$  was assumed to be approximately 2‰ (based on vadose zone samples), and  $\epsilon$  was assumed to be approximately -18‰ - the fractionation factor associated with riparian denitrification (Kendall 2007). Substituting these values for their respective parameters, the fraction of remaining  $\text{NO}_3^-$ , and thereby the fraction of  $\text{NO}_3^-$  denitrified in the deepest aquifer sample was calculated was 0.91 or 91% of remaining  $\text{NO}_3^-$ . That is, the fraction of  $\text{NO}_3^-$  denitrified in the deepest sample was approximately 9%. Assuming that the  $\text{NO}_3^-$  in all other deep aquifer samples originated from a source with similar isotopic composition (e.g., 2‰), that  $\text{NO}_3^-$  must have been subjected to an even lesser degree of denitrification. Collectively,  $\text{NO}_3^-$ , DO,  $\text{N}_2$ , and isotopic data show evidence of inconsistent



denitrification within the deep aquifer. It is likely that subsurface heterogeneity plays a role in varying DO conditions, organic matter availability, and therefore denitrification within the deep aquifer.

## **4.4 Conclusions and Applications**

### **4.4.1 Conclusions**

At my project site, the shallow aquifer appears to behave similarly to a drainage pipe, funneling fertilizer-derived  $\text{NO}_3^-$  through an oxic vadose zone and shallow aquifer, with little potential for denitrification along the flow path. This implies that any excess  $\text{NO}_3^-$  leached beyond the root zone of crops will eventually make its way from the field into Indian River. As a limiting nutrient in algal growth, significant loading of N to a water body can promote algal growth, initiating the cascade of impacts associated with eutrophication (Anderson et al. 2002). The significant flux of groundwater-driven  $\text{NO}_3^-$  from the field to Indian River contributes to eutrophic conditions in the river and ultimately, in Indian River Bay.

Certainly not all fertilizer-N applied to the field moves into Indian River. A large portion is assimilated by crops, provided that it remains within the root zone. However, due to the porous, unconsolidated nature of the subsurface, and in light of the high  $\text{NO}_3^-$  concentrations observed in the shallow aquifer throughout

this study, precipitation-driven leaching appears to be a significant factor in  $\text{NO}_3^-$  transport throughout the system.  $\text{NO}_3^-$  concentrations in the shallow aquifer were consistently higher than natural soil concentrations throughout the study period. Increases in precipitation and storm intensity associated with climate change would certainly accelerate the process of  $\text{NO}_3^-$  leaching through the vadose zone to the aquifer.

In the deep aquifer however,  $\text{NO}_3^-$ , DO,  $\text{N}_2$ , and isotopic data suggest that denitrification occurred to some degree.  $\text{NO}_3^-$  and DO concentrations were not consistently correlated, indicating that denitrification did not occur throughout the deep aquifer, but rather at certain points within. This suggests the possibility of hot spots of denitrification, potentially associated with subsurface heterogeneity. Overall, it appears that  $\text{NO}_3^-$  in deeper, older groundwater has a greater potential to be denitrified than groundwater within the shallow aquifer.

Valiela's nitrogen loading model (NLM) (1997), calibrated with watershed N loads and losses relevant to land uses in the Cape Cod region, requires modification in order to be applicable to Delmarva. Giordano et al. (2011) applied NLM to watersheds in Virginia, using its original N loss coefficients. However, my research shows that minimal N loss associated with agriculturally-derived N in shallow groundwater, certainly well below the loss coefficients (61% loss vadose zone, 34% loss aquifer) in the original model. My

data further indicate that the extent of denitrification varies in deeper, older groundwater. It can therefore be concluded that N loss in groundwater cannot be captured by a comprehensive loss coefficient. Rather, losses appear to be highly variable and dependent upon many factors including subsurface composition, aquifer conditions, and groundwater age, and must instead be determined on a site-by-site basis for incorporation into the NLM.

#### **4.4.2 Applications**

Based on this study, subsurface composition, shallow aquifer conditions, and the proximity of agricultural land to a surficial water body, are significant factors influencing N loading to surficial water bodies in southern Delaware. At my project site, the agricultural field was adjacent to Indian River, meaning that groundwater discharge occurred fairly quickly following recharge. The substrate was sandy and porous with good recharge potential (Kasper and Strohmeier 2007), creating a highly oxic environment throughout the vadose zone and shallow aquifer. The crop and fertilizer regime were typical of Delmarva – soybeans, to winter wheat, to corn, to wheat (Kasper and Strohmeier 2007). Much of southern Delaware's agricultural land is comparably managed and overlies similarly-characterized substrate and shallow aquifer conditions (Kasper and Strohmeier 2007).

A reduction in nitrogen loads throughout the region might be facilitated by more careful fertilizer management on agricultural land, specifically on properties adjacent to surficial water bodies. At our site, significant  $\text{NO}_3^-$  concentrations were measured in vadose zone groundwater throughout the study period, independent of changes in crop cover. This suggests that a reservoir of N within the soil. An inventory of  $\text{NO}_3^-$  in the soil prior to each application of fertilizer would help farmers to determine the minimum amount of N needed to maximize crop growth. More importantly, this would reduce the risk of  $\text{NO}_3^-$  leaching and loss to groundwater.

Through better understanding and managing agricultural N loading to groundwater, overall N loads to the Inland Bays can be reduced, ultimately improving Bay health and preserving these unique ecosystems that we depend on for food, shelter, and recreation.

**Table 2. Blue text indicates rainfall during the week prior to sampling, and red text indicates rainfall on days of sampling.**

	January	June	November
day	rainfall (inches)	rainfall (inches)	rainfall (inches)
1	0.00	0.00	0.07
2	0.00	0.15	0.07
3	0.00	1.00	0.00
4	0.00	0.00	0.00
5	0.00	0.00	0.00
6	0.00	0.00	0.00
7	0.00	1.16	0.20
8	0.00	0.46	0.00
9	0.00	0.00	0.00
10	0.00	0.23	0.00
11	0.24	0.00	0.00
12	0.01	0.00	0.02
13	0.00	0.22	0.00
14	0.13	0.14	0.00
15	0.65	0.00	0.00
16	0.45	0.04	0.26
17	0.66	0.05	0.00
18	0.17	1.32	0.32
19	0.00	0.00	0.00
20	0.00	0.00	0.00
21	0.00	0.00	0.00
22	0.00	0.00	0.17
23	0.00	0.00	0.00
24	0.00	0.00	0.00
25	0.00	0.00	0.00
26	0.03	0.00	0.40
27	0.00	0.00	1.22
28	0.11	0.00	0.00
29	0.00	0.00	0.00
30	0.00	0.05	0.00
31	0.26	—	—
<b>Total</b>	<b>2.71</b>	<b>3.27</b>	<b>2.73</b>

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