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Nitrogen biogeochemistry in a restored Mississippi River delta: a modeling approach

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NITROGEN BIOGEOCHEMISTRY IN A RESTORED MISSISSIPPI RIVER DELTA:
A MODELING APPROACH

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The Department of Oceanography and Coastal Sciences

by
Benjamin Branoff
B.S. University of Florida, 2009
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ABSTRACT

There is evidence that significant reductions (about 50%) in surface water nitrate concentrations within coastal deltaic wetlands receiving diverted Mississippi River water can be contributed to denitrification. Yet there is also contrasting evidence that other processes could be responsible for this nitrate reduction. As Louisiana plans the implementation of major Mississippi River sediment diversions, a thorough understanding of nitrogen dynamics is necessary to reduce risks of coastal eutrophication and offshore hypoxia. A mechanistic numerical computer model has been developed to simulate nitrogen biogeochemistry within the wetlands of the prograding Wax Lake Delta. This model is calibrated to observed fluxes within laboratory experiments and validated against observed gradients in field observations, as well as against literature reports of other estuarine systems. Calibration of biogeochemical rate constants to the extremes of their bounds set by literature values, as well as the differences in effective rates exhibited between core incubation simulations and ecosystem simulations, suggests that laboratory experiments alone cannot account for full ecosystem biogeochemistry. Sensitivity analysis showed that, within soil core incubation simulations, nitrification had the greatest influence on nutrient fluxes. Dissimilatory nitrate reduction to ammonium (DNRA) had a similar influence on nitrate flux as denitrification and neither of these processes affected ammonium flux. In ecosystem simulations, denitrification exhibited the largest biogeochemical rate at $50 \mu\text{mol m}^{-2} \text{h}^{-1}$, with vegetation uptake, DNRA, and nitrification at 27, 17, and $0.6 \mu\text{mol m}^{-2} \text{h}^{-1}$, respectively. Retention efficiency of the study site fluctuated between 4% of loaded nitrogen in December and 16% in May. Temperature was found to have little effect on this efficiency, however loading rates and residence times were found to influence the nitrogen retention efficiency according to the same relationships of other wetland systems. Understanding the observed differences of nitrogen biogeochemistry operating at the laboratory

and landscape scales, will aid in the interpretation of measured results. Further, consideration of DNRA as a significant influence on surface water nitrate, and understanding the influences of residence time and nitrogen loading rate, will help in determining the fate of nitrogen in similar systems.

INTRODUCTION

Background

The general structure of the wetland nitrogen cycle is well understood, however the relative significance of specific processes to the ultimate fate of nitrogen within wetlands remains unclear, leading to uncertainties in nitrogen mass balances within different landscapes (Brock, 2001; van Breemen et al., 2002; Kroeze et al, 2003; Burgin and Hamilton, 2007). This uncertainty in the fate of nitrogen is particularly complex in the deltaic wetlands of Louisiana, where dynamics of the Mississippi River over the last 6000 years has created varying soil biogeochemical properties across the coast (McPhee, 1989). Managers in Louisiana are proposing sediment diversions there to ameliorate the growing problems of wetland degradation and to sustain the myriad ecosystem services that these wetlands provide. Such diversions will mimic the highly complex deltaic systems of the Mississippi River, but they will likely be designed to exhibit specific environmental parameters such as water residence time and nitrogen loading rates. Yet, the dynamics of nitrogen cycling as a result of diverting nitrate-enriched river water into coastal bays and estuaries is still largely unknown and this understanding will be important in determining the ultimate fate of river born nitrogen and thus the success of these proposed projects in reducing Louisiana's persistent and growing problems of coastal eutrophication and offshore hypoxia.

The function of coastal deltaic wetland ecosystems as a nitrogen source or sink depends on complex inter- and intra-relationships between their physical, chemical and biological components, each of which is governed by a separate and unique set of laws (Chen and Lu, 2003; Reddy and DeLaune, 2009). These laws incorporate various environmental parameters,

such as temperature (Kadlec, 1999), residence time (Dettman, 2001), nitrogen concentrations (Scott et al., 2008), loading rates (Spieles and Mitsch, 2000), and the seasonality associated with each of these variables (Ferguson and Eyre, 2007; Fulweiler and Nixon, 2011). This suite of environmental controls makes estimating seasonal biogeochemical activity difficult. Along the Louisiana deltaic coast, environmental parameters are often controlled by the influence of the Mississippi River and its distributaries. Actively prograding deltaic wetlands that are immediately influenced by Mississippi River water, for example, will likely experience lower temperatures, shorter water residence times, elevated nitrogen concentrations, and higher nitrogen loading rates than wetlands within abandoned, retrograding deltas of greater marine influence (Henry 2012). As a result, the wetland nitrogen cycle may operate differently in coastal basins of different stages of the delta cycle, and thus the ultimate fate of nitrogen as river water flows to the nearshore environments will vary.

Recently, the dominant features of anthropogenic engineering along the coast have served to eliminate natural deltaic processes in some areas, while mimicking them elsewhere (McPhee, 1989). The outcome has been one of the largest wetland loss problems in the world, with nearly one-third of the original Louisiana deltaic wetlands now submerged under water. From 1932 to 2010, Louisiana lost roughly 4,750 km² of coastal land, which is equivalent to 25% of the 1932 land area (Couvillion et al., 2010). Since 1985, the rate of loss has been 43 km² a year. The reasons for this loss are both natural and anthropogenic as the deltaic nature of the Louisiana coast experiences natural fluctuations of river flooding and storm disturbances across a landscape of human settlement that has taken advantage of the rich energy and fisheries resources in the region (Boesch et al., 1983; Turner and Cahoon, 1988; Nyman et al. 1993). Engineering along the Mississippi River and its distributaries, which is essential for flood protection from both the

river and the sea, has compounded the problem by disturbing the natural dynamic flow of water and sediment that historically nourished the deltaic wetlands of this coast (Kesel, 1989).

Additionally, the chemistry of the Mississippi River has changed over the last four decades with increases in river nitrate stimulating a large seasonal hypoxic dead zone in the northern Gulf of Mexico (Rabalais et al., 2002). Given the problems of wetland loss facing Louisiana's coast and the proposed solutions using river diversions, understanding these differences in the fate of nitrogen with age of coastal basins will be important to ultimately predicting outcomes of various management scenarios to eutrophication of coastal waters.

These problems of wetland loss and coastal eutrophication, and the potentially severe economic repercussions (Farber, 1996) have led both the public and the state and federal governments to enact coastal wetland management policies such as the Coastal Wetland Planning Protection and Restoration Act (CWPPRA), the Louisiana Coastal Protection and Restoration Authority (LACPRA) and the Louisiana Coastal Area (LCA), to propose solutions that will restore the dynamic linkages of the Mississippi River to the deltaic coast. The mission of these groups and the policies they encourage, are to enhance the ecosystem services provided by Louisiana's coastal wetlands, primarily by preventing further wetland loss, restoring degraded wetland areas or creating entirely new wetlands in strategic areas. One of the central strategies of these planning documents is to use the natural sediment resources of the river to rebuild land by the use of river diversions (Turner and Boyer, 1997; Martin, 2002; DeLaune et al., 2003; Paola et al. 2011). Some of these diversions have already been implemented in the past, while others have been approved in current State legislation and await future implementation.

The 2012 Louisiana Comprehensive Master Plan for a Sustainable Coast describes the State's plan for obtaining a sustainable coast through the use of various engineering projects

meant to enhance the coast's ecosystem services with both natural and created wetlands restoration. Within the plan, State legislature has approved \$3.8 billion for the implementation of sediment diversions that will use up to 50% of the Mississippi River's peak flow (LACPRA, 2012). These diversions are projected to build 777 km² of land. Although the land building potential and subsequent improvements to ecological components are fairly well established (Lane and Day, 1999; DeLaune et al, 2003; Lane et al., 2006; LDNR, 2006), the nutrient biogeochemistry of deltaic coasts requires further analysis to determine the effect on (Turner, 2010; Swarzenski et al. 2008) and ultimate fate of nitrogen in wetlands receiving diverted Mississippi River water.

It is hypothesized that by diverting water from the Mississippi River into degrading wetlands, these habitats can promote nitrogen removal, mainly through denitrification but also through burial and plant uptake (Day et al. 2004). This management strategy suggests that river-pulsing events from the Mississippi river to the deltaic floodplain, in addition to other methods (e. g. flood control, riparian wetland restoration, modification of farm practices upstream) can address both problems of coastal land loss and water quality deterioration. However, other studies have concluded nitrogen removal in the water column and benthic sediments via denitrification has minimal impact on the fate of nitrogen at high loading rates and high nitrate concentrations (80 -145 μ M nitrate) (Turner et al. 2004; Roy and White, 2012). Although it is reported that nitrate concentrations are rapidly reduced as diverted river water flows through coastal watersheds (e.g., Smith, 1985; Lane et al. 2002, Lane et al. 2003, Lane et al. 2004), it is not clear if this reduction is caused by denitrification or other factors such as dilution with ambient water, phytoplankton uptake, or plant uptake. These mechanisms represent nitrogen

recycling and transformations rather than a sink, since nitrogen is not lost from the system through denitrification.

The Wax Lake Delta is the result of a river diversion from the Atchafalaya River, which is itself a distributary of the Mississippi River (Fig. 1). The Wax Lake Outlet was constructed in 1941 by the U.S. Army Corps of Engineers as part of the Mississippi River and Tributaries Project (USACE, 2011). The outlet was designed to carry 30% of the Atchafalaya River's flow as a means of lowering the peak flood height in nearby Morgan City. The resulting delta became subaerial in 1973 alongside the Atchafalaya Delta (Roberts et al., 2003) and in 2005 represented nearly 100 km² of newly formed coastal wetlands (Kim et al., 2009). Biogeochemically, these wetlands are unique among other coastal systems in that they are only 40 years old at a maximum and thus consist almost entirely of nitrogen limited primary substrates that are subjected to elevated nitrate concentrations (50 - 100μM) (Henry, 2012). As a result, nitrogen biogeochemistry in these emerging deltaic landscapes has not yet been clearly defined.



Figure 1. The Wax Lake (a) and Atchafalaya (b) Deltas have formed as a result of a Mississippi River diversion. The study sight consists of the upper portions of Mike Island as shown to the right. The location of an active tidal creek is indicated by the arrow.

As of 1998, the delta was receiving anywhere from 30 to 45% of the Atchafalaya River flow, corresponding to roughly 9 to 14% of the Mississippi River flow (Roberts, 1998). This makes the Wax Lake Delta much more comparable to the size of sediment diversions proposed in the Master Plan (3 to 27% of river flow), than the much smaller freshwater diversions at Caernarvon, Davis Pond, Grand Bay and Pass a Loutre (1.6%, 2.1%, 0.51% and 0.51%, respectively)(Turner and Boyer, 1997), where most of the scientific investigations have been conducted. However, the Wax Lake Delta is fundamentally different than the proposed river diversions, in that it is constantly receiving diverted Mississippi River, whereas the proposed diversions would be pulsed systems, receiving diverted Mississippi river water for short periods throughout the year.

A review of denitrification measurements throughout Louisiana has shown extreme variability in measured rates depending primarily on the methods used (Rivera-Monroy et al., 2010). Further, multiple studies comparing conventional methods of measuring biogeochemical rates, both in-situ and within laboratories, have shown considerable differences (Parkin et al., 1984; Raison et al. 1987; Miller-Way et al., 1994; Fisher and Reddy, 2000), which leads to the conclusion that laboratory measurements alone cannot account for the full breadth of ecosystem biogeochemistry (Kadlec, 2012). This variability, as well as the uncertainty in the fate of nitrogen in deltaic wetlands, presents a need for more thorough understanding in: a) measured nitrogen biogeochemical rates within the wetlands of the Wax Lake Delta, covering spatial and temporal gradients to determine the relationships of these rates and their environmental controls on the ultimate fate of nitrogen within these prograding systems, and b) the relationship between these laboratory measured rates and the actual operating rates within the ecosystem. Additionally, a comparison of the above information to that of other coastal wetland systems

would be helpful in determining the relative efficiency of Louisiana's coastal wetlands in removing excess nitrogen from downstream coastal waters.

This thesis describes the development of a biogeochemical model to simulate fate of nitrogen in a prograding deltaic coast, the Wax Lake Delta. The model operates mechanistically by simulating each process in the nitrogen cycle through the use of various differential equations and incremental time steps. However, the model also incorporates important environmental controls such as the seasonality associated with temperature, vegetation dynamics and hydrology. In doing so, the model provides insight into the relative magnitude of the various biogeochemical rates as well as the temporal and spatial gradients observed in these rates. It is calibrated with observations taken in the field as well as in controlled laboratory experiments. This calibration explores the link between biogeochemical rates measured in the laboratory and those operating at the landscape scale. It is then validated against observations made within the Wax Lake Delta as well as against reported observations from other systems within the literature.

Through this model, I test hypotheses associated with the role of selective processes in removing nitrogen, particularly nitrate, from a river-dominated deltaic coast. I compare variations in rates of nitrogen processes that result in concentrations observed in laboratory core incubations to those rates that result in observed concentrations of nitrogen within the ecosystem. I also show how these nitrogen processes in both cores and the ecosystem are influenced by environmental controls and how their relative significance to nitrogen cycling changes seasonally. Temperature and ambient nitrogen concentrations affect the rates of biogeochemical processes, which determine the seasonal changes in rates and resulting fate of nitrogen. Water flow and the corresponding residence times within deltaic wetlands also influence the processing and removal of nitrogen from the ecosystem. Nitrogen loading rates have also been shown to

significantly impact wetland nitrogen removal efficiencies. By simulating all of these environmental variables and calibrating the biogeochemical parameters based on measured values in both core incubations and the field, I am able to suggest potential landscape scale rates as well as test the following hypotheses: a) denitrification is the primary process responsible for large reductions in surface water nitrogen within prograding wetlands receiving diverted Mississippi River water on the Louisiana coast (Smith, 1985; Lane et al, 2002; Lane et al., 2004). b) nitrogen retention within the Wax Lake Delta can be controlled through water residence time (Dettmann, 2001) and nitrogen loading rates (Spieles and Mitsch, 2000). c) Soil core incubations do not accurately reflect nitrogen biogeochemistry at full ecosystem scales, and appropriate precautions must be made when interpreting these results (Parkin et al., 1984; Raison et al. 1987; Miller-Way et al., 1994; Fisher and Reddy, 2000; Kadlec, 2012).

I tested these hypotheses using simulation models of nitrogen cycling in an emerging landscape along the Mississippi River delta. The Wax Lake Delta field site consists of the upper portions of Mike Island (29.506251,-91.443672), one of the primary subaerial deltaic splays. As of spring 2012, one tidal creek (29.511069,-91.443876) supplied the interior of Mike Island with river water from the primary channel. Other, now inactive tidal creeks up river from this are known to have been active and their remnants can be seen in aerial photography. These tidal creeks, along with the occasional extreme tidal pulsings and southerly winds are assumed to be the primary source of river water to the island interiors, which are otherwise bounded by natural levees.

Nitrogen Biogeochemistry

Nitrogen is of particular importance because of its widespread use by nearly all life on Earth, which is most likely a result of its versatility as an element. This is evident in its wide range of valence states (-3 to +5), a trait that allows it to form a large number of bonds with various other elements, as well as its natural occurrence as both a gas and a dissolved solute. Previous studies have shown that Louisiana's coastal wetlands are nitrogen limited for most of the year (Lane et al., 2002; DeLaune et al., 2005), making nitrogen the primary controlling nutrient in these ecosystems. Therefore, by understanding the specific processes of the nitrogen cycle in these systems, we may also better understand the system as a whole.

The nitrogen cycle is a suite of complex processes involved in the gradual oxidation of organic nitrogen to various inorganic forms, including the ultimate reduction to nitrogen gas (Reddy and DeLaune, 2009)(Fig. 2). Nitrogen can also be fixed back into organic matter, completing the cycle. Nitrogen enters a wetland in both organic and inorganic forms, however about 70% of the nitrogen carried in rivers globally is in the form of dissolved organic nitrogen (Stepanauskas et al., 1999). In the particulate form, organic nitrogen may accumulate in soil, eventually massing as peat. In subtropical wetlands however, such as those of Louisiana, this particulate nitrogen is most likely broken down by various bacterial communities through the process of enzyme hydrolysis, which separates individual organic molecules from larger, biologically derived macromolecules through the use of enzymes (Campbell and Reece, 2005). The organic nitrogen is then in a soluble form, available to mineralizing bacteria and in some cases, plant uptake. Studies in arctic settings have shown the ability of plants there to supplement their nitrogen demand with the uptake of amino acids (Kielland and Chapin, 1992; Nadelhoffer et al., 1992; Henry and Jeffries, 2002), however the importance of this process in the

nitrogen cycle is likely insignificant (Jones et al., 2005). Mineralization is a microbial process in which organic nitrogen is used, oxidized and expelled in an inorganic form as NH_4^+ (Reddy and Patrick, 1984).

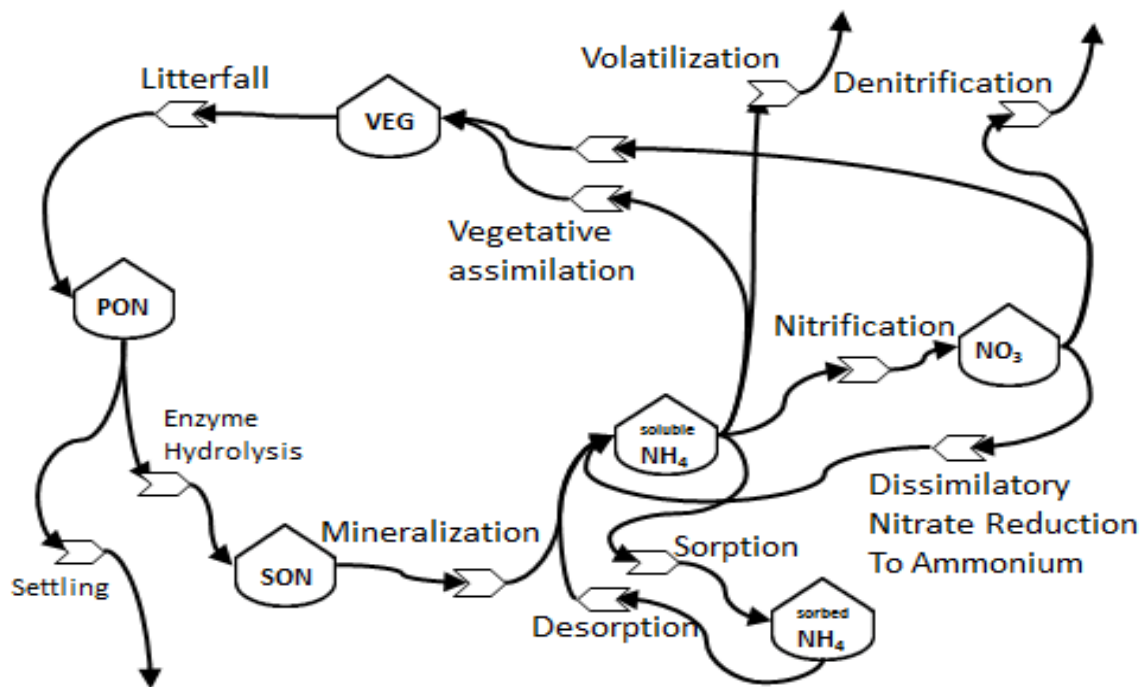


Figure 2. Unit model of the nitrogen cycle as described by Martin and Reddy (1997) and represented in the symbolic language of Systems Ecology (Odum, 1983). Organic Nitrogen (PON and SON) is converted to inorganic forms of ammonium (NH_4) and nitrate (NO_3), first via mineralization and then nitrification. Both ammonium and nitrate can be assimilated into vegetation, where it assumes an organic form and completes the cycle as litterfall. Removal of nitrogen from the system is accomplished via volatilization of ammonium, denitrification of nitrate and settling of PON. Alternate pathways include sorbtion and desorption of ammonia to and from the soil, and dissimilatory reduction of nitrate to ammonium.

Microbially, ammonium is nitrified in an aerobic process in the water column or in a thin layer of soil at the interface with overlying water (Reddy and Patrick, 1984). This process is called nitrification, which is a two-step process of further nitrogen oxidation that results in nitrite, NO_2^- , and nitrate, NO_3^- , the most oxidized forms of nitrogen. Ammonium may also partition between a soluble form and an adsorbed form on anionic soil particles (Kadlec and

Wallace, 2009). This process is largely controlled by the equilibrium dynamics between the adsorbed and soluble fractions of ammonium (Berner, 1975). Ammonium may also convert to ammonia, NH_3 , where it will likely volatilize to the atmosphere (Rao et al., 1984), or it can be assimilated into organic nitrogen by the surrounding photosynthetic organisms (Bowden, 1987). Finally, anammox is a process of anaerobic oxidation of ammonium to N_2 gas, although little is known about this process within Louisiana freshwater wetlands, and so it is not represented in this model.

Once nitrified to nitrite and subsequently nitrate, nitrogen has three potential pathways that will reduce its most oxidized form. Microbially, nitrate can be reduced to nitrogen gas, N_2 , which will be released to the atmosphere, in the process of denitrification. Or, nitrate can be reduced back to ammonium in the process of dissimilatory nitrate reduction to ammonium, allowing it to participate in the pathways explained above. Both of these nitrate pathways are anaerobic reactions and thus take place in the lower soil layers.

Denitrification in wetlands has been a focal point of nitrogen biogeochemistry since it was first suggested as the primary nitrogen removal mechanism of coastal ecosystems (Seitzinger, 1988; Cornwell et al. 1999). However, measured rates of this process vary depending on the method used and this is evident in the variety of measurements taken within similar ecosystems (Cornwell et al., 1999; Rivera-Monroy et al., 2010). As a result, some have suggested that we may be overemphasizing the role of this process in nitrogen removal (Burgin and Hamilton, 2007).

Finally, nitrate can also be assimilated into vegetation in the same manner as ammonium. Within vegetation, nitrogen may have many fates depending on climate, perennial or annual

lifecycle, or magnitude of nitrogen loading (Bowden, 1987). Many of the dominant species within Louisiana's freshwater marshes and especially those of the flooded soils in the Wax Lake Delta (*Sagittaria latifolia*, *Potamogeton nodosus*, *Typha latifolia*) are perennials. Species of these genera have been known to exhibit translocation of nitrogen from aboveground biomass during senescence to the perennial tissues belowground, known as retranslocation. This returns a portion of nitrogen back to belowground reserves that had been translocated in spring (Schenk, 1972; Smith et al, 1987; Caffrey and Kemp, 1990). However, some nitrogen is lost as leaching and litterfall at the end of the growing season, with leaching being a release of soluble organic nitrogen, and litterfall being that of particulate organic nitrogen (Bowden, 1987). The addition of these constituents completes the wetland nitrogen cycle by recycling the nitrogen previously assimilated in inorganic or organic forms.

Modeling Nitrogen Biogeochemistry

Given the importance of nitrogen in coastal ecological dynamics and the uncertainties associated with measuring the various processes of its cycle, biogeochemical modeling offers a method of providing insight by testing various hypotheses with new insights of ecosystem dynamics. There are a variety of methods and designs for modeling wetland nitrogen cycling (Rousseau et al., 2004). In its simplest form, modeling may provide a mass balance for a particular system, in which all of the nitrogen is accounted for based solely on empirical uncalibrated equations. An example would be the use of average biogeochemical rates taken from the literature. However, these models are rarely accurate for a given ecosystem and may only provide preliminary data on nitrogen sources and sinks. A much more accurate and robust model would operate mechanistically and be based on recorded observations from a specific system, for a specific type of system. These models simulate every biogeochemical process in the cycle at

incremental time steps, with as many environmental controls included as possible. Such models not only estimate potential mass balances, but they also estimate spatial and temporal gradients of specific rates, which may be very important at the landscape scale and over multiple seasons. Assuming that rates of nitrogen cycle are properly calibrated and estimates of nitrogen concentrations are tested against known observations, these models could provide accurate whole system simulations that can be used to test hypotheses described above (Dettmann, 2001; Spieles and Mitsch, 2000). Such simulations are complex, however, and require not only elevated computer processing capabilities but also accurate estimates of rate constants and nitrogen behavior in water and sediments of the ecosystem.

Such mechanistic models have been around since at least the 1970's to describe what was then referred to as diagenesis, or the transformations of recently deposited sediments and their contents (Vanderborght et al., 1977). Since then, increasingly complex and specific models have been developed to simulate nitrogen processing in wetlands (Bender, 1976; Martin and Reddy, 1997). Researchers have noted the need for highly complex ecosystem models that incorporate the dynamisms associated with wetland nitrogen cycle, including physical controls of hydrology with chemical and physical controls of biogeochemistry (Schubert et al., 2009). Such models offer insight not only into the mass balance of nitrogen in specific systems, but also into the spatial and temporal relationships between various ecological parameters and the nitrogen cycle. H.T. Odum advocated this systems based approach to understanding ecosystem function, which contributed significantly to the discipline of ecological engineering and especially to constructed wetland design (Taylor, 1988). As the science of ecological engineering and wetland restoration has progressed, it has become increasingly apparent how complex these systems are and how

essential it is to understand a wide variety of ecological components for successful restoration (Zedler, 2000).

METHODS

Description of the Model

Model Architecture

The model is written in the Visual Basic programming language and is based on a single fundamental unit- model representation of the wetland nitrogen cycle, which was modified from Martin and Reddy, 1997 (Fig. 2). Each process in the model is governed by a differential equation to determine change in a compartmental storage concentration over a small time step. Storages of nitrogen are represented within virtual layers, or compartments, within the modeled system. Two primary architectures are presented, a vertical flux model with no movement of overlying water, and a horizontal flow model in which the overlying water layer flows horizontally. Each version uses the same set of equations, when applicable. These equations are approximated iteratively using the Runge-Kutta fourth order method (Butcher, 2005). The equations and the processes they represent are described below and summarized in Table 1.

First Order Rate Processes

First order rate processes are those that are dependent on the reactant concentration and the rate constant. They are defined by the differential equation, Eq. (1).

$$\frac{dN}{dt} = kN \quad (1)$$

where $\frac{dN}{dt}$ is the change in nitrogen concentration over time, k is the first order rate constant with units of t^{-1} , and N is the concentration of a given nitrogenous compound.

Table 1. Equations used in the model.

| # | Equation | Description |
|----|--|--|
| 1 | $\frac{dN}{dt} = kN$ | First order processes |
| 2 | $J_N = D \frac{N_1 - N_2}{d_x}$ | Diffusive flux |
| 3 | $NH_3 = NH_4^+ \times 5.8 \times 10^{pH-10}$ | Volatilization |
| 4 | $Veg\ uptake_{NH_4} = Ndemand \times layerdepth\% \times \frac{N_{NH_4}}{k_m + N_{NH_4}} \times \frac{N_{NH_4}}{N_{NH_4} + N_{NO_3}}$ | Vegetation uptake of ammonium |
| 5 | $Veg\ uptake_{NO_3} = Ndemand \times layerdepth\% \times \frac{N_{NO_3}}{k_m + N_{NO_3}} \times \frac{N_{NO_3}}{N_{NH_4} + N_{NO_3}}$ | Vegetation uptake of nitrate |
| 6 | $\frac{NH_4\ sorption}{desorption} = \left((partitionk \times NH_{4\ sorbed}) - NH_{4\ soluble} \right) \times spectrate$ | Ammonium sorption |
| 7 | $Temperature\ (^{\circ}C) = 19 - 11 \cos \left(2\pi \left(\frac{day - 18.34}{365} \right) \right)$ | Daily temperature |
| 8 | $NO_3\ (\mu M) = 75.38 - 24.24 \cos \left(2\pi \left(\frac{day + 36.6}{365} \right) \right)$ | Daily nitrate |
| 9 | $NH_4\ (\mu M) = 1.62 + 0.79 \cos \left(2\pi \frac{day - 0.5}{365} \right)$ | Daily ammonium |
| 10 | $Water\ stage(m) = \begin{cases} 0.51 - 0.28 \cos \left(2\pi \left(\frac{day + 56.9}{365} \right) \right) & 0 < day \leq 245 \\ 0.41 - 0.16 \cos \left(2\pi \left(\frac{day - 84.3}{365} \right) \right) & 245 < day \leq 365 \end{cases}$ | Daily water elevation relative to NAVD88 |
| 11 | $flow\ rate\ \frac{m^3}{s} = 3.7132 \times water\ elevation^{1.6334}, \quad water\ elevation < 1$ | Flow rate through the system as a function of the water elevation. |
| 12 | $Vegetation\ N\ Biomass\ \left(\frac{mol}{m^2} \right) = 0.09 - 0.08 \cos \left(2\pi \left(\frac{day - 49.4}{365} \right) \right)$ | Daily vegetation N biomass |
| 13 | $Vegetation\ N\ Uptake\ \left(\frac{\mu mol}{m^2 h} \right) = \frac{2000000\pi}{365} 0.08 \sin \left(\frac{2\pi(day - 49.4)}{365 \times 24} \right)$ | Daily vegetation N uptake |

Table 1 continued. Equations used in the model.

| # | Equation | Description |
|----|--|--|
| 14 | $f_{denitrification} = \begin{cases} Te^{-6}, & 0 \leq T < 10 \\ 0.0822T - 0.7356, & 10 \leq T < 20 \\ -0.000471T^2 + 0.032359T + 0.45441, & 20 \leq T < 40 \end{cases}$ | Temperature effect on potential denitrification rate |
| 15 | $f_{nitrification} = \begin{cases} 0.0005T^2 + 0.0096T + 0.03, & 0 \leq T < 35 \\ 0.00043T^2 - 0.4277T + 10.709, & 35 \leq T < 50 \end{cases}$ | Temperature effect on potential nitrification rate |
| 16 | $f_{mineralization} = -0.00004T^3 + 0.0023T^2 - 0.0037T + 0.0689$ | Temperature effect on potential mineralization rate |
| 17 | $f_{DNRA} = 0.025T$ | Temperature effect on potential DNRA rate |
| 18 | $f_{volatilization} = 0.0567e^{0.0732T}$ | Temperature effect on potential volatilization rate |
| 19 | $f_{decay} = \begin{cases} 0.1203e^{0.0628T}, & 0 \leq T < 28 \\ -0.0389T + 1.8389, & 25 \leq T < 40 \end{cases}$ | Temperature effect on potential decay rate |
| 20 | $f_{litterfall} = 0.00054e^{0.0245day}$ | Litterfall as percentage of biomass |
| 21 | $RT = \frac{V}{Q}$ | Residence time |
| 22 | $z = 0.000005x^2 - 0.00022y + 0.12$ | Modeled Mike Island surface elevations |

Processes in this model that are defined by first order kinetics are: enzyme hydrolysis of particulate organic nitrogen (PON) to soluble organic nitrogen (SON), mineralization of SON to ammonium (NH_4^+), nitrification of NH_4^+ to nitrate (NO_3^-), denitrification of NO_3^- to nitrogen gas (N_2), dissimilatory nitrate reduction to ammonium (DNRA), the decay of vegetation litterfall to PON, and the settling of PON. Each process may have a separate rate constant, k.

Diffusive Flux

Diffusive flux of dissolved nitrogenous components between two vertical layers was modeled using Fick's law as defined by Eq. (2).

$$J_N = D \frac{N_1 - N_2}{D_x} \quad (2)$$

where D is diffusion coefficient, in units of $\frac{m^2}{h}$, N_1 and N_2 are soluble nitrogen concentrations in two adjacent layers, and d_x is the average distance between the layers. For the purposes of this model, d_x was taken to be half of the combined layer depths or $d_x = \frac{d_1 + d_2}{2}$. For cases in which the upper layer is the water layer, $d_x = \frac{d_2}{2}$ to account for the assumption that the water layer is fully mixed.

Volatilization

Volatilization of ammonia (NH_3) is assumed to occur immediately upon the formation of the gas from its parent compound, ammonium (NH_4^+). The conversion of Ammonia from Ammonium is governed by the equation (3):

$$NH_3 = NH_4^+ \times 5.8 \times 10^{pH-10}. \quad (3)$$

Eq. (3) results in little formation of NH_3 at pH values less than 7 and a large shift in the equilibrium concentration of NH_3 and NH_4^+ between pH values of 8 and 9, which have not been recorded at Wax Lake Delta.

Vegetative Assimilation

The assimilation of NH_4^+ and NO_3^- by various photosynthetic organisms is governed by Michaelis-Menten kinetics as represented in Eq. (4) & Eq. (5).

$$Veg\ uptake_{NH_4} = Ndemand \times layerdepth\% \times \frac{NH_4}{k_m + NH_4} \times \frac{NH_4}{NH_4 + NO_3} \quad (4)$$

$$Veg\ uptake_{NO_3} = Ndemand \times layerdepth\% \times \frac{NO_3}{k_m + NO_3} \times \frac{NO_3}{NH_4 + NO_3}, \quad (5)$$

where N_{demand} is the maximum nitrogen demand by photosynthesis within the system, in units of $\frac{\mu mol}{m^2 h}$. $Layerdepth\%$ is the percentage of that N demand which will be supplied by the given layer. This is taken as the % of the plant mass found in a given layer. NH_4 and NO_3 are the concentrations of nitrate and ammonium within the layer and k_m is the half saturation constant for the compound in question. In Michaelis-Menten kinetics, this is the concentration at which uptake rate is half of the maximum rate or N demand. For the purposes of this model, separate half saturation constants were assigned to water and soil layers to account for differences in uptake rates between leaves and roots (Thursby and Harlin, 1984). k_m is in units of $\frac{\mu mol}{m^2}$. Although N demand changes seasonally, k_m is assumed to remain constant (Lycklama, 1963; van den Honert and Hooymans, 1955).

Ammonium soil adsorption/desorption

Ammonium may exist in two states within wetland soils, in a soluble form within the soil pore-water, or in a sorbed form attached to the soil particles (McBride, 1994). The dynamics of this behavior is modeled using Eq. (6).

$$\frac{NH_4_{sorption}}{desorption} = \left((partitionk \times NH_4_{sorbed}) - NH_4_{soluble} \right) \times spectrate \quad (6)$$

Seasonal Simulations

Being driven primarily by the Mississippi River, the Wax Lake Outlet and its delta exhibit seasonal fluctuations of water elevation, temperature, nitrogen concentrations, and vegetation coverage. All are accounted for in the model by simulating the mean monthly values obtained from observations or from previous studies nearby. Water Quality parameters such as

temperature and inorganic nitrogen concentrations were modeled to simulate observations made at the United States Geological Survey's (USGS) National Water Information System gauge at the Wax Lake Outlet (USGS 073815925; 29.698528, -91.373463). Recordings were averaged into monthly values from the most recent ten years of data. Surface water temperature, nitrate and ammonium as modeled are shown in Figs. 3, 4 and 5, respectively, and the equations used to model them are (7), (8) and (9).

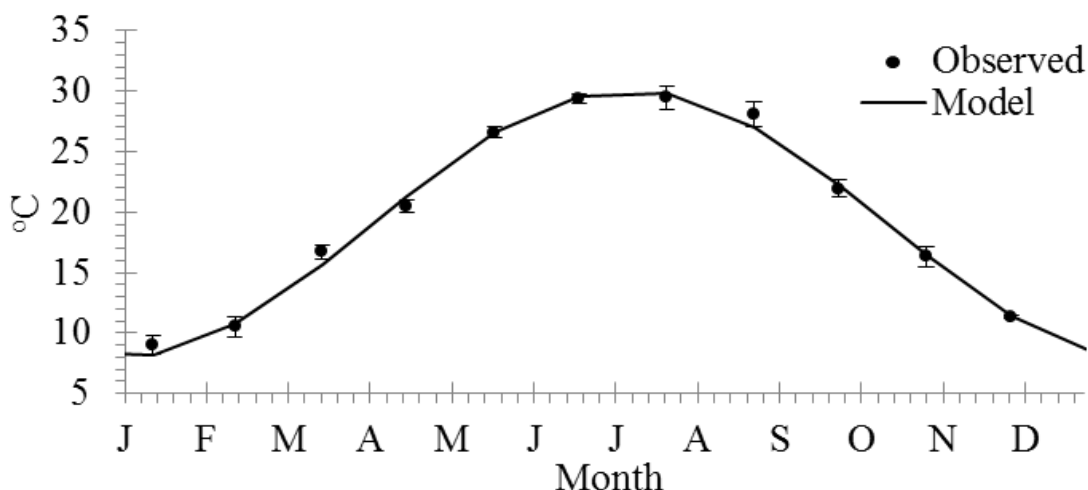


Figure 3. Mean monthly values of water temperature recorded at USGS station 073815925 for the period of December 4, 1972 – March 7, 2012, with modeled values using equation (7).

Water elevation in the system was modeled to simulate observations made at the Louisiana Department of Natural Resources Coastal Resource Monitoring Station in the Wax Lake Delta (CRMS 0479; 29.522907,-91.449745). Observations were averaged into monthly values since the beginning of the program in 2008 (Fig. 6; Eq. 10). Flow rate through the system was modeled as a correlation between the water elevation measured at CRMS 0479 and the recorded flow rates measured in the tidal creek (Fig. 7). Seasonal fluctuations in vegetative nitrogen demand and litterfall were modeled based on a combination of reports of vegetation coverage and mortality for a southeastern Louisiana fresh-water marsh (Sasser and Gosselink,

1984; Evers et al., 1998). Vegetative nitrogen demand was determined by first fitting a curve to published data of vegetation biomass with time of year (Sasser and Gosselink, 1984). This curve was then fit to data provided by Evers et al., 1998 and further reduced under the assumption that vegetation coverage on Mike Island was only 25% of land area compared to 50% cited in

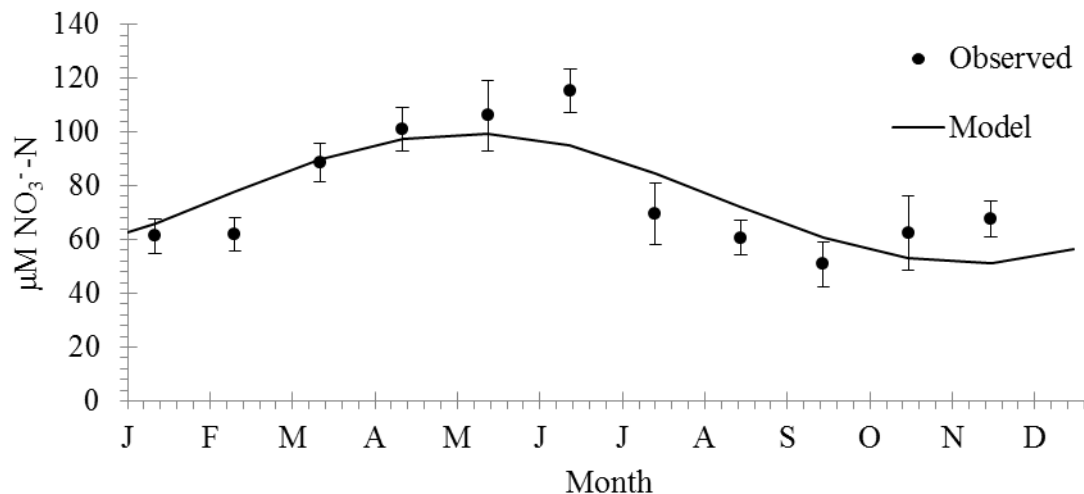


Figure 4. Mean monthly values of water nitrate concentration recorded at USGS station 073815925 for the period of October 28, 1977 – February 8, 2011, with modeled values using equation (8).

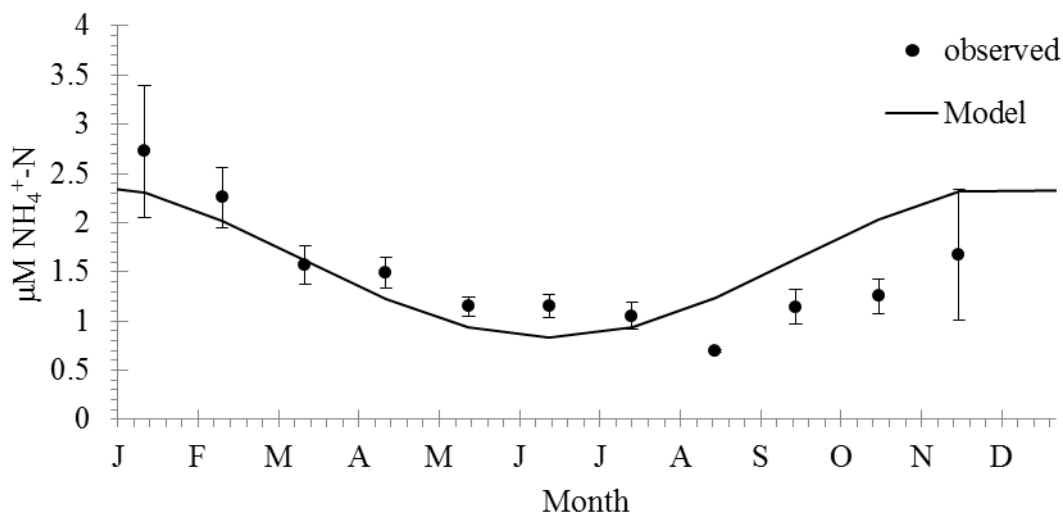


Figure 5. Mean monthly values of water ammonium concentration recorded at USGS station 073815925 for the period of July 14, 1981 – March 7, 2012, with modeled values using equation (9).

published reports. The derivative of this curve was then taken to be change (growth) in biomass for each day of the year. By assuming that nitrogen comprises roughly 1.25% of vegetative dry biomass (McJannet et al., 1995), nitrogen demand ($\mu\text{mol N m}^{-2} \text{d}^{-1}$) is determined by multiplying this percentage by the daily change in dry biomass (Fig. 8; Eqs. 12 & 13). Seasonal changes in litterfall were also derived from Sasser and Gosselink, 1984, by calculating the percentage of biomass that is dying at any given day of the year (Fig. 9).

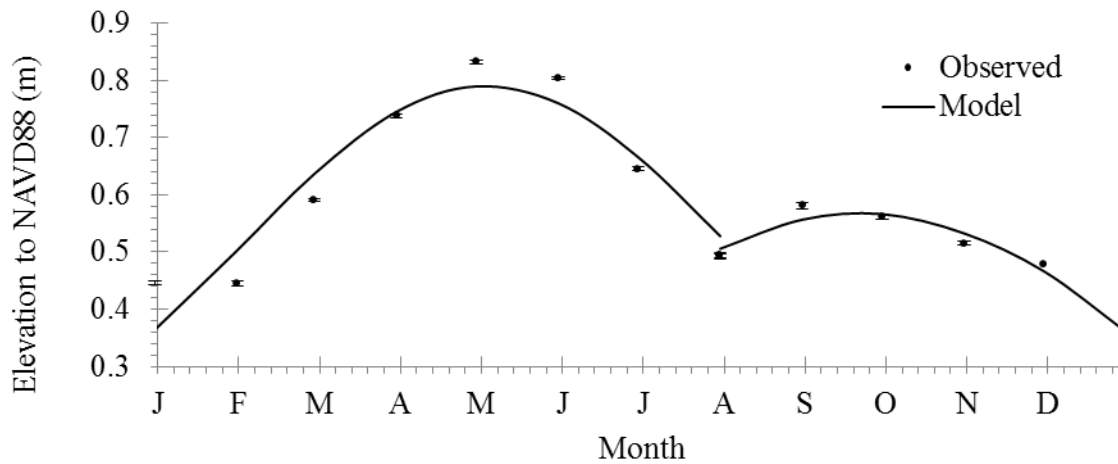


Figure 6. Mean monthly values of water elevations recorded at CRMS station 0479 for the period of March 26, 2008 – January 25, 2012, with modeled values using equation (10). Standard errors are shown but are often too small to distinguish.

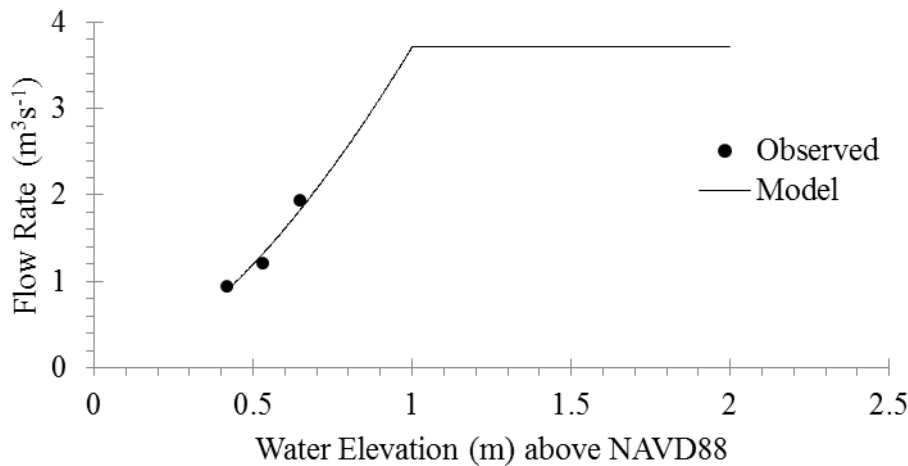


Figure 7. Relationship between water elevation in the delta and the flow rate through Mike Island. Flow rate is assumed to level off at 1 meter, which is the elevation of the natural levees. Modeled values use equation (11).

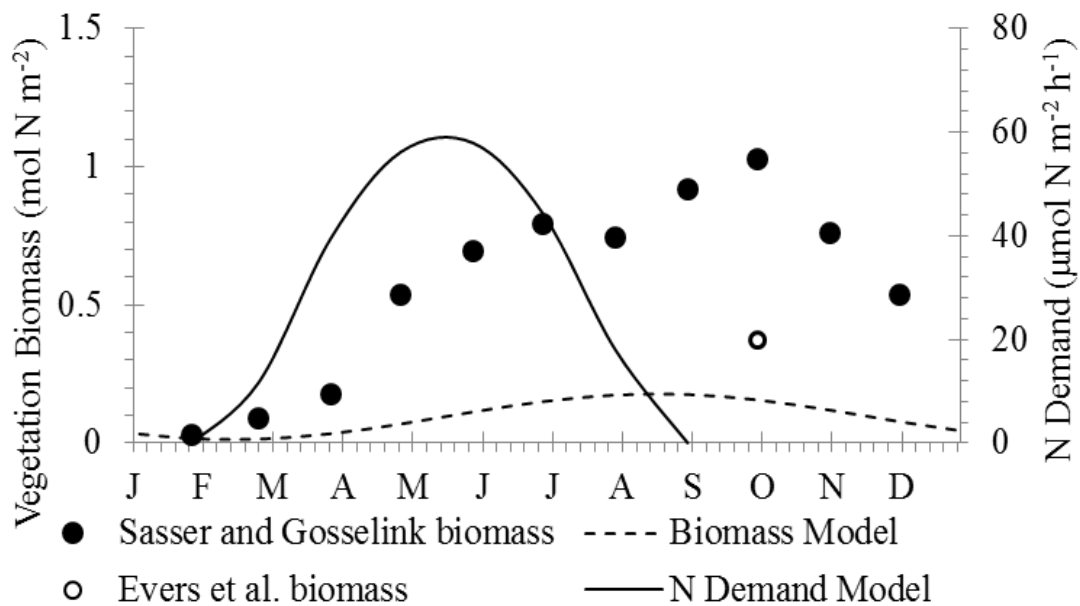


Figure 8. Vegetation within the system is modeled after reports by Sasser and Gosselink, 1984 and Evers et al. 1998. Nitrogen uptake, Eq. (13), is taken as the derivative of the nitrogen biomass within the system on a given day, Eq. (12).

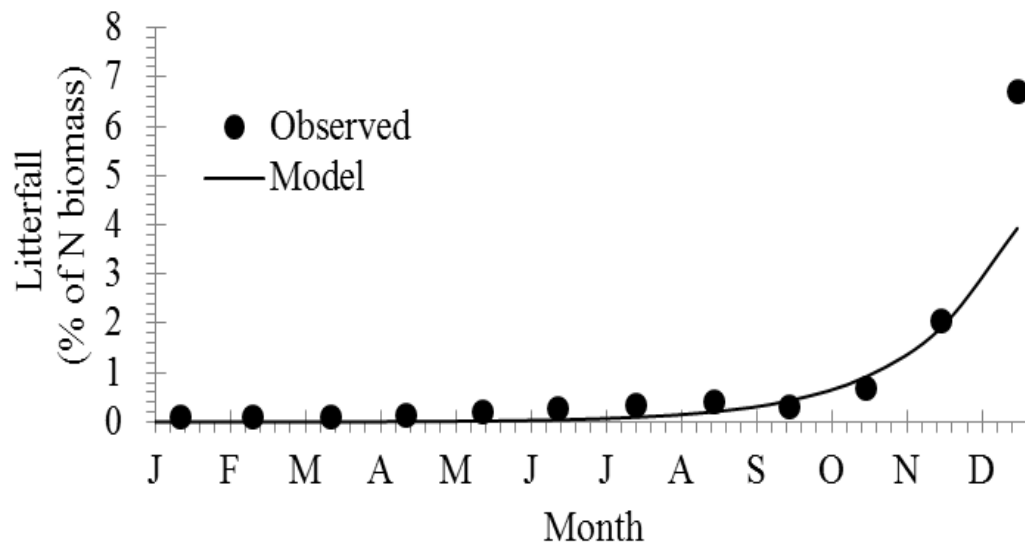


Figure 9. Percent of vegetation converted to litterfall on a given day in a southeastern Louisiana freshwater wetland, modified from Sasser and Gosselink, 1984, and modeled using equation (20).

Temperature Dependence

The rates of many biological processes are dependent upon the temperature at which they are performed (Shapley, 1924; Christopherson et al., 1973; Gillooly et al., 2001). This is especially true for the enzyme-based activities of soil microbiology (Burns and Dick, 2002). Typical biogeochemistry models use an Arrhenius equation to simulate the change in a biological rate for every 10 or 20 °C change in temperature (Q_{10} and Q_{20} , respectively). The model presented here however, uses laboratory observations of denitrification activity with varying temperatures (Rivera-Monroy, V.H., personal observations) as well as literature reports on the same relationship with nitrification (Jones and Hood, 1980), mineralization (De Neve et al., 2003), DNRA (Tomaszek and Gruca-Rokosz, 2007) volatilization (Valero and Mara, 2007) and decomposition (Carpenter and Adams, 1979) (Fig. 10; Eqs. 14,15,16,17,18 & 19). These reductions were applied to the ideal rate constant of the process as calibrated. To test the effect of temperature on removing nitrogen from the Mike Island ecosystem, all other environmental variables were held constant, while temperature exhibited its normal seasonal fluctuations, and the resulting removal efficiencies were compared.

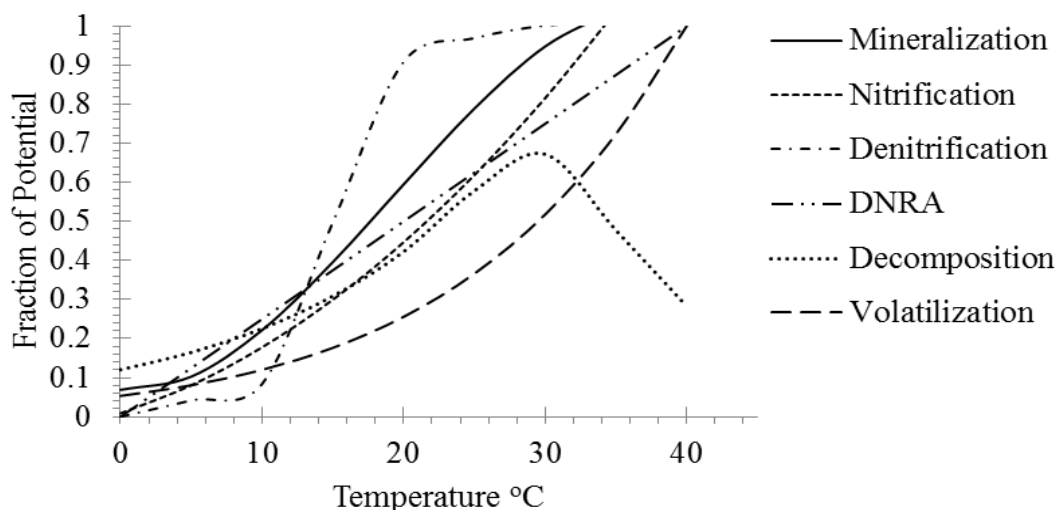


Figure 10. Modeled temperature effects on potential biogeochemical rates.

Vertical Flux Model

Wetland biogeochemistry is spatially distributed between soils and the overlying water. To distinguish wetland surface-water from soil pore-water and to represent the cycle in a vertical profile, the unit model (Fig. 2) is replicated and stacked in a series of vertical layers (Fig. 11).

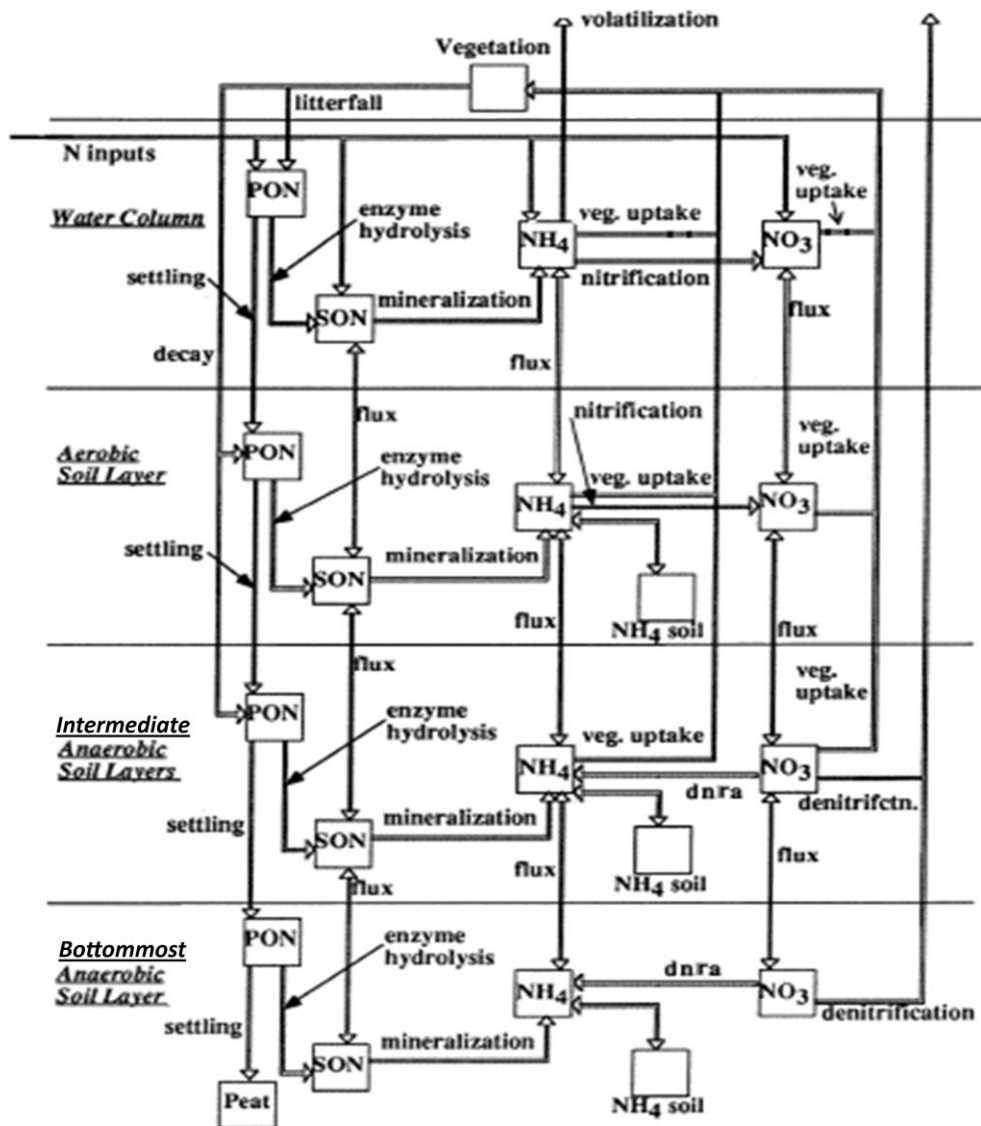


Figure 11. Vertical representation of the nitrogen cycle as modified from Martin and Reddy, 1997. Modifications include the addition of vegetation assimilation from the surface water, the addition of dissimilatory nitrate reduction to ammonium (DNRA), and dynamic layer numbers and depths.

Each layer represents a specific depth of soil or water with a specific combination of nitrogen processes. Ammonium volatilization, for instance, only occurs in the water layer and nitrification only occurs in layers that are aerobic. Additionally, denitrification and DNRA only occur in anaerobic layers, and vegetative assimilation only occurs in layers with leaves or roots. It is evident that the bottom layer in the series is incapable of transferring mass any lower. This allows the model to estimate the accumulated nitrogen mass as burial in peat.

The assemblage of these unit-models in vertical series results in a representation of the nitrogen cycle with soil depth referred to as the vertical flux model. This representation is unique in that the surface water is immobile, and it was used to simulate core incubation experiments in which soil cores from the study site were incubated in the laboratory and monitored for changes in surface water nitrogen concentrations.

Horizontal Flux Model

To accurately simulate nitrogen flux from upstream to downstream locations in a wetland ecosystem, a horizontal representation must also be incorporated to account for flow of surface water over wetland sediment. This was accomplished by replicating the vertical flux model into a spatial series of longitudinal wetland cells, and connecting the upper water layer of each cell. Surface water flow over a wetland ecosystem is simulated by allowing the contents of the water layer of an upstream cell to flow into the adjacent downstream cell. Soil layers do not communicate horizontally. Timing between the transfer of surface water contents from upstream to a downstream cell is controlled by freshwater residence time, which is determined by water flow rate and cell volume (Eq. 21). Volumetric flow rate in each cell is assumed to be constant throughout the model area.

Physical dimensions of the model area are represented by a three dimensional planar surface described by the quadric:

$$z = ax^2 + by^2 + cxy - dx - ey + f, \quad (21)$$

where z is the elevation at any given point described by the Cartesian coordinates, (x, y) .

The coefficients: a, b, c, d, e & f (0.000005, 0, 0, 0, 0.00022, 0.12) define the curvature of the surface along three axes. This surface is modeled after a Kriging interpolation of a collection of elevation measurements taken at the field site (Fig. 12), which represents an area 800 meters wide by 1000 meters long. The quadric surface allows for immediate calculation of depth at any given point and thus an average depth for any given section. This is necessary as the water volume of the basin changes according to the water elevation (Fig. 13). This representation also allows for changes to be made to the modeled area, as was necessary for later analyses.

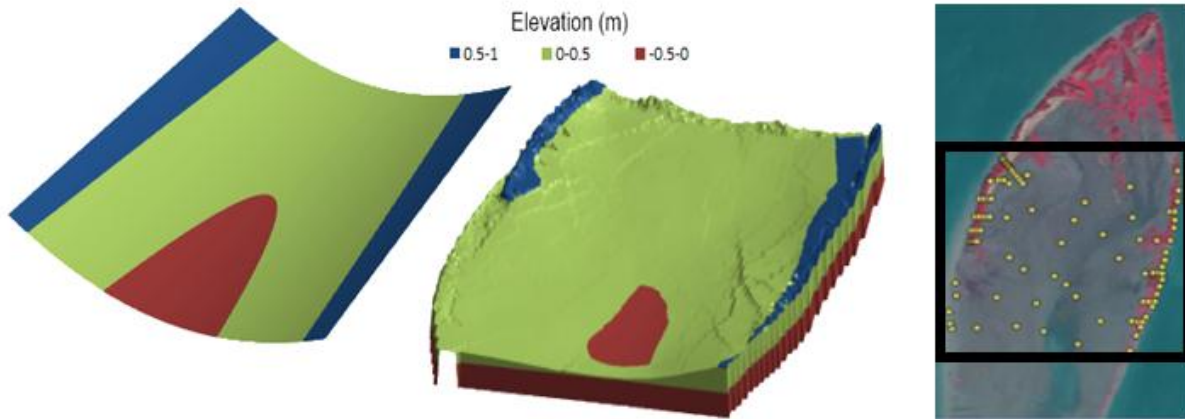


Figure 12. A quadric surface (left), represented by the general equation: $z = ax^2 + by^2 + cxy - dx - ey + f$, provides an approximation of the bathymetry and sub-aerial elevations of the study site for rapid assessment of site hydrology with changing water levels. In this representation $a = 0.000005$, $b = c = d = 0$, $e = -0.00022$ & $f = 0.12$. The quadric is modeled after a Kriging interpolation (center) of known elevations (right), in which the top left $(-400,0)$ and lower right $(400,1000)$ corners are represented by the coordinates $(29.510723, -91.444767)$ and $(29.501078, -91.439509)$, respectively.

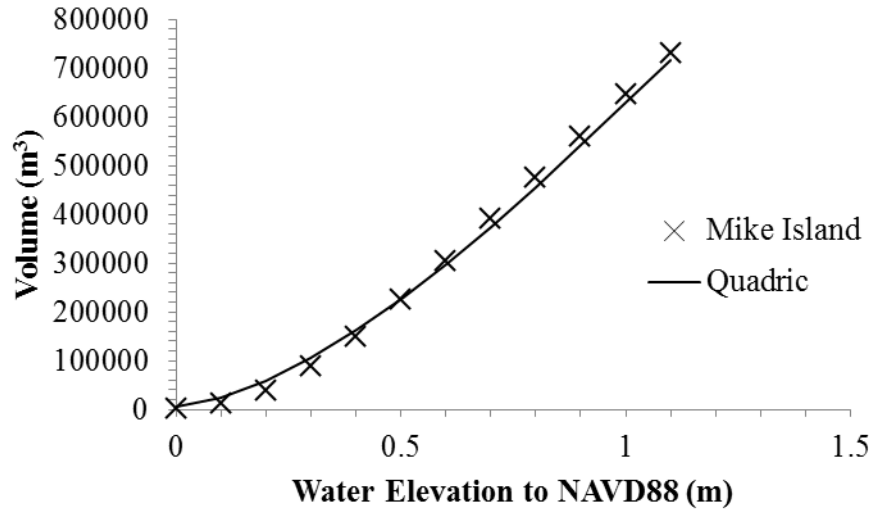


Figure 13. The quadric representation provides a significant approximation of the field site dimensions. As the water elevation of the Kriging interpolation and the quadric changes, the corresponding basin volumes match with an r^2 of 0.999.

To satisfy mass balance of surface water above the wetland landscape of Mike Island, each cell must be of equal volume. This ensures that as the residence time expires, the amount of water received by one cell is not more or less than the amount the cell currently holds. Therefore, the dimensions of each cell must be dynamic and capable of changing with water level. This is accomplished by finding the relationship between the cumulative volume of the modeled system and its length (Fig. 14). The second order polynomial of the form:

$$y = ax^2 + bx,$$

describes the relationship. However, the coefficients a & b will change as the water level changes. Therefore, separate relationships must be determined for coefficients and water levels (Fig. 15).

Knowing water elevation, the volume of the first cell of a given length can be determined by solving the above polynomial, with the cumulative volume as y , the cell's length as x and the

coefficients a & b determined from the polynomials shown in Fig. 15. The goal is to give every cell equal volume. Therefore, with the uniform cell volume determined, the length of the remaining cells is found by solving the polynomial for x via the quadratic equation.

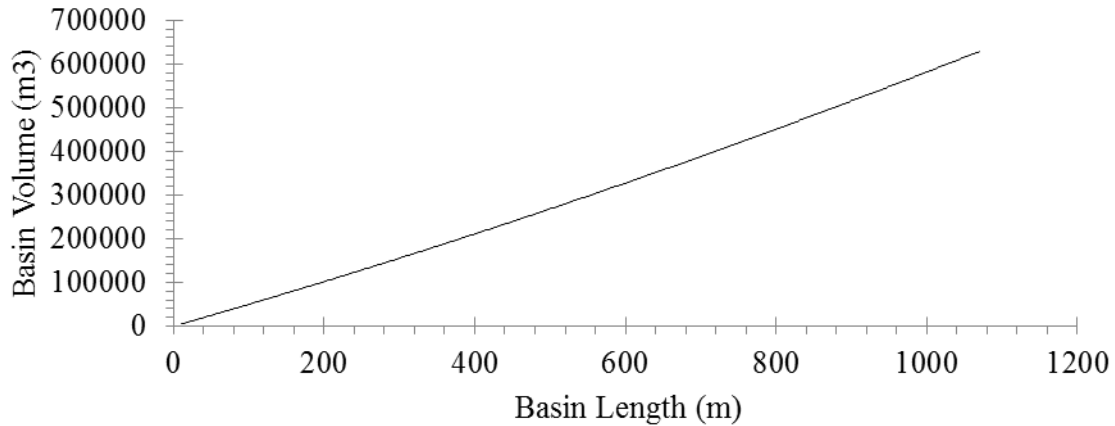


Figure 14 Quadric basin volume as a function of its length follows a second order polynomial. Cell lengths are determined by setting the first cell's length and then solving for the remaining cell lengths via the polynomial and the quadratic equation, such that each cell has an equal volume. This example shows the relationship when the water elevation is 0.5m, however the coefficients of the polynomial will change as the water elevation changes. These relationships are shown in figure 15.

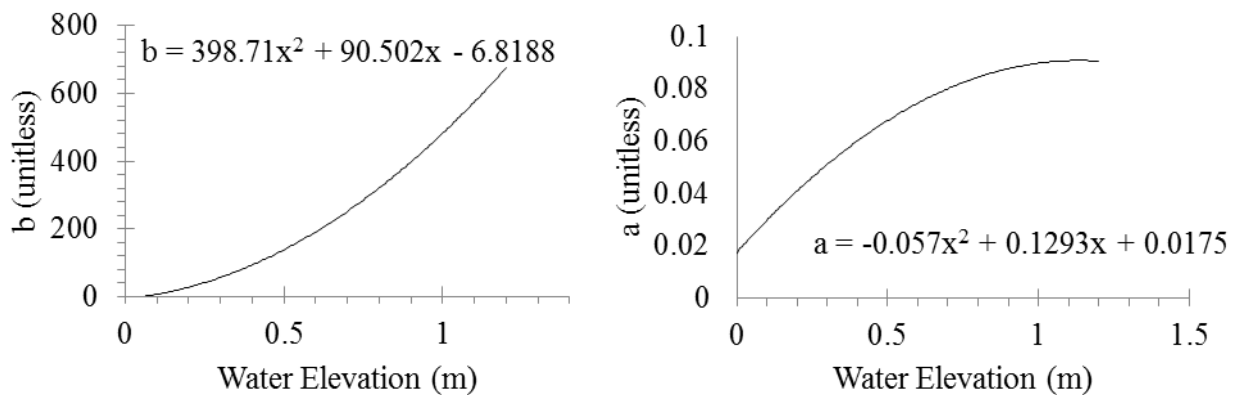


Figure 15 The coefficients for the polynomial shown in figure 14 will change as the water elevation changes according to the above relationships.

$$\text{Cumulative Volume} = a(\text{Cell Length}_n + \text{Cumulative Length}_{n-1})^2 + b(\text{Cell Length}_n + \text{Cumulative Length}_{n-1})$$

$$0 = a(\text{Cell Length}_n)^2 + 2a(\text{Cumulative Length}_{n-1} + b)(\text{Cell Length}_n) + b(\text{Cumulative Length}_{n-1}) + a(\text{Cumulative Length}_{n-1})^2 - \text{Cumulative Volume}$$

$$0 = Ax^2 + Bx + C$$

$$x = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

$$A = a$$

$$B = 2a(\text{Cumulative Length}_{n-1} + b)$$

$$C = b(\text{Cumulative Length}_{n-1}) + a(\text{Cumulative Length}_{n-1})^2 - \text{Cumulative Volume},$$

With the length of the first cell provided, the length of each downstream cell can be determined by systematically solving the above quadratic equation. Furthermore, as the water elevation changes, these cell dimensions can change accordingly to maintain proper basin and cell dimensions. The model performs these calculations for the initial user setup. If the water elevation changes during the run, the model will recalculate the cell dimensions to simultaneously maintain the original basin length as well as equal cell volumes.

Calculation Process

Each process in the nitrogen cycle is evaluated according to the governing equations and the required inputs. This results in a change in mass of nitrogen for the given time step. A step size of 0.01h^{-1} was determined to be the largest possible without altering results of the simulation, and was used throughout the modeling process. The change in storages for each layer and for each cell are then evaluated according to processes associated with storage in each

cell. This is represented by the following generalized sequence, which is repeated iteratively, increasing the time by the time step, dt, for each loop. Coding for the calculations can be found in the appendix.

For $t = 0$ to simulation duration

$$\Delta \text{Litterfall} = f_{\text{litterfall}} N_{\text{Plant biomass}} dt$$

for each horizontal cell

for each vertical layer, n

$$\Delta \text{Decay}_n = k_{\text{decay}} \cdot \text{Litterfall} \cdot dt$$

$$\Delta \text{Enzyme Hydrolysis}_n = k_{\text{enzyme hydrolysis}} \cdot N_{\text{PON}} \cdot dt$$

$$\Delta \text{Diffusion}_{\text{SON},n} = D_{\text{SON}} \cdot \frac{N_{\text{SON layer } n} - N_{\text{SON layer } n+1}}{d_x} \cdot dt$$

$$\Delta \text{Settling}_n = k_{\text{settle layer } n} \cdot N_{\text{PON}} \cdot dt$$

$$\Delta \text{Volatilization}_n = N_{\text{NH}_4} \cdot 5.8 \cdot 10^{\text{pH}-10} \cdot dt$$

$$\Delta \text{Mineralization}_n = k_{\text{mineralization}} \cdot N_{\text{SON}} \cdot dt$$

$$\Delta \text{Partition}_n = \left((k_{\text{partition}} \cdot N_{\text{NH}_4 \text{ sorbed}}) - N_{\text{NH}_4 \text{ soluble}} \right) \cdot \text{spectrate} \cdot dt$$

$$\Delta \text{Nitrification}_n = k_{\text{nitrification}} \cdot N_{\text{NH}_4} \cdot dt$$

$$\Delta \text{Diffusion}_{\text{NH}_4,n} = D_{\text{NH}_4} \cdot \frac{N_{\text{NH}_4 \text{ layer } n} - N_{\text{NH}_4 \text{ layer } n+1}}{d_x} \cdot dt$$

$$\Delta \text{DNRA}_n = k_{\text{DNRA}} \cdot N_{\text{NO}_3} \cdot dt$$

$$\Delta \text{Diffusion}_{\text{NO}_3,n} = D_{\text{NO}_3} \cdot \frac{N_{\text{NO}_3 \text{ layer } n} - N_{\text{NO}_3 \text{ layer } n+1}}{d_x} \cdot dt$$

$$\Delta \text{Denitrification}_n = k_{\text{denitrification}} \cdot N_{\text{NO}_3} \cdot dt$$

$$\Delta \text{veg uptake}_{\text{NO}_3,n} = N_{\text{demand}} \cdot \text{layerdepth}\%_n \cdot \frac{N_{\text{NO}_3}}{k_m + N_{\text{NO}_3}} \cdot \frac{N_{\text{NO}_3}}{N_{\text{NH}_4} + N_{\text{NO}_3}} \cdot dt$$

$$\Delta \text{veg uptake}_{\text{NH}_4,n} = N_{\text{demand}} \cdot \text{layerdepth}\%_n \cdot \frac{N_{\text{NH}_4}}{k_m + N_{\text{NH}_4}} \cdot \frac{N_{\text{NH}_4}}{N_{\text{NH}_4} + N_{\text{NO}_3}} \cdot dt$$

next layer

for each vertical layer, n

$$N_{\text{PON},n} = N_{\text{PON},n} + \Delta \text{Decay}_n - \Delta \text{Enzyme Hydrolysis}_n - \Delta \text{Settling}_n$$

$$N_{\text{SON},n} =$$

$$N_{\text{SON},n} + \Delta \text{Diffusion}_{\text{SON},n} - \Delta \text{Diffusion}_{\text{SON},n-1} +$$

$$\Delta \text{Enzyme Hydrolysis}_n - \Delta \text{Mineralization}_n$$

$$N_{\text{NH}_4 \text{ soluble},n} = N_{\text{NH}_4 \text{ soluble},n} + \Delta \text{Mineralization}_n +$$

$$\Delta \text{Diffusion}_{\text{NH}_4,n} - \Delta \text{Diffusion}_{\text{NH}_4,n-1} - \Delta \text{Nitrification}_n -$$

$$\Delta \text{Volatilization}_n + \Delta \text{DNRA}_n + \Delta \text{Partition}_n - \Delta \text{veg uptake}_{\text{NH}_4,n}$$

$$N_{\text{NH}_4 \text{ sorbed},n} = N_{\text{NH}_4 \text{ sorbed},n} - \Delta \text{Partition}_n$$

$$N_{NO_3,n} =$$

$$N_{NO_3,n} + \Delta Nitrification_n + \Delta Diffusion_{NO_3,n} - \Delta Diffusion_{NO_3,n-1} -$$

$$\Delta Denitrification_n - \Delta DNRA_n - \Delta veg\ uptake_{NO_3,n}$$

$$Plant\ biomass = plant\ biomass + \Delta veg\ uptake_{NO_3,n} + \Delta veg\ uptake_{NH_4,n}$$

next layer

next cell

$$Plant\ biomass = plant - \Delta Litterfall$$

$$Litterfall = Litterfall + \Delta Litterfall$$

$$t = t + time\ step$$

next t

In the vertical flux model, this process continues until the experimental duration is reached, at which point the simulation is stopped. Nutrient fluxes are determined by the slope of a regression of their surface water concentrations over time. Biogeochemical rates are determined by keeping track of the total amount of nitrogen treated by each process, in each layer.

The same is true for the horizontal flow model, however additional computations must be made to account for the flow of water over the wetland. When the time reaches a multiple of the residence time, the contents from each upstream water cell are transferred into the next downstream water cell. The most upstream water cell contents are determined by the input nitrogen concentration and the flow rate as the following example for nitrate:

$$NO_3 = NO_3\ input \left(\frac{\mu mol}{m^3} \right) \cdot input\ flow\ rate \left(\frac{m^3}{h} \right) \cdot residence\ time\ (h)$$

This calculation is done for each constituent of nitrogen and recorded for each loading incidence, to keep track of the total nitrogen loaded to the system. As each residence time expires, the contents of the most downstream cell leave the system. When initiating a

simulation, this process is allowed to repeat until enough time has passed to allow for water to completely flow through the entire longitudinal series of water cells. At this point, the model begins to keep track of total nitrogen that enters and leaves the system. It also begins to keep track of the processes for each layer, in each cell. These values, which are stored in the computer's memory, are used for various analyses once the simulation is complete. When a simulation experiment is complete, nitrogen inputs to the most upstream cell are stopped and water remaining in the cells is allowed to flow out of the simulated wetland. This ensures that a mass balance of all loaded nitrogen and its fate can be determined.

When a simulation run is complete, output of nitrogen concentrations are used to determine the fate of nitrogen in surface water as it moves across Mike Island. Multiple calculations are made to determine the nitrogen mass balance of the simulated deltaic wetland as well as average biogeochemical rates for an experiment. A mass balance is determined simply by summing all nitrogen storages in each cell of the simulated deltaic wetland as well as all exported nitrogen throughout the simulation, which is equal to the total nitrogen loaded as demonstrated in the following equation:

$$N_{loaded} = N_{exported} + \sum_{cell=1}^{cell\ number} N_{plant\ storage} + N_{soil\ storage} + N_{water\ storage}$$

The amount of nitrogen lost, or exported, from the deltaic wetland is defined by the cumulative nitrogen that was denitrified, volatilized in each cell or loaded downstream. Any remaining nitrogen is expected to remain in the system, primarily in soil and vegetation. The average biogeochemical rates for the deltaic wetland are determined by dividing the cumulative

nitrogen transformed by a process (sum for all the cells) by the total simulation area and simulation time. For instance, the average denitrification rate is determined by:

$$\text{Average Denitrification} = \frac{\text{Total N Denitrified } (\mu\text{mol})}{\text{Area } (\text{m}^2) \times \text{simulation time} (\text{h})}$$

The results of a simulation experiment and analyses are then displayed for interpretation.

Calibration and Validation

Calibration was accomplished by simulating laboratory incubations of sediment cores from Mike Island using the vertical flux representation of the model. A series of simulations were run using a combination of diffusion coefficients and rate constants from the literature (Table 2). Those parameters which best matched the observed core incubation results, would be considered for simulations in the horizontal flow model. A sensitivity analysis was then performed by observing the response in nutrient fluxes to changes in the rate constants and diffusion coefficients. Because the Wax Lake Delta nitrogen budget is comprised overwhelmingly of inorganic forms, only those diffusion coefficients and rate constants pertaining to inorganic nitrogen forms (NO_3^- and NH_4^+), were varied.

Soil cores were collected and processed by Dr. Edward Castañeda-Moya. The cores were taken in triplicates at the study site locations (Fig. 17), and brought back to an environmental growth chamber at Louisiana State University for processing. Cores were uniformly 10.3 cm in diameter with 10 cm of soil and an overlying water layer of 15-20 cm. The overlying water of the cores was dosed with nitrate and ammonium concentrations at time zero to mimic those concentrations measured in the field. The cores were then maintained at field site water temperatures and monitored regularly over a 24 h period for surface water nitrate, ammonium

and nitrogen gas fluxes. Nitrate and ammonium were recorded and measured from the overlying water colorimetrically using a Flow IV OI Analytical Autoanalyzer (Strickland and Parsons 1972; Parsons et al. 1984). Dissolved nitrogen gas in the water was measured via the MIMS method (Membrane Introduction Mass Spectrometry), using a Pfeiffer Prisma QME 200 quadrupole mass analyzer as based on the technique of Kana et al. (1994) and modified with a copper reduction column and furnace heated to 600°C (Eyre et al. 2002). Linear regressions were used to report the change in these compounds' concentrations over the course of the

Table 2. Model parameters calibrated for and tested in the sensitivity analysis. Parameter bounds were set by the literature values.

| | Min | Max | Mean | Source | |
|-------------------------|---|-----------------|-----------------|--------------------------|-------------------------------|
| DNRA (h ⁻¹) | Denitrification (h ⁻¹) | 0.00417 | 0.03542 | 0.01646 | Gale et al. (1983) |
| | | 0.00002 | 0.00100 | 0.00006 | Reddy et al. (1982) |
| | | 0.00100 | 0.04000 | 0.02050 | Stanford at al. (1975) |
| | | 0.10417 | 0.10417 | 0.10417 | Martin and Reddy (1997) |
| | | 0.15458 | 0.15458 | 0.15458 | Reddy and Rao (1983) |
| | | 0.00042 | 0.00042 | 0.00042 | Dettman (2001) |
| | | 0.00960 | 0.00960 | 0.00960 | Dincer and Kargi (2000) |
| | | 0.01313 | 0.02167 | 0.01740 | Reddy et al. (1980) |
| | | 0.00002 | 0.15458 | 0.02464 | All Sources |
| | Nitrification (h ⁻¹) | 0.01040 | 0.01040 | 0.01040 | Reddy and Rao (1983) |
| | | 0.00420 | 0.05000 | 0.02708 | Martin and Reddy (1997) |
| | | 0.00100 | 0.00230 | 0.00217 | Flowers and Ocallaghan (1983) |
| | | 0.04790 | 0.04790 | 0.04790 | Dincer and Kargi (2000) |
| | | 0.00104 | 0.05000 | 0.01494 | All Sources |
| | 0.00420 | 0.05210 | 0.02813 | Pett-Ridge et al. (2006) | |
| | NO ₃ Diffusion (m ² h ⁻¹) | 4.00E-08 | 8.08E-08 | 5.88E-08 | Reddy et al. (1980) |
| | | 1.80E-06 | 1.80E-05 | 1.80E-05 | Clark and Barley (1968) |
| | | 4.68E-08 | 4.68E-08 | 4.68E-08 | Patrick and Reddy (1976) |
| | | 4.00E-08 | 1.80E-05 | 3.34E-06 | All Sources |
| | NH ₄ Diffusion (m ² h ⁻¹) | 1.44E-10 | 1.08E-09 | 6.12E-10 | Clark and Barley (1968) |
| | | 2.46E-09 | 9.00E-09 | 5.73E-09 | Reddy et al. (1980) |
| | | 3.53E-08 | 3.53E-08 | 3.53E-08 | Krom and Berner (1980) |
| | | 1.44E-10 | 3.53E-08 | 9.59E-09 | All Sources |

experiment. Fluxes were calculated by taking the slope of these regressions over the area of the core.

In validation, calibrated parameters were used in the horizontal flux model to simulate ecosystem biogeochemistry. The results were then compared to observations of surface and pore water concentrations at Mike Island. Surface and pore-water samples were managed by Azure Bevington and collected by various individuals, including myself, at various times throughout the year (Fig. 16). Surface water was collected by submerging scintillation vials to no more than 10 cm below the surface. Pore-water was collected by drawing water from a glass pipette, which was submerged at 2 and 10 cm below the sediment-water interface. All samples were collected in triplicate and stored on ice until laboratory processing.

Pore water equilibrators (peepers; Hesslein, 1976) were used to determine the pore water profiles, or the concentrations of nitrate and ammonium with soil depth up to 20 cm. Peepers were deployed at the same time of the core extractions (Fig. 18). They were allowed to equilibrate for one week before the internal water samples were extracted and taken back to the lab. Nitrate and ammonium were measured colorimetrically using a Flow IV OI Analytical Autoanalyzer (Strickland and Parsons 1972; Parsons et al. 1984).

Volumetric flow rate of the system was estimated by assuming that the flow rate was constant throughout the area and that it was equal to that of the input flow rate through the tidal creek. The flow rate of the tidal creek was estimated through the use of a SonTek Argonaut acoustic doppler velocimeter (ADV) and a SonTek FlowTracker handheld ADV. The instrument was allowed to record the flow velocity at a point of roughly 60% of the creek's depth for a period of one month (April 19th – May 21st, 2012). This velocity was then

extrapolated across the channel according to the velocity relationship determined with the FlowTracker at multiple locations along the channel cross-section. A channel profile was taken at the point of these velocity measurements to determine the cross-sectional area (figure 19). The channel volumetric flow rate was calculated by multiplying the measured or extrapolated velocities by the respective cross-sectional areas (Fig. 7).

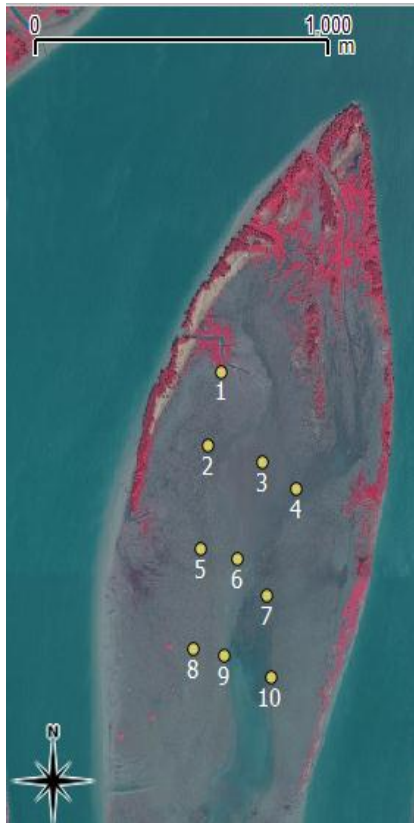


Figure 16. Surface and pore-water collection sites on Mike Island.

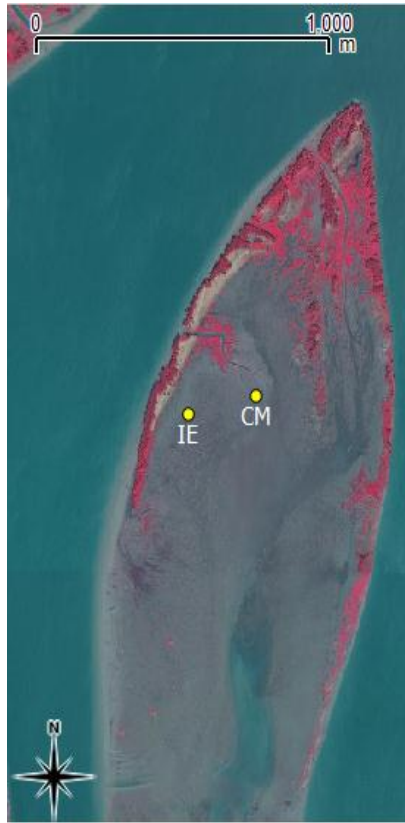


Figure 17. Sediment core collection sites.
CM = Creek Mouth, IE = Island



Figure 18. Sediment pore water peeper sites.

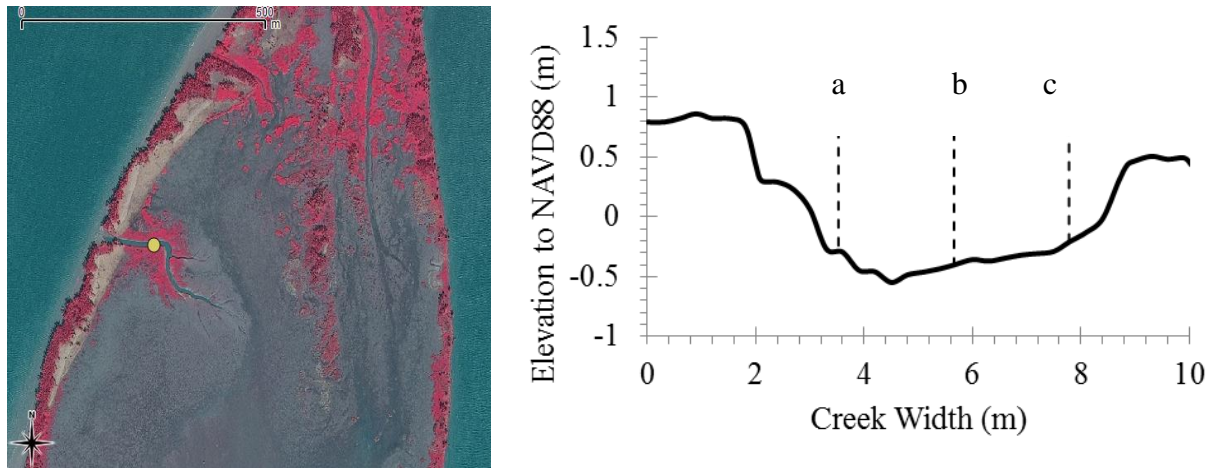


Figure 19. Site of the flow measurements taken in the tidal creek and a depth profile of the creek at that point. The Argonaut long term ADV was deployed at site C, while handheld measurements of current velocity were taken at points a, b and c with the FlowTracker ADV.

RESULTS

Sensitivity Analysis

After bounding the rate constants for nitrification, denitrification, DNRA, and the diffusion coefficients for nitrate and ammonium, a sensitivity analysis was run to determine the effect of each parameter on the flux of nutrients within core incubation simulations (Table 3).

Table 3. Results of the sensitivity analysis, in which the nitrification (nit.), denitrification (denit.), dissimilatory nitrate reduction to ammonium (DNRA), NO_3^- diffusion, and NH_4^+ diffusion parameters were varied according to bounds set by the literature. Sensitivity units are $\frac{\mu\text{mol m}^{-2} \text{h}^{-1}}{\text{h}^{-1}}$, for nitrification, denitrification and DNRA, and $\frac{\mu\text{mol m}^{-2} \text{h}^{-1}}{\text{m}^2 \text{h}^{-1}}$, for the diffusion coefficients.

| | Rate | NO_3^- Flux $\mu\text{mol m}^{-2} \text{h}^{-1}$ | NH_4^+ Flux $\mu\text{mol m}^{-2} \text{h}^{-1}$ | N_2 Flux $\mu\text{mol m}^{-2} \text{h}^{-1}$ |
|--|--------------|--|--|---|
| Nit. h^{-1} | 0.001 | -9.45 | -3.08 | 15.29 |
| | 0.0255 | 0.23 | -12.14 | 15.32 |
| | 0.05 | 7.63 | -18.97 | 15.36 |
| | Sensitivity: | 348.55 | -342.22 | 1.39 |
| Denit. h^{-1} | 0.00002 | -3.25 | -8.54 | 0.02 |
| | 0.0773 | -4.20 | -8.54 | 32.26 |
| | 0.15458 | -4.71 | -8.54 | 41.84 |
| | Sensitivity: | -9.44 | 0.00 | 270.57 |
| DNRA h^{-1} | 0.0041667 | -3.26 | -8.54 | 19.04 |
| | 0.028125 | -3.63 | -8.54 | 15.31 |
| | 0.0520833 | -3.92 | -8.54 | 12.61 |
| | Sensitivity: | -13.94 | 0.00 | -134.06 |
| NO_3^- Diff. $\text{m}^2 \text{h}^{-1}$ | 4E-08 | 6.01 | -8.54 | 12.57 |
| | 9.02E-06 | -22.79 | -8.54 | 19.28 |
| | 0.000018 | -47.90 | -8.54 | 24.53 |
| | Sensitivity: | -3000000.00 | 0.00 | 665724.00 |
| NH_4^+ Diff. $\text{m}^2 \text{h}^{-1}$ | 1.44E-10 | -3.63 | -8.55 | 15.31 |
| | 1.771E-08 | -3.63 | -8.53 | 15.31 |
| | 3.528E-08 | -3.63 | -8.51 | 15.31 |
| | Sensitivity: | 0.00 | 1000000.00 | 0.00 |

Results from the sensitivity analysis show that, of the first order rate constants, nitrification has the greatest influence on nitrogen fluxes, changing the flux of nitrate, ammonium, and nitrogen gas by 349, -342, and $1.39 \mu\text{mol m}^{-2} \text{h}^{-1}$, respectively, for every h^{-1} change in the constant. Neither the denitrification nor DNRA rate constants had any effect on the flux of ammonium, however, DNRA showed to be comparable to denitrification in influencing the flux of nitrate from overlying water. Nitrate and ammonium diffusion constants expressed relatively equal, but opposite, effects on fluxes. Nitrate diffusion did not affect ammonium flux and vice-a-versa, but nitrate diffusion affected nitrate flux by $-3000000 \mu\text{mol m}^{-2} \text{h}^{-1}$ for every $\text{m}^2 \text{h}^{-1}$ change in the coefficient, and ammonium diffusion affected ammonium flux by $1000000 \mu\text{mol m}^{-2} \text{h}^{-1}$ for every $\text{m}^2 \text{h}^{-1}$ change in the coefficient.

Calibration and Validation

Calibration

Calibration was done by determining model parameters of nitrification, denitrification, DNRA, nitrate diffusion and ammonium diffusion, which resulted in the best match between model outputs and observations of soil core incubation experiments. All other values were taken from the previous Martin and Reddy (1997) report. The vertical flux model simulates the core incubation experiments by mimicking the physical dimensions of each core as well as initial nitrogen concentrations and incubation duration. Linear regressions were performed on simulated water concentrations to calculate benthic fluxes, just as was done in the actual core incubations. Core benthic fluxes were determined for these vertical flux simulations by taking the slope of these regressions for nitrogen concentrations over the area of the virtual core, resulting in flux units of $\mu\text{mol m}^{-2} \text{h}^{-1}$. Rate constants and diffusion coefficients were optimized

to find a consistent set that most accurately matched observed values of all cores (Table 4). This assumes that soil parameters do not change from core to core or from month to month. The only values that were changed within the core simulations were water temperature and initial nitrogen concentrations.

Table 4. Model parameters optimized in the core incubation simulations. These rate constants were used in the ecosystem simulations along with other parameters unique to Mike Island. (Min = mineralization, Nit. = nitrification, Denit. = denitrification, DNRA = dissimilatory nitrate reduction to ammonium).

| | Enzyme Hydrolysis | Rate Constants (h^{-1}) | | | | Depth (cm) |
|-------------|-------------------|------------------------------------|-------|--------|------|------------|
| | | Min. | Nit. | Denit. | DNRA | |
| Water | 0.00001 | 0.008 | 0.001 | 0 | 0 | 18 |
| Aerobic | 0.00001 | 0.008 | 0.001 | 0 | 0 | 1 |
| Anaerobic 1 | 0.00001 | 0.008 | 0 | 0.155 | 0.05 | 2 |
| Anaerobic 2 | 0.00001 | 0.008 | 0 | 0.155 | 0.05 | 2 |
| Anaerobic 3 | 0.00001 | 0.008 | 0 | 0.155 | 0.05 | 2 |
| Anaerobic 4 | 0.00001 | 0.008 | 0 | 0.155 | 0.05 | 2 |
| Anaerobic 5 | 0.00001 | 0.008 | 0 | 0.155 | 0.05 | 2 |

Enzyme hydrolysis and mineralization were modeled with the first order rate constants of $1 \times 10^{-5} \text{ h}^{-1}$ and 0.008 h^{-1} , respectively, within all water and soil layers. Nitrification was modeled in the aerobic layers only with a rate constant of 0.001 h^{-1} . Denitrification and dissimilatory nitrate reduction to ammonium were simulated in the anaerobic layers only with rate constants of 0.155 h^{-1} and 0.05 h^{-1} , respectively. Diffusion of the soluble organic nitrogen, ammonium and nitrate were simulated using molecular coefficients of 1×10^{-6} , 3.5×10^{-8} and $1.8 \times 10^{-5} \text{ m}^2 \text{ h}^{-1}$, respectively (Table 5). Vegetation dynamics within the cores were not modeled, under the assumption that no photosynthetic organisms were active.

The average nitrate flux across all observed and simulated cores was -178 ± 30 and $-58 \mu\text{mol m}^{-2} \text{h}^{-1}$, respectively (Figs. 20,21, 22 & 23; Table 6). Ammonium fluxes were 139 ± 96 and -8 , and di- nitrogen gas fluxes were 62 ± 19 and $81 \mu\text{mol m}^{-2} \text{h}^{-1}$ for observed and simulated cores respectively. Average nitrification, denitrification and DNRA rates across all core simulations were 1.00, 81.02 and $16.20 \mu\text{mol m}^{-2} \text{h}^{-1}$, respectively (Table 7).

Table 5. Additional model parameters used in the core incubation simulations.

| | | |
|--------------------------|----------|---|
| SON Diffusion, D_{SON} | 1.00E-06 | m^2/h |
| NH4 Diffusion, D_{NH4} | 3.50E-08 | m^2/h |
| NO3 Diffusion, D_{NO3} | 1.80E-05 | m^2/h |
| pH | 6.7 | |
| NH4 Partition Spectrate | 1.37 | $\frac{\text{gNH}_4 \text{ soluble}}{\text{g NH}_4 \text{ sorbed}}$ |
| PON Water Settling | 0.04 | h^{-1} |
| PON Aerobic Settling | 4.24E-04 | h^{-1} |
| PON Soil Settling | 2.1E-06 | h^{-1} |
| Core Diameter | 10.3 | cm |
| Time Step | 0.01 | h |
| Tmax | 21.5 | h |

Table 6. Observed and modeled fluxes for the core incubations experiments. All values are in $\mu\text{mol m}^{-2} \text{h}^{-1}$. Oct. = October, Dec. = December, Apr. = April, Jul. = July, CM = Creek Mouth and IE = Island Edge (Fig. 17).

| | Observed NO3 | | | Model NO3 | | | Observed NH4 | | | Model NH4 | | | Observed N2 | | | Model N2 | | |
|--------|-----------------|-------|----|--------------|--|--|-----------------|-------|-----|--------------|--|--|----------------|-------|----|-------------|--|--|
| Oct CM | -207 | \pm | 14 | -48 | | | 492 | \pm | 259 | -9 | | | 0 | \pm | 0 | 80 | | |
| Oct IE | -274 | \pm | 36 | -47 | | | 278 | \pm | 247 | -9 | | | 0 | \pm | 0 | 79 | | |
| Dec CM | -75 | \pm | 32 | -35 | | | 221 | \pm | 135 | -12 | | | 61 | \pm | 6 | 44 | | |
| Dec IE | -164 | \pm | 13 | -37 | | | 34 | \pm | 34 | -22 | | | 102 | \pm | 35 | 44 | | |
| Apr CM | -167 | \pm | 17 | -78 | | | -2 | \pm | 14 | -2 | | | 103 | \pm | 22 | 86 | | |
| Apr IE | -215 | \pm | 47 | -77 | | | 71 | \pm | 25 | -2 | | | 145 | \pm | 69 | 86 | | |
| Jul CM | -116 | \pm | 31 | -73 | | | 21 | \pm | 21 | -2 | | | 48 | \pm | 14 | 115 | | |
| Jul IE | -203 | \pm | 49 | -72 | | | -6 | \pm | 34 | -3 | | | 34 | \pm | 4 | 114 | | |
| Mean | -178 | \pm | 30 | -58 | | | 139 | \pm | 96 | -8 | | | 62 | \pm | 19 | 81 | | |

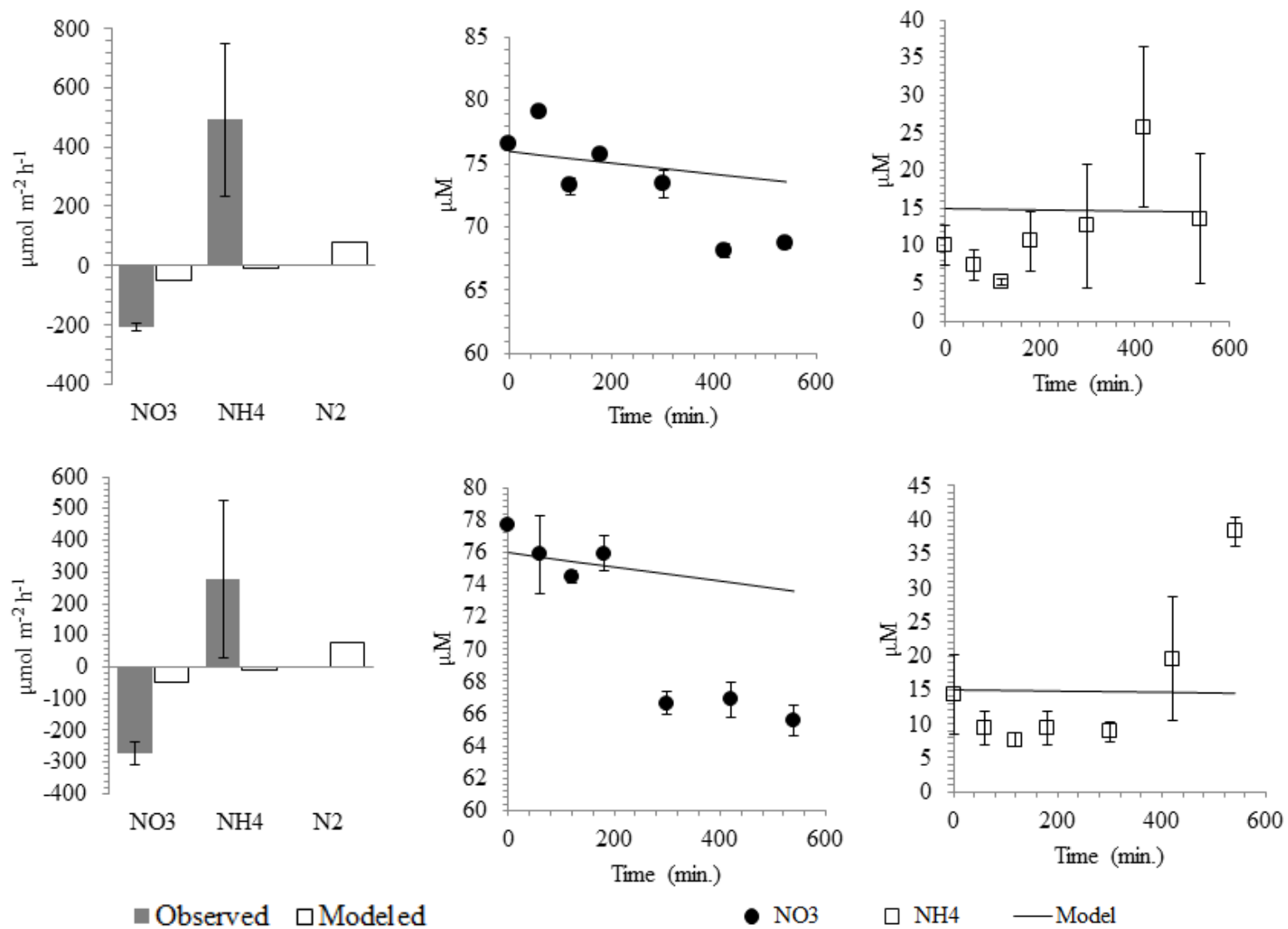


Figure 20. Observed and modeled results of the October, 2010 core incubation experiments at creek mouth (top) and island edge (bottom) (Fig.17). Fluxes (left), were obtained by taking the slope of the concentrations over time (right).

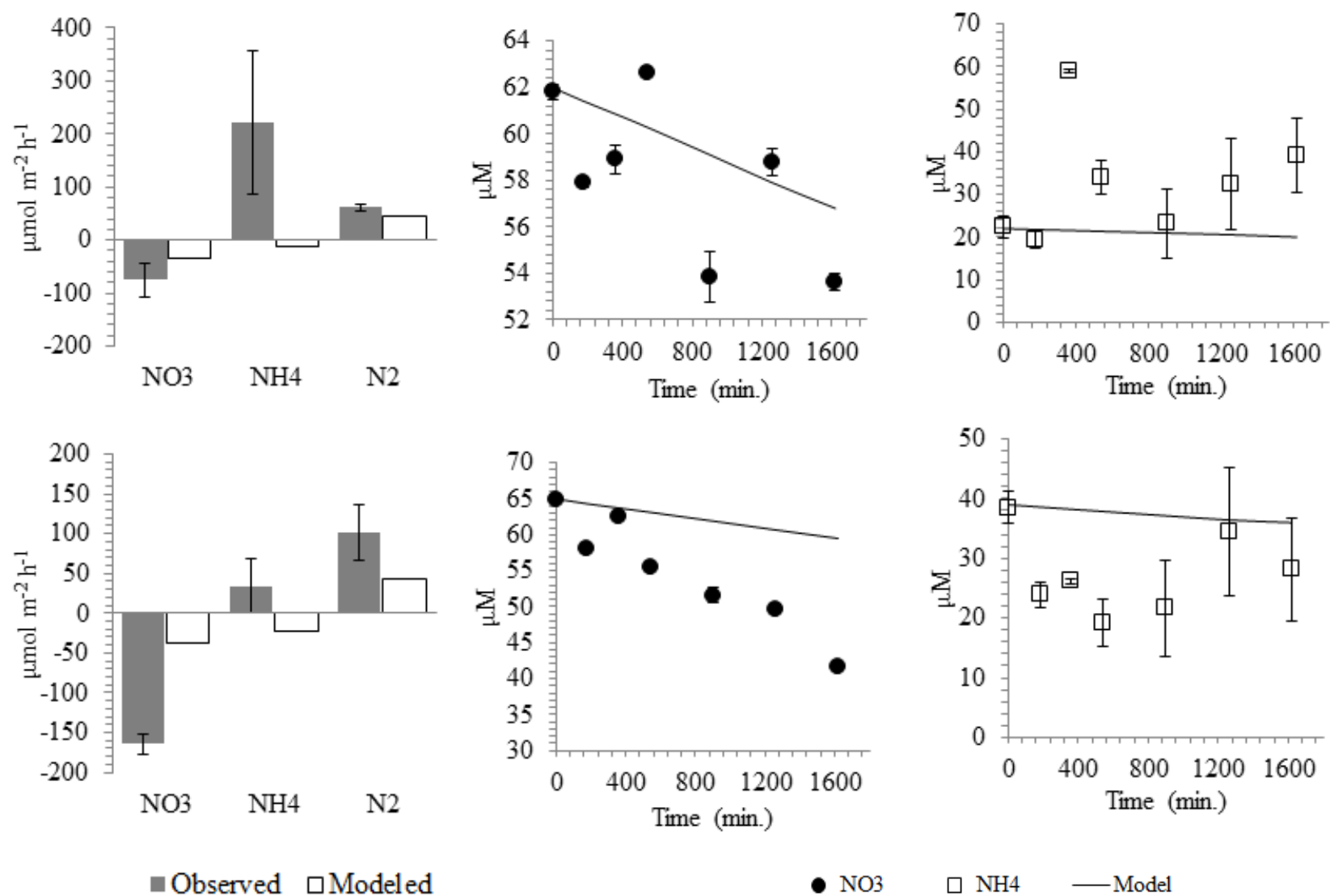


Figure 21. Observed and modeled results of the December, 2010 core incubation experiments at the creek mouth (top) and island edge (bottom) (Fig.17). Fluxes (left), were obtained by taking the slope of the concentrations over time (right).

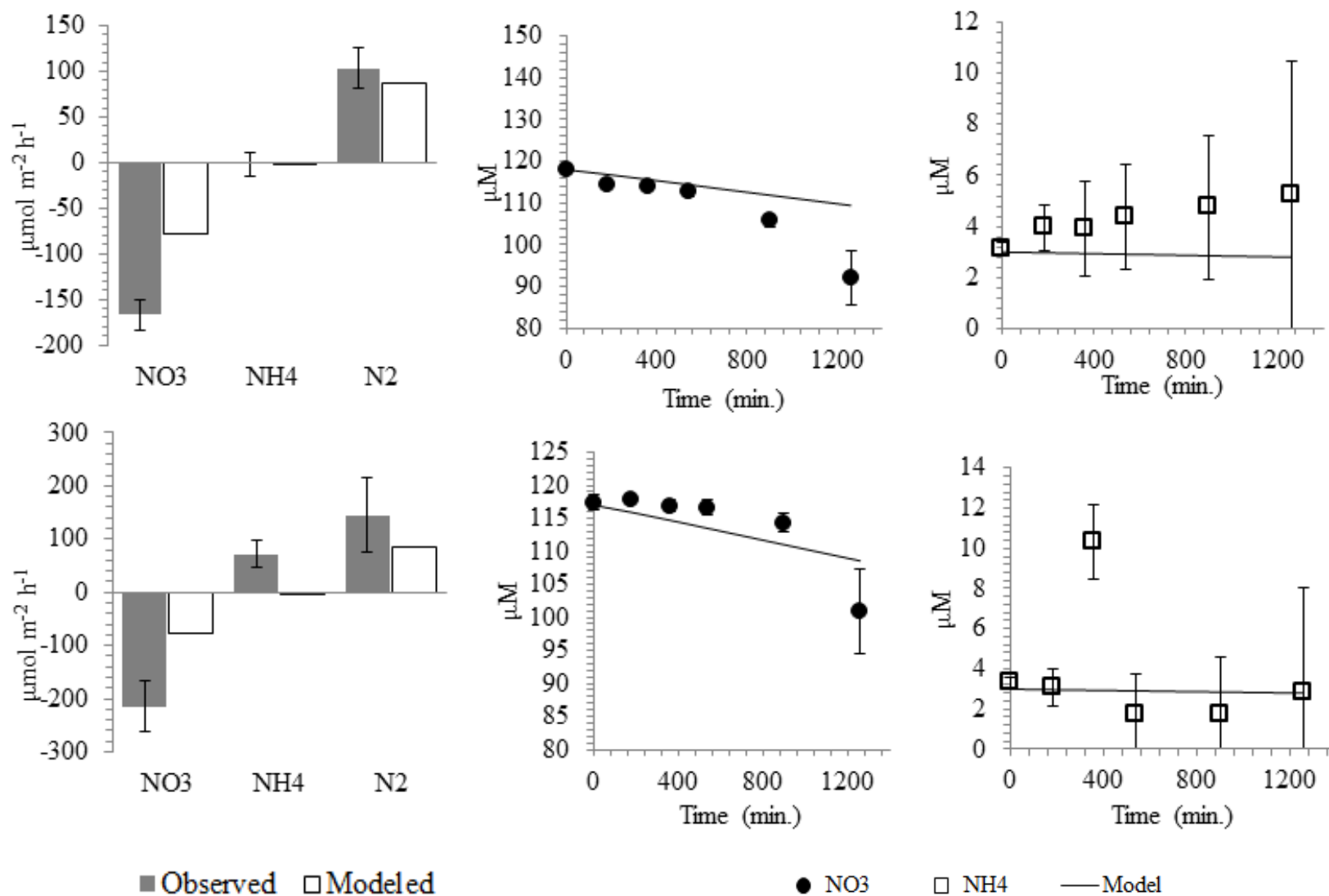


Figure 22. Observed and modeled results of April, 2011 core incubation experiments at the creek mouth (top) and island edge (bottom) (Fig.17). Fluxes (left), were obtained by taking the slope of the concentrations over time (right).

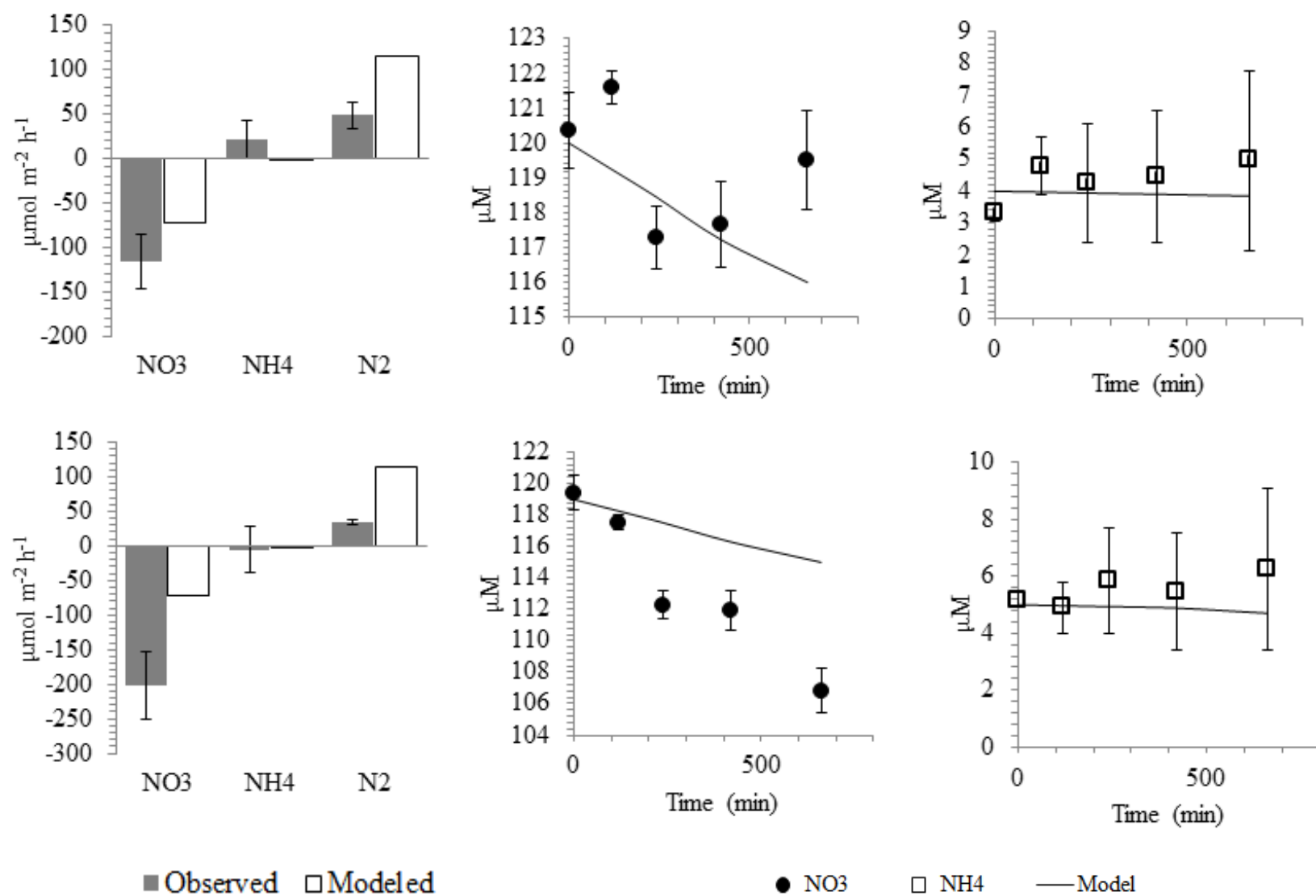


Figure 23. Observed and modeled results of July, 2011 core incubation experiments at the creek mouth (top) and island edge (bottom) (Fig.17). Fluxes (left), were obtained by taking the slope of the concentrations over time (right).

Table 7. Calculated rates resulting in the simulated fluxes shown in Table 6. All values are in $\mu\text{mol m}^{-2}\text{h}^{-1}$.

| | Nitrification | Denitrification | DNRA |
|--------|---------------|-----------------|-------|
| Oct CM | 1.52 | 79.68 | 16.06 |
| Oct IE | 1.52 | 79.26 | 15.98 |
| Dec CM | 1.23 | 43.82 | 9.75 |
| Dec IE | 2.18 | 44.14 | 10.15 |
| Apr CM | 0.30 | 86.30 | 15.77 |
| Apr IE | 0.30 | 85.90 | 15.70 |
| Jul CM | 0.42 | 114.67 | 23.11 |
| Jul IE | 0.52 | 114.40 | 23.06 |
| Mean | 1.00 | 81.02 | 16.20 |

Validation

Validation was accomplished through two separate comparisons of model results with published data and observations. In the first, a rate constant of 0.3 mo^{-1} or 0.00042h^{-1} was used for the denitrification and DNRA processes to simulate a scenario similar to that reported by Dettman, 2002. Input flow rates were then varied to produce an array of residence times and corresponding nitrogen export efficiencies also comparable to those reported by Dettman, 2002. In the second comparison, calibrated inputs from the core incubation simulations were used on the horizontal flux model, and the results of surface- and pore-water nitrogen concentrations were compared to those observed at Mike Island. In these simulations, input surface water nitrogen concentrations were set to match those observed at the creek mouth, and the model was allowed to operate for a thirty day period using the parameters from the calibration (Tables 4 & 5), as well as previously described seasonal inputs from the month of observations.

Results from the validation show the model performing well when compared to literature reports and observations made at Mike Island. Model results compare well to the same

relationships reported by Dettmann, 2002 using the same first order rate constant (Fig. 24). Similarly, surface water nitrogen concentrations in March (Fig. 25), and soil pore water nitrogen profiles from April (Fig. 26), show good fit between simulation results and field results of spatial and temporal nitrogen gradients. These results confirmed the model's accuracy in capturing fundamental nitrogen biogeochemistry within the field site and as compared to other estuarine systems.

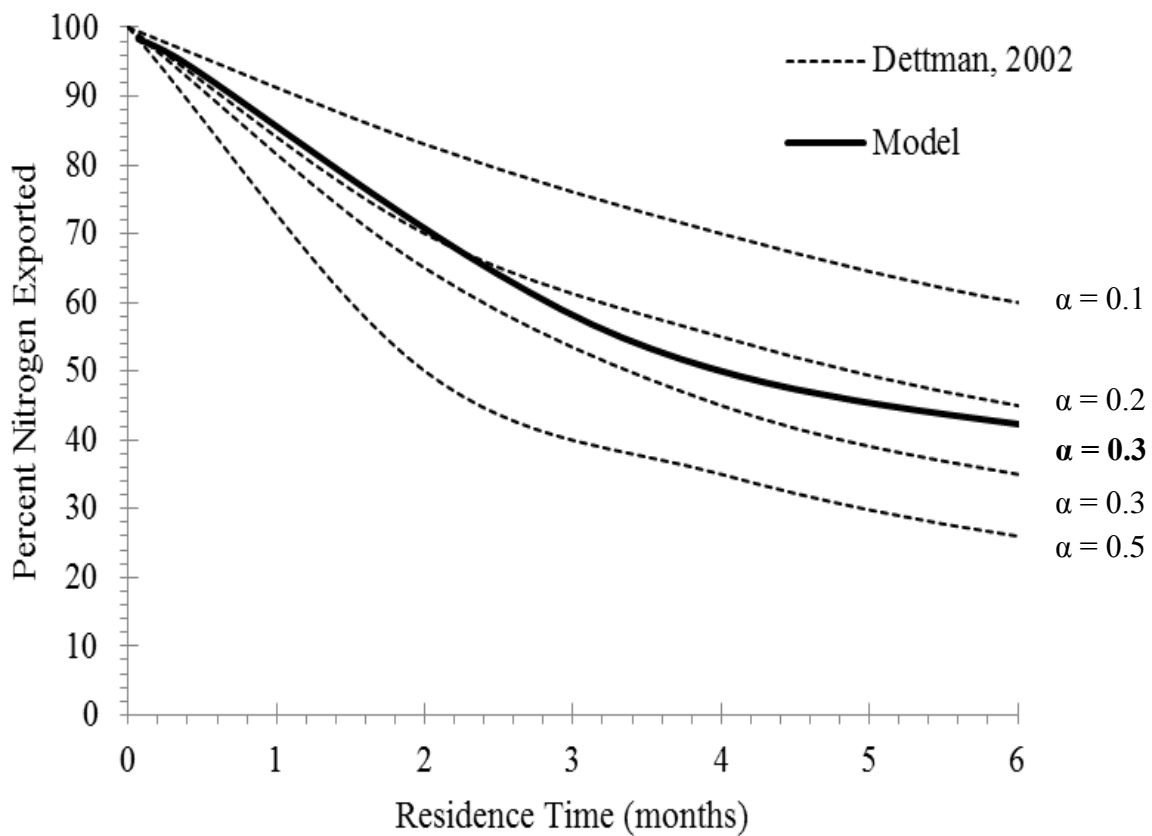


Fig. 24. Validation of the model against reports by Dettmann, 2002. A first order rate constant of 0.3 mo^{-1} or 0.00042h^{-1} was used for denitrification and DNRA, and the input flow rate was varied to produce an array of residence times. The result is a relationship between residence time and the percent of nitrogen exported downstream.

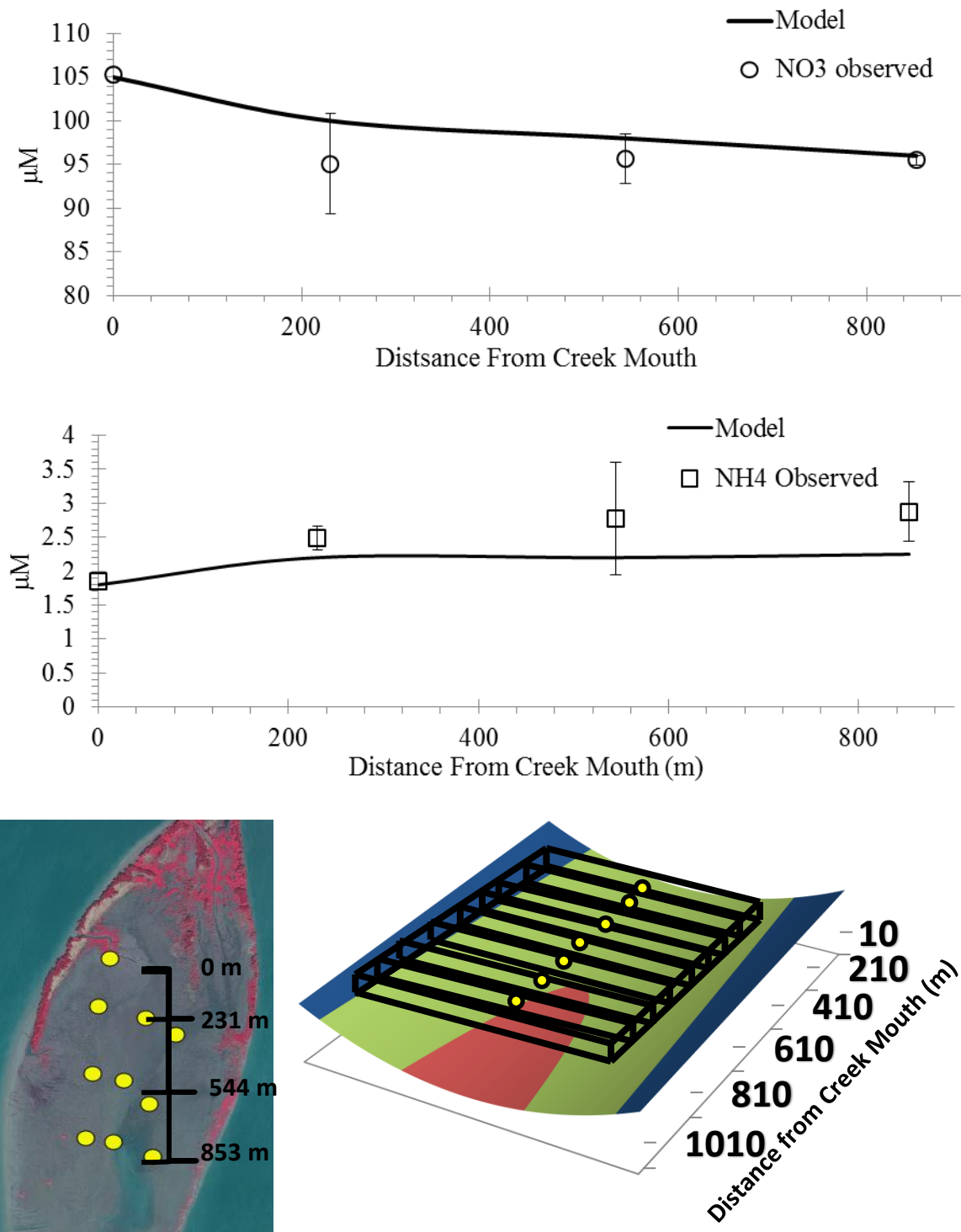


Figure 25. Observed and modeled surface water nitrate and ammonium concentrations for March (above), taken as an average of observations made at the field sites shown at bottom left and within the corresponding cells shown at bottom right.

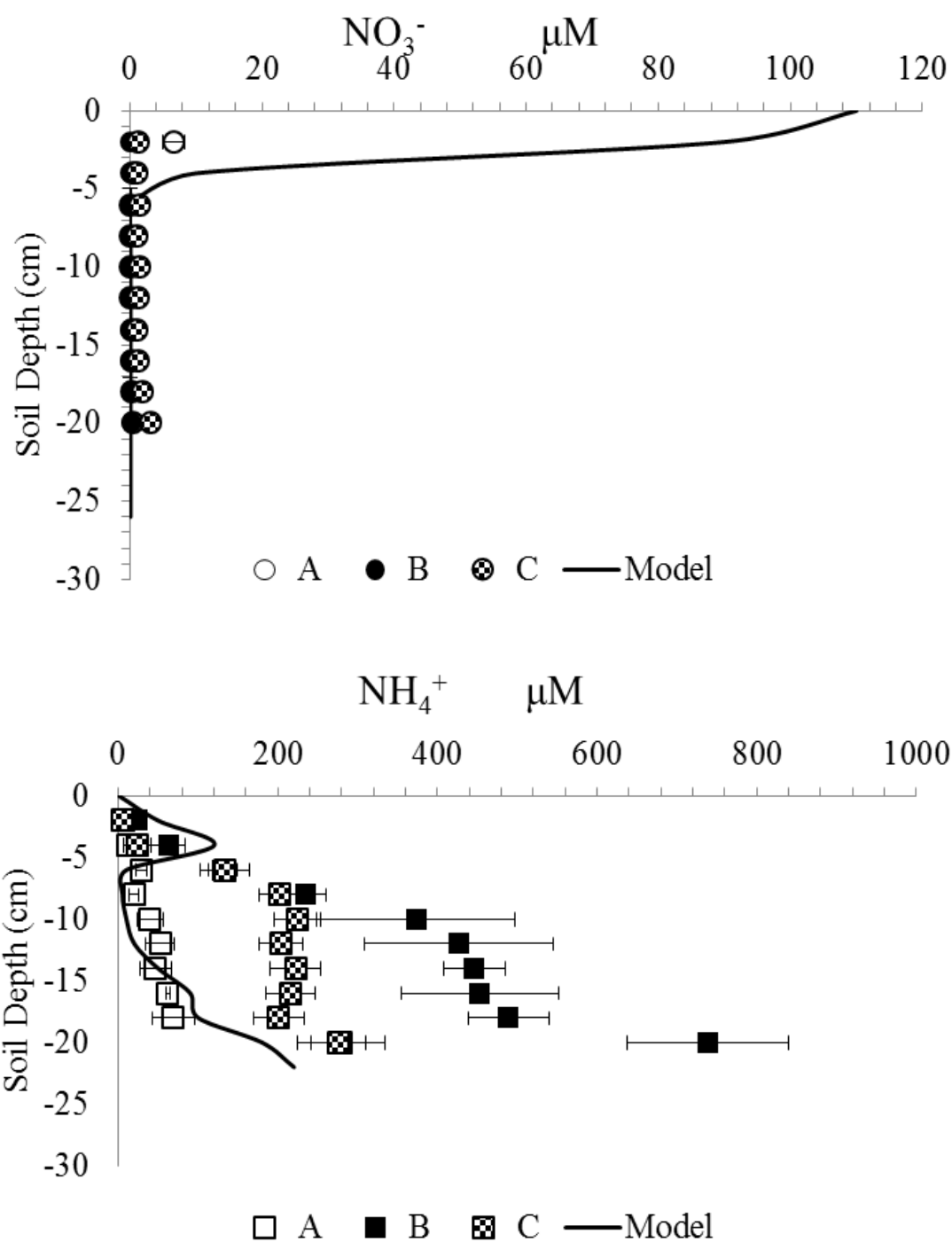


Figure 26. Soil profiles of NO_3^- and NH_4^+ concentrations as measured via the pore water equilibrators at sites A, B and C (Fig. 18), and as modeled for the month of April.

Mike Island Annual Simulations

Once calibrated, the model was run through a one year simulation using the parameters in Tables 4 and 5, and the previously described seasonal inputs. Denitrification expressed the largest instantaneous rate of $49.6 \mu\text{mol m}^{-2}\text{h}^{-1}$, with vegetation uptake, DNRA, and nitrification expressing maximum instantaneous rates of 26.5, 17, and $0.6 \mu\text{mol m}^{-2}\text{h}^{-1}$, respectively (Fig 27, Table 8). As annual averages, denitrification also expressed the largest rate of $31.6 \mu\text{mol m}^{-2}\text{h}^{-1}$, with DNRA, vegetation uptake, and nitrification expressing rates of 9.6, 7.7, and $0.3 \mu\text{mol m}^{-2}\text{h}^{-1}$, respectively. The month of May showed the greatest biogeochemical activity, with a combined nitrification, denitrification, DNRA, and vegetation processing rate of $85.8 \mu\text{mol m}^{-2}\text{h}^{-1}$. December showed the lowest biogeochemical rates, with a combined rate of $21.9 \mu\text{mol m}^{-2}\text{h}^{-1}$. May also expressed the largest percent of maximum rates, at 77% and January showed the lowest percent of maximum rates at 27%. Nitrification reached its maximum in September, denitrification in May, DNRA in February and vegetation uptake in May.

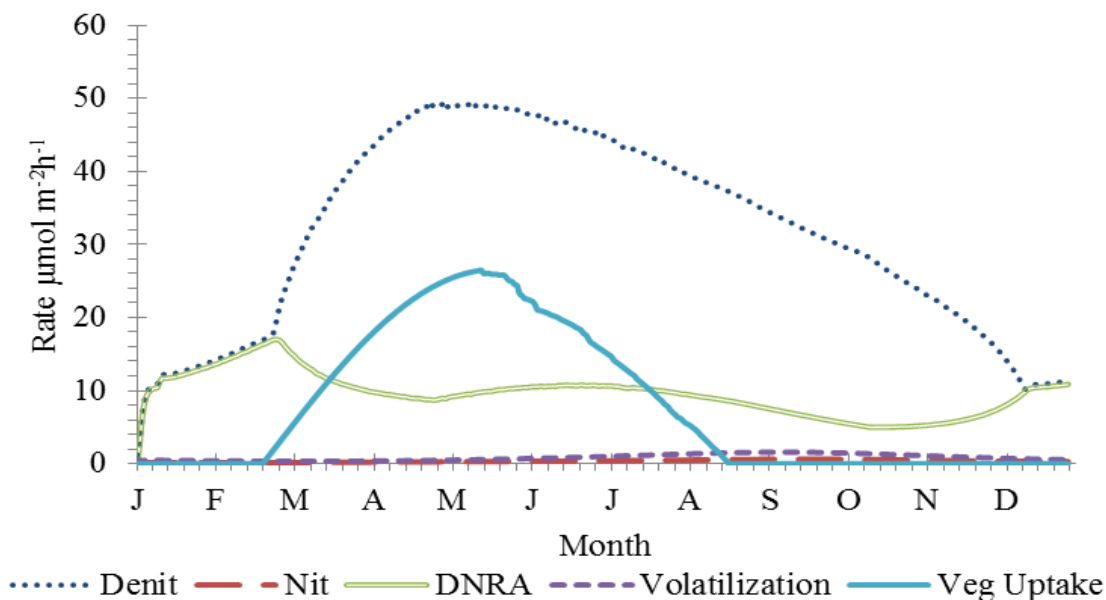


Figure 27. Daily biogeochemical rates simulated throughout the year

Table 8. Summary of the daily biogeochemical rates displayed in figure 27 as monthly means of the mass transfer rates as well as the percentage of the maximum attained rate.

| | Nitrification | | Denitrification | | DNRA | | Veg Uptake | | | |
|------|-------------------------|-------|-------------------------|-------|-------------------------|-------|-------------------------|-------|--------------|---------------|
| | $\frac{\mu mol}{m^2 h}$ | % Max | $\frac{\mu mol}{m^2 h}$ | % Max | $\frac{\mu mol}{m^2 h}$ | % Max | $\frac{\mu mol}{m^2 h}$ | % Max | | |
| Max | 0.6 | 100% | 49.6 | 100% | 17.0 | 100% | 26.5 | 100% | | |
| Min | 0.1 | 19.2% | 0.0 | 0.0% | 0.0 | 0.0% | 0.0 | 0.0% | Sum of Rates | Mean of % Max |
| J | 0.1 | 20.6% | 11.5 | 23.1% | 11.0 | 64.8% | 0.0 | 0.0% | 22.6 | 27.1% |
| F | 0.1 | 20.9% | 17.5 | 35.2% | 15.5 | 91.4% | 1.0 | 3.6% | 34.1 | 37.8% |
| M | 0.2 | 28.7% | 35.8 | 72.2% | 11.8 | 69.5% | 11.5 | 43.6% | 59.4 | 53.5% |
| A | 0.2 | 38.6% | 47.0 | 94.8% | 9.2 | 53.8% | 21.8 | 82.4% | 78.3 | 67.4% |
| M | 0.3 | 46.4% | 48.8 | 98.3% | 11.2 | 66.1% | 25.5 | 96.2% | 85.8 | 76.8% |
| J | 0.3 | 55.1% | 46.5 | 93.8% | 10.6 | 62.5% | 19.3 | 72.9% | 76.8 | 71.1% |
| J | 0.4 | 69.2% | 42.4 | 85.5% | 10.2 | 60.1% | 10.9 | 41.2% | 64.0 | 64.0% |
| A | 0.5 | 88.3% | 37.6 | 75.8% | 8.7 | 51.3% | 1.9 | 7.3% | 48.8 | 55.7% |
| S | 0.6 | 98.9% | 32.5 | 65.5% | 6.7 | 39.5% | 0.0 | 0.0% | 39.8 | 51.0% |
| O | 0.5 | 89.0% | 27.3 | 55.0% | 5.2 | 30.4% | 0.0 | 0.0% | 33.0 | 43.6% |
| N | 0.4 | 67.8% | 20.5 | 41.3% | 5.9 | 34.5% | 0.0 | 0.0% | 26.8 | 35.9% |
| D | 0.3 | 50.9% | 12.0 | 24.3% | 9.6 | 56.5% | 0.0 | 0.0% | 21.9 | 32.9% |
| Mean | 0.3 | 56.2% | 31.6 | 63.7% | 9.6 | 56.7% | 7.7 | 28.9% | | |

Additional secondary annual simulations were run with variations in the relationship between denitrification rate and temperature. In the first secondary variation, denitrification was given a relationship similar to that observed in literature studies (Veraart et al., 2011; Nowicki, 1994), rather than those observed in our lab (Fig. 28). The second variation included a denitrification rate that varied the same as DNRA with changing temperatures (Fig. 29).

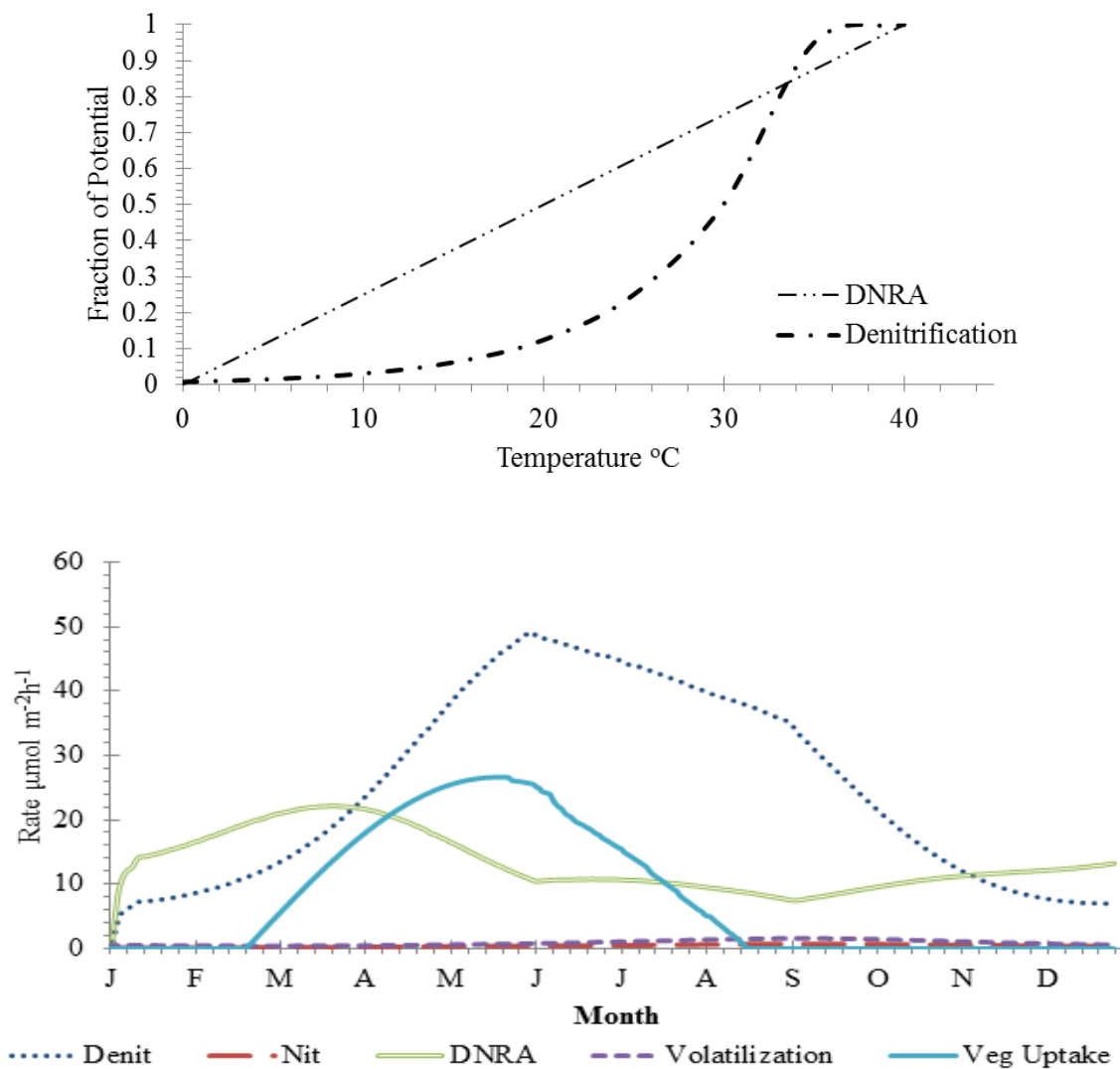


Figure 28. The denitrification-temperature relationship as described by Veraart et al. (2011) and Nowicki (1994) (top), and the resulting daily biogeochemical rates simulated throughout the year using this relationship and keeping all other variables as previously described (bottom).

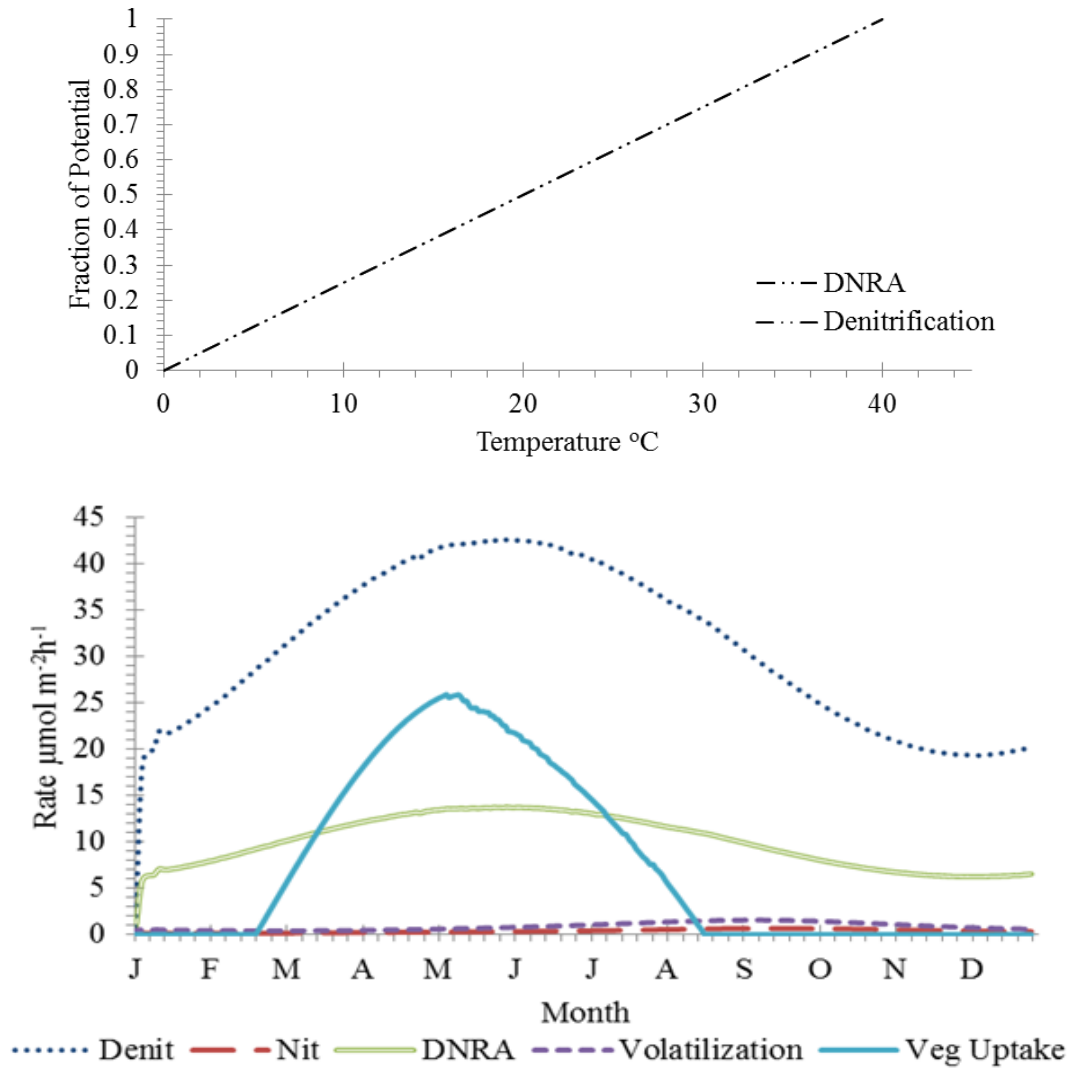


Figure 29. The denitrification-temperature relationship as equal to that of DNRA (top) and resulting daily biogeochemical rates simulated throughout the year using this relationship and keeping all other variables as previously described (bottom).

In the primary run (Fig 27., Table 8), Denitrification and DNRA expressed nearly equal rates from January to March, and again in December, diverging by as much as $40 \mu\text{mol m}^{-2}\text{h}^{-1}$ otherwise. The diverging points were representative of times when the water temperature neared 10°C (Fig. 3). Above this temperature, denitrification activity begins to increase more quickly than that of DNRA (Fig., 10), which in turn, allows denitrification to process and remove what

little nitrate is available in the anaerobic layers. The result is a competitive advantage for nitrate, which favors denitrification at temperature greater than 10°C. In the secondary runs, in which the temperature relationship for denitrification was varied (Figs. 28 and 29), the same general trends were maintained. Denitrification remained the dominant average biogeochemical rate, due to the greater rate constant of denitrification (0.155h^{-1}) compared to that of DNRA (0.05h^{-1}). However, in the case in which other literature observations were used for the denitrification-temperature relationship (Fig. 28), DNRA expressed a greater rate than denitrification from January to April, and again in November and December. Additionally, denitrification did not reach its peak rate until June in this secondary run, compared to May in the primary run. The peak for DNRA was also slightly delayed. In the second secondary run (Fig. 29), both denitrification and DNRA reach their peak in June and expressed identical seasonal variations. All remaining analyses pertain to the primary rate-temperature relationships (Fig. 10).

Percent of loaded nitrogen that is exported downstream varies from a low in late May of 84% to a high in December of 97% (Fig. 30). Export of loaded nitrogen seems to be highly correlated with denitrification and vegetation uptake activities. An exaggerated dip in exported nitrogen occurs in early summer, when these biogeochemical processes are most active.

The percent of loaded nitrogen that is exported is affected by temperature logarithmically, varying by 4.0% from 10 – 30°C (Fig. 31). Nitrogen export responds to loading rates as indicated by roughly 20% retention at a loading rate of $0.1\text{ kg N ha}^{-1}\text{ d}^{-1}$ compared to 4% retention at $4\text{ kg N ha}^{-1}\text{ d}^{-1}$ and less than 1% retention at loading rates greater than $40\text{ kg N ha}^{-1}\text{ d}^{-1}$ (Fig. 32). The percent of nitrogen exported decreases from nearly 100% at residence times less than a day, to roughly 30% at a residence time of 1 month and less than 10% at residence times

greater than 2.5 months (Fig. 33). The wetland length needed to achieve these residence times is 15km for every month.

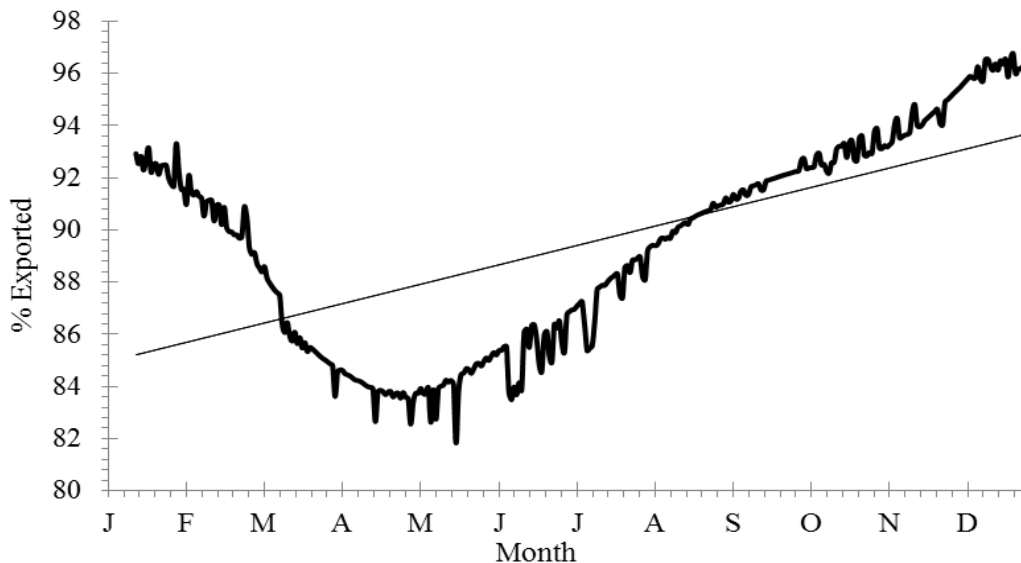


Figure 30. Simulated percentage of loaded nitrogen that is exported downstream for each day throughout the year based on horizontal flux model of a deltaic wetland at Wax Lake Delta. .

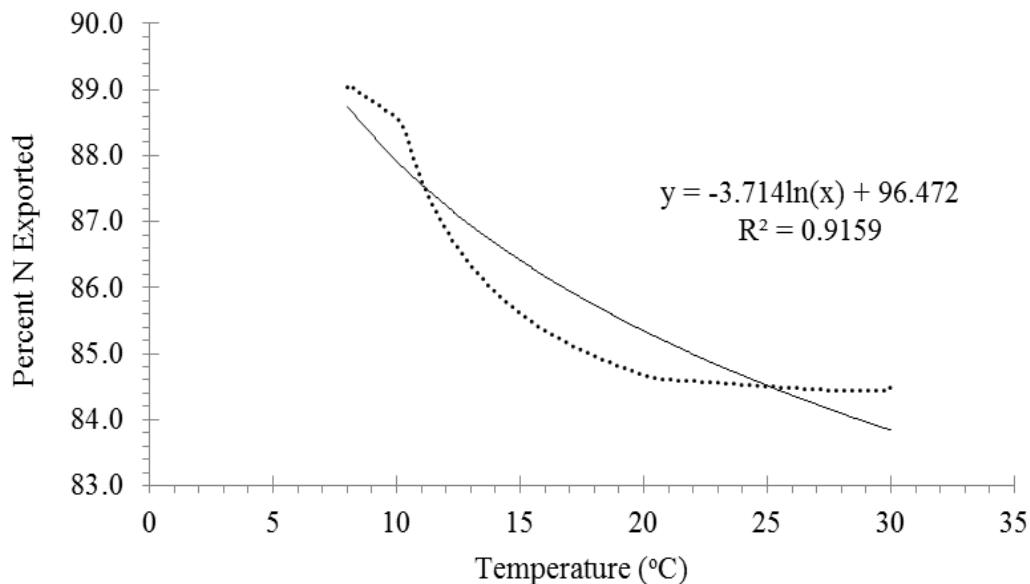


Figure 31. Relationship between temperature and percent of loaded nitrogen that is exported. All other seasonal variables are held constant.

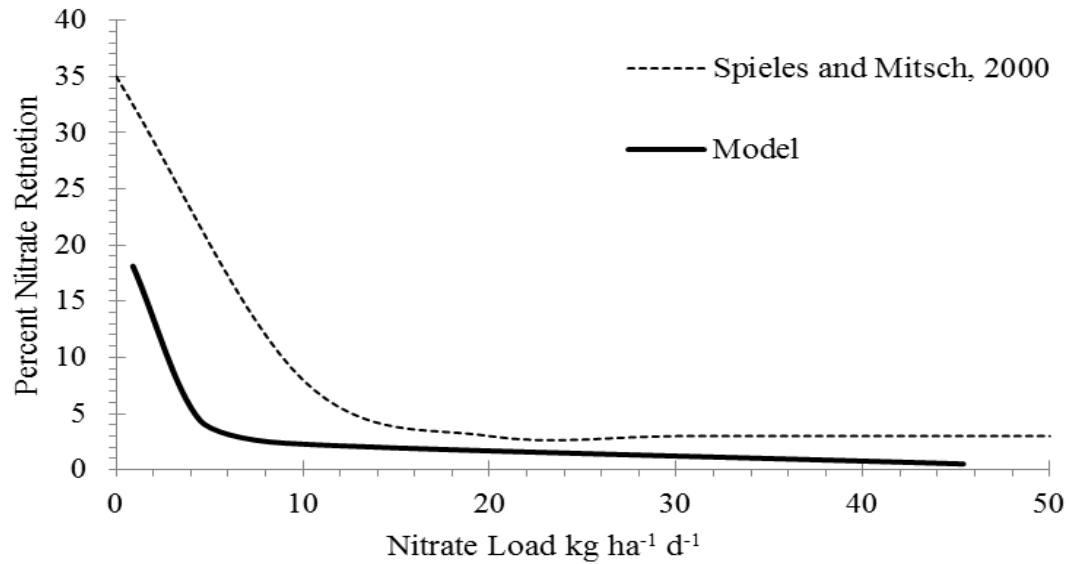


Figure 32. Modeled relationship between loaded nitrogen and % nitrogen retention within the Mike Island deltaic wetland study site and values from Spieles and Mitsch, 2000, in which a 0.004h^{-1} denitrification rate was used. The loading rate is determined by the input nitrogen concentrations and flow rate.

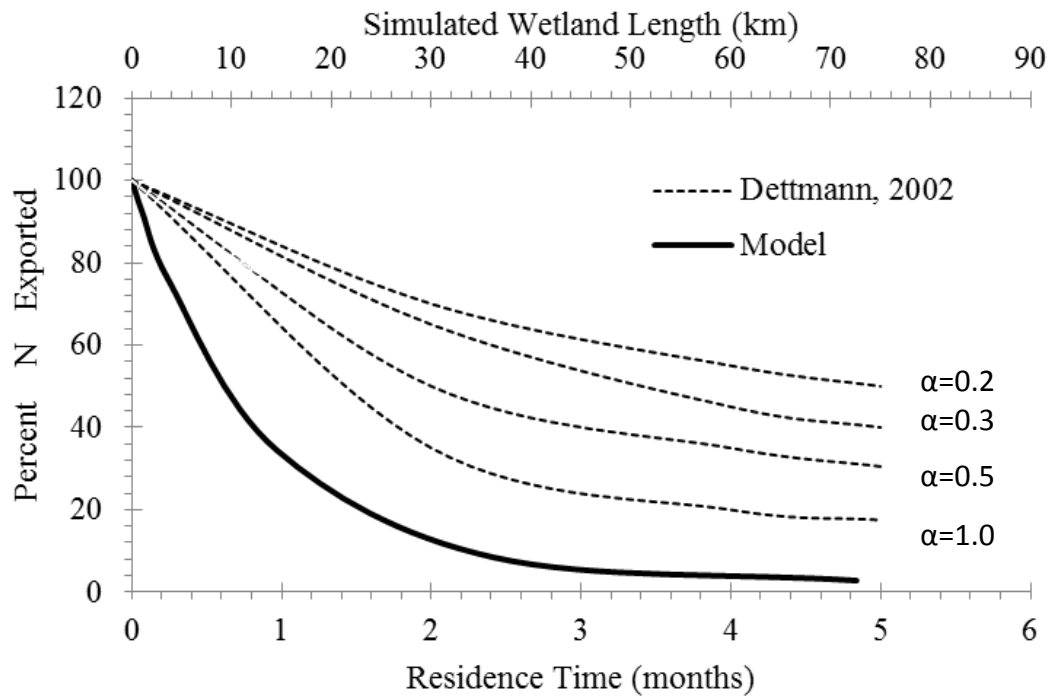


Figure 33. Modeled relationship between residence time and percent nitrogen exported within the system for the Mike Island study site and comparable values from Dettmann, 2002. Residence time varies by changing the length of the quadric and thus the simulated wetland.

DISCUSSION

Sensitivity Analysis

Of the first order processes, nitrification was most influential in controlling nutrient fluxes within the soil core incubation simulations, which was primarily exhibited in nitrate and ammonium fluxes. This is surprising considering nitrification only acts upon ammonium, which represents a small percentage of total nitrogen in the Wax Lake Delta. However, this dominating influence may be explained by the presence of nitrification in the aerobic soil layer, which represents a small boundary between overlying water and the majority of underlying soil. By transforming ammonium to nitrate within this small boundary, the resulting fluxes are amplified.

DNRA showed to be more influential in removing nitrate from overlying water, than both nitrification and denitrification. Similar patterns were observed in a recent Wax Lake Delta study in which roughly 30% of the nitrate flux was accounted for by denitrification, leaving 70% of the soil nitrate demand unaccounted for and likely due to DNRA (Henry, 2012). This competitive equilibrium for nitrate by different microorganisms has been suggested previously (Canavan et al, 2007; Megonigal et al., 2004; Tiedje, 1988), and is an important consideration in modeling and understanding wetland nitrogen dynamics. It also reinforces the argument that the role denitrification plays in removing surface water nitrogen from wetland environments may have been overestimated in the past (Kroeze, 2003; Burgin and Hamilton, 2007).

Denitrification, DNRA, and nitrate diffusion rates had no effect on the flux of ammonium. All of these processes are operating within a cycle and each is tied to the others through a series of direct or indirect pathways. Therefore, a change in the rate of one process, should eventually lead to changes in all nutrient concentrations. Explanations for these results

could lie in the duration of the core incubations, and the corresponding simulations. At a target length of 24 hours and with diffusion operating at rates of $1 \times 10^{-5} - 1 \times 10^{-10} \text{ cm}^2 \text{ h}^{-1}$, significant quantities of soluble nitrogen are unable to transfer vertically for effective changes in their concentrations. This presents a question in the appropriate length of soil core incubations. Is 24 hours long enough to effectively capture all biogeochemical processes, including diffusion?

Calibrated Parameters

Although bounds for model parameters were set by literature reports, calibrations of these parameters resulted in values that were at the extremes of their upper and lower bounds. This suggests that more accurate simulations of the soil core incubations could have been achieved with rates outside of the literature bounds. Studies regarding rate constants and diffusion coefficients within the Wax Lake Delta would provide more confidence in placing these specific values within the bounds set by the literature. In lieu of such studies, however, the model parameters optimized for both the vertical flux model and the Mike Island observations shown in Tables 4 and 5, are taken as the most accurate representation of biogeochemical parameters in Mike Island until a more detailed investigation shows otherwise.

The fact that rate constants came from the extremes of their literature set ranges, could be explained by the environmental conditions of the various studies from which they came. Denitrification was given the highest first order rate constant, 0.155 h^{-1} , as a result of the calibration. This value came from a study of nitrogen processes in flooded organic Florida soils, in which the nitrate concentration was 21-57 μM (Reddy and Rao, 1983). These concentrations are at the lower end of the surface water nitrate concentrations in Mike Island, which range from 50 – 100 μM . Therefore, it is possible that the denitrification rate constant for the Wax Lake

Delta could be higher, due to elevated nitrate concentrations. The same is possibly true for the DNRA rate of 0.05h^{-1} , which is the maximum reported value for humid tropical forest soils (Pett-Ridge, et al., 2006). Because this rate represents a terrestrial soil, with less moisture content and nitrate than those of the Wax Lake Delta, it is likely that the actual Wax Lake Delta rate is higher. Unfortunately, little has been reported for first order rate constants of DNRA. In the case of nitrification, which showed to be the most influential first order rate, a constant of 0.001h^{-1} resulted from the calibration. This represents the lower end of the range determined by the literature review. The studies constituting this range, however, were conducted in environmental conditions very different from those in the Wax Lake Delta, such as in pig slurries or synthetic waste water where the ammonium concentrations ($0 - 550\text{ }\mu\text{M}$) are far greater than those observed at the Wax Lake Delta ($0 - 4\text{ }\mu\text{M}$).

Simulated Rates

Even with a consistent set of calibrated soil parameters in the vertical flux and horizontal flow models, discrepancies between biogeochemical rates within soil core simulation results (Table 7) and Mike Island ecosystem simulation results (Table 8) were apparent. Nitrification in the soil core incubations was three times as much as that within the Mike Island simulations (1.0 and $0.3\text{ }\mu\text{mol m}^{-2}\text{h}^{-1}$, respectively). Denitrification in the core incubations was more than twice that of the Mike Island simulations, at 81 and $31\text{ }\mu\text{mol m}^{-2}\text{h}^{-1}$, respectively. DNRA in the soil core incubations was almost twice as much as that in the Mike Island simulations (9.6 and $16.3\text{ }\mu\text{mol m}^{-2}\text{h}^{-1}$, respectively). This deviation is most likely due to the variations in biogeochemical controls within the ecosystem simulations, such as temperature, nitrogen inputs, residence times and vegetation uptake. The difference between these rates underscores the problem of using laboratory based experiments to estimate biogeochemical rates within an ecosystem (Cornwell et

al., 1999; Groffmen et al., 2006; Kadlec, 2012). Instead, results from these methods should be interpreted as potential rates within a constrained set of conditions and extrapolation to the landscape scale requires more detailed inclusion of ecosystem dynamics.

Denitrification and volatilization are the only processes capable of removing nitrogen from wetlands by transferring it into the atmosphere. Denitrification is the dominant removal mechanisms within this model, removing up to $50 \mu\text{mol m}^{-2}\text{h}^{-1}$ in late spring and early summer. This is most likely due to the increased nitrate concentrations and moderate temperatures at this time. Volatilization is modeled at removing $2.5 \mu\text{mol m}^{-2}\text{h}^{-1}$ at its highest rate in late summer, which seems to primarily be a function of temperature. Other studies of the Wax Lake system (Lane et al., 2002) as well as other wetland systems in Louisiana (Buresh and Patrick, 1981) have suggested that denitrification is the primary player in apparent nitrogen removal. Yet other studies have found confounding results, that denitrification must be operating amongst other rates of greater magnitude to account for the observed nitrogen fluxes (Lenaker, 2009; Henry, 2012). This model suggests that most surface water nitrate reductions result from a combination of denitrification, DNRA, and vegetation uptake, with roughly two thirds of the reduction due to denitrification. This has important implications when estimating wetland nitrogen removal, because vegetation uptake and DNRA merely store, rather than completely remove nitrogen from the system,

Soil Core Incubations as Biogeochemical Indicators

Intact soil core incubations are used to estimate fate of nitrogen in wetland ecosystems by measuring changes in core surface water nutrient concentrations over time (Robertson et al., 1988; Moore et al., 1998; Hopkinson and Wetzel, 1982). Although precaution is taken to

preserve the natural integrity of the soil, some disturbance leads to artifacts in final estimates of biogeochemical rates (Parkin et al., 1984; Raison et al. 1987; Miller-Way et al., 1994; Fisher and Reddy, 2000). When combined with natural variability at the landscape scale, soil cores are often poor representations of ecosystem biogeochemistry (Kadlec, 2012). In this study, simulations of soil core incubations were used to calibrate model parameters. Results show that rates within the soil cores are much higher than those within the ecosystem from which the cores came, even with a consistent set of model parameters between the two. Further, the core incubation simulations did not always accurately represent observed fluxes, especially in the case of ammonium. Despite these differences however, the parameters were successfully validated against observation made in the field. This suggests that soil cores accurately represent true ecosystem level biogeochemistry, only when all of the environmental controls within that system are accounted for. Water residence time, nitrogen concentration, temperature and vegetation coverage all play important roles in governing biogeochemistry. Only by including all of these processes, is the biogeochemical model able to accurately simulate observations made in the field, using parameters calibrated through soil core incubations. As a result, more accurate and reliable conclusions can be drawn on the fate of nitrogen within the system.

Residence Time, Loading Rate, and Nitrogen Fate

The percentage of loaded nitrogen that is retained, rather than exported downstream indicates a steady increase in exported nitrogen from January to December and a strong correlation with highly active biogeochemistry from March to August. Throughout the year, the model shows a maximum nitrogen retention efficiency of roughly 16% in May. The timing of this retention coincides with that of planned river diversions, which will operate when the river is experiencing peak flows in April and May. By diverting river water through deltaic wetlands at

this time, when biogeochemistry is most active and nitrogen is retained within the system, a maximum amount of nitrogen can be removed from surface waters.

Temperature showed little effect on the percent of nitrogen retained, with only a 4% decrease of exported nitrogen from 10 to 30 °C. This is surprising considering the effects of temperature on the individual rates of the nitrogen cycle, however similar patterns have been reported (Kadlec, 1999; Fulweiler and Nixon, 2011). Changes in the effect of temperature on denitrification rates did result in slight variations in the relationship between denitrification and DNRA rates throughout the year. When using literature cited values for the denitrification-temperature relationship, instead of laboratory observations, DNRA exhibited a greater rate than denitrification in winter months. This suggests the importance of including appropriate temperature effects when modeling biogeochemistry.

Loading rates and residence times have profound effects on the amount of nitrogen removed from the system. A maximum retention value of 16% might suggest that much more efficient systems must be operating within the Wax Lake Delta to obtain the observed surface water nitrogen reductions of up to 47% by Lane et al., 2002. However, freshwater residence time within the Mike Island model only fluctuate by an hour over the course of a year. When this residence time is increased to compare with those of other coastal systems, a 45% retention efficiency could be achieved at residence times of just under two weeks (Fig. 33). Yet the wetland length needed to obtain a two week residence time is roughly 5km, which is five times greater than the modeled area. This underscores the importance of considering the spatial scale when estimating nitrogen removal at the landscape level.

When compared to other riverine wetlands as well as other estuarine systems, the Wax Lake Delta process nitrogen similarly across varying loading rates and residence times. Generally, percent of loaded nitrogen that is retained within the system decreases as loading rates increase and residence times decrease. However, the apparent retention efficiency of the Wax Lake Delta compares differently when considering the two independent variables, loading rate and residence time. In terms of loading rate, the Wax Lake Delta seems to be less efficient at retaining nitrogen than the systems reported by Spieles and Mitsch, 2000. However, when considering residence times, Mike Island is operating much more efficiently than systems reported on by Dettman, 2002. This indicates that a low loading rate and a high residence time would be optimal in maximizing the percent of loaded nitrogen that is retained in or removed from the system.

Wetlands process nitrogen according to a complex suite of biogeochemical laws, operating simultaneously and according to varying environmental controls. This complexity compounds the difficulty in using laboratory measurements to estimate landscape level biogeochemistry, in both reality and virtually within numerical models. Precautions should be made when attempting to interpret biogeochemical rates obtained within soil cores, to comparable ecosystem level rates. By using core result to calibrate mechanistic models, and with the inclusion of fundamental environmental variability within the models, soil cores can be pivotal in understanding nitrogen biogeochemistry.

Within the Wax Lake Delta, however, this model reaffirms the hypotheses that denitrification alone cannot account for reductions in surface water nitrate, nor is it likely that denitrification is the dominant process contributing to this trend. DNRA, rather, is a likely candidate for elevating the soil nitrogen demand and thus the corresponding flux of nitrate from

surface waters. Yet DNRA does not remove nitrogen from the system, temporarily storing it rather as ammonium in the soil. In this sense, denitrification remains the primary mechanisms of completely removing nitrogen from the Wax Lake Delta system. Temperature has little influence on the percentage of nitrogen exported from the system, however its relationship to biogeochemical rates is an important consideration when comparing those rates at varying temperatures. Residence time and loading rate relationships are consistent with literature reports and suggest that by keeping a moderate loading rate and a high residence time, a large portion of loaded nitrogen can be retained in the system rather than exported downstream.

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APPENDIX – Visual Basic Coding for Primary Model Functions

```

'Declare all variables
'Dimensional variables
Dim WaterDepth(), SoilDepth(), CellWidth, CellLength(), FlumeLength, CellArea(cells),
    TotalWaterSurfaceArea, WaterElevation, CellWaterVolume, TotalSoilDepth,
    CurrentDepth, RootDepth, FlowThroughTime As Single
'Input concentration variables
Dim NO3in, NH4in, SONin, PONin As Single
'First order rate variables, one for each layer
Dim PONTtoSON_(), SONtoNH4_(), NH4toNO3_(), NO3toNH4_(), NO3toN2_(), PONsettle1,
    PONsettle2, PONsettle3 As Single
'Other rate constants and vegetation controls
Dim PlantNdecay, SONdif, NH4dif, NO3dif, Litterfall, PercPlantWater, PercPlant(),
    PercPlantAero, PercPlantAnaero, PlantBioMass As Single
'Analysis variables for calculating and plotting daily rates
Dim TotalNitrogenLoaded, DailyNitrogenLoaded, DailyNitrogenRemoved, TotalDenitrified,
    TotalVolatilized, TotalFinalSoilNitrogen,
    TotalFinalWaterNitrogen, TotalInitialNitrogen, NitrogenOutput, NitrogenOutput_t,
    NitrogenInput_t, totalSettled,
    RemovalFromDenitrification(), ConversionFromNitrification(),
    ConversionFromDNRA(), Denitrification_t, Nitrification_t,
    DNRA_t, decay_t, volatilization_t, litterfall_t, uptake_t, SoilStorage_t,
    WaterStorage_t As Single
'layer variable, 0 = water and #layers = the bottom most layer
Dim z As Integer
'integers
Dim layers, cells, month, days As Integer
'Miscellaneous variables
Dim i, Tmax, Tinit, pH, pK, Temp, NH4PartitionCoeff, Spectrate, Ndemand, RootsKm,
    LeavesKm As Single
'Timing controls
Dim RT, T, dT, InputRate As Decimal
'Each wetland cell is a unit capable of containing the above variables
Dim Cell(cells) As Unit
'stats for calculating fluxes and other analyses
Dim SumT, SumNO3Conc, SumNH4Conc, SumTimeNO3Conc, SumTimeNH4Conc, SumTT, NO3slope,
    NH4slope, NO3intercept, NH4intercept, WaterNO3stor_uM, WatersolNH4stor_uM As
    Single
'For interpreting user defined equations into the VB language for the computer to
solve
Dim SC As New MSScriptControl.ScriptControl

Private Sub RunButton_click(ByVal sender As System.Object, ByVal e As System.EventArgs)
Handles RunButton.Click
    'Run Bathymetry analyzation to determine the intitial cell volumes and dimensions
    T = 0
    If SeasonalElevationCheckBox.Checked = True Then
        If T >= 0 And T < 214 Then
            WaterElevation = Seasonal(T / 24, ElevationEquationTextBox1)
        Else
            WaterElevation = Seasonal(T / 24, ElevationEquationTextBox2)
        End If
        WaterElevationTextBox.Text = WaterElevation
        Button2_Click(Nothing, Nothing)
        DataGridView1.Update()
    
```

```

Else
    WaterElevation = WaterElevationTextBox.Text
    Button2_Click(Nothing, Nothing)
    DataGridView1.Update()
End If

'Initialize all variables
Initialize()

'Begin Calculations of storage values from t = 0 to Tmax
RunFlume()

'Compute and Output Mass Balance
MassBalance()

'Show the results window
Form2.Show()

End Sub

Public Sub Initialize()
    Try
        'number of layers and cells
        layers = LayersTextBox.Text
        cells = CellNumberTextBox.Text
        ReDim Cell(cells)
        'river inputs
        NO3in = NO3InputTextBox.Text
        NH4in = NH4InputTextBox.Text
        SONin = SONInputTextBox.Text
        PONin = PONInputTextBox.Text
        'cell dimensions
        ReDim WaterDepth(layers), PONtoSON_(layers), SONtoNH4_(layers),
            NH4toNO3_(layers), NO3toNH4_(layers), NO3toN2_(layers)
        ReDim CellLength(cells), CellArea(cells)
        ReDim RemovalFromDenitrification(cells, layers)
        ReDim ConversionFromNitrification(cells, layers)
        ReDim ConversionFromDNRA(cells, layers)
        For c = 0 To cells - 1
            Cell(c) = New Unit(layers, Tmax) ' Must fill the array with objects
            before use
            Cell(c).depth(0) = DataGridView1.Rows(c).Cells(5).Value
            CellLength(c) = CInt(DataGridView1.Rows(c).Cells(1).Value)
            CellArea(c) = DataGridView1.Rows(c).Cells(6).Value
            FlumeLength += CellLength(c)
        Next
        CellWaterVolume = DataGridView1.Rows(1).Cells(3).Value
        'the first cells surface water concentrations are the input concentrations
        If SeasonalAmmoniumCheckBox.Checked = True Then
            Cell(0).PONstor(0) = PONin * 1000 * CellWaterVolume
            Cell(0).SONstor(0) = SONin * 1000 * CellWaterVolume
            Cell(0).solNH4stor(0) = Seasonal(StartTimeTextBox.Text,
                AmmoniumEquationTextBox) * 1000 * CellWaterVolume
            Cell(0).sornh4stor(0) = 0 * 1000 * CellWaterVolume
            Cell(0).No3stor(0) = Seasonal(StartTimeTextBox.Text,
                NitrateEquationTextBox) * 1000 * CellWaterVolume
            Cell(0).layervolume(0) = CellWaterVolume
        Else

```

```

Cell(0).PONstor(0) = PONin * 1000 * CellWaterVolume
Cell(0).SONstor(0) = SONin * 1000 * CellWaterVolume
Cell(0).solNH4stor(0) = NH4in * 1000 * CellWaterVolume
Cell(0).sornh4stor(0) = 0 * 1000 * CellWaterVolume
Cell(0).No3stor(0) = NO3in * 1000 * CellWaterVolume
Cell(0).layervolume(0) = CellWaterVolume
End If

'set the aerobic layers characteristics
Cell(0).depth(1) = 0.01
Cell(0).layervolume(1) = CellArea(0) * Cell(0).depth(1)
Cell(0).PONstor(1) = 0 * 1000 * Cell(0).layervolume(1)
Cell(0).SONstor(1) = 0 * 1000 * Cell(0).layervolume(1)
Cell(0).solNH4stor(1) = Cell(0).solNH4stor(0) * 1.5 ' 1000 *
Cell(0).layervolume(1)
Cell(0).sornh4stor(1) = 0 * 1000 * Cell(0).layervolume(1)
Cell(0).No3stor(1) = 0 * 1000 * Cell(0).layervolume(1)
'set the anaerobic layer characteristics
For z = 2 To layers
    Cell(0).depth(z) = 0.03
    Cell(0).layervolume(z) = CellArea(0) * Cell(0).depth(z)
    Cell(0).PONstor(z) = 0 * 1000 * Cell(0).layervolume(z)
    Cell(0).SONstor(z) = 0 * 1000 * Cell(0).layervolume(z)
    Cell(0).solNH4stor(z) = Cell(0).solNH4stor(z - 1) * 1.5 ' * 1000 *
    Cell(0).layervolume(z)
    Cell(0).sornh4stor(z) = 0 * 1000 * Cell(0).layervolume(z)
    Cell(0).No3stor(z) = 0 * 1000 * Cell(0).layervolume(z)
Next

'set the other cells initial storages. Text boxes are in uM, so they are
converted tom umols.
'the ammonium concentrations in the lower layers must increase with depth to
mimic the natural behavior
For c = 1 To cells - 1
    With Cell(c)
        z = 0
        .depth(z) = .depth(0)
        .PONstor(z) = 0 * 1000 * CellWaterVolume
        .SONstor(z) = 0 * 1000 * CellWaterVolume
        .solNH4stor(z) = 2 * 1000 * CellWaterVolume
        .sornh4stor(z) = 0 * 1000 * CellWaterVolume
        .No3stor(z) = 0 * 1000 * CellWaterVolume
        .layervolume(z) = CellWaterVolume
        z = 1
        .depth(z) = 0.01
        .layervolume(z) = CellArea(c) * .depth(z)
        .PONstor(z) = 0 * 1000 * CellWaterVolume
        .SONstor(z) = 0 * 1000 * CellWaterVolume
        .solNH4stor(z) = .solNH4stor(z - 1) * 1.5
        .sornh4stor(z) = 0 * 1000 * CellWaterVolume
        .No3stor(z) = 0 * 1000 * CellWaterVolume
        For z = 2 To layers
            .depth(z) = 0.03
            .layervolume(z) = CellArea(c) * .depth(z)
            .PONstor(z) = 0 * 1000 * CellWaterVolume
            .SONstor(z) = 0 * 1000 * CellWaterVolume
            .solNH4stor(z) = .solNH4stor(z - 1) * 1.5
            .sornh4stor(z) = 0 * 1000 * CellWaterVolume

```

```

        .No3stor(z) = 0 * 1000 * CellWaterVolume
    Next z
End With
Next
'the maximum extent of the roots. This will be used to determine how far
down plants are capable of drawing nitrogen.
RootDepth = 0.3
'The residence time is a function of the flow rate and the cell volume
RT = Math.Round((1 / InletRateTextBox.Text) * CellWaterVolume / (60 * 60), 2)
'the flow through time is a function of the flow rate and the total system
volume
FlowThroughTime = (1 / InletRateTextBox.Text) * CellWaterVolume * cells / (60
    * 60)
'The total simulation duration, in hours. January 1st = 0, December 31st =
365*24
Tmax = SimulationTimeTextBox.Text * 24
'The initial time of the
Tinit = StartTimeTextBox.Text * 24
'find the integer number of the month by dividing the start day by the number
of days in a month
month = Tinit / 30.416667
'If the total flowthrough time is greater than the simulation duration, then
the water would not have a chance to flow completely through the system
If FlowThroughTime > (Tmax - Tinit) Then
    MessageBox.Show("Total Flow Through Time: " &
        FlowThroughTime.ToString("F2") & " hr, is more than the simulation
        duration, " & Tmax & " hr")
    Exit Sub
End If

'Set the rates for each process in each layer according to the user inputs.
For z = 0 To 5
    PONtoSON_(z) = tabPage4.Controls.Item("PONtoSONTextBox" & z).Text()
    SONtoNH4_(z) = tabPage4.Controls.Item("SONtoNH4TextBox" & z).Text()
    NH4toNO3_(z) = tabPage4.Controls.Item("NH4toNO3TextBox" & z).Text()
    NO3toNH4_(z) = tabPage4.Controls.Item("NO3toNH4TextBox" & z).Text()
    NO3toN2_(z) = tabPage4.Controls.Item("NO3toN2TextBox" & z).Text()
Next
'Any layers greater than 5 will mimic the 5th layer in terms of rates.
For z = 6 To layers
    PONtoSON_(z) = tabPage4.Controls.Item("PONtoSONTextBox" & 6).Text()
    SONtoNH4_(z) = tabPage4.Controls.Item("SONtoNH4TextBox" & 6).Text()
    NH4toNO3_(z) = tabPage4.Controls.Item("NH4toNO3TextBox" & 6).Text()
    NO3toNH4_(z) = tabPage4.Controls.Item("NO3toNH4TextBox" & 6).Text()
    NO3toN2_(z) = tabPage4.Controls.Item("NO3toN2TextBox" & 6).Text()
Next

'each anaerobic layer is 3cm, plus the aerobic layer of 1cm
TotalSoilDepth = 0.03 * (layers - 1) + 0.01
'Particulate organic nitrogen settling rates as determined by the user
PONsettle1 = PONSettling1TextBox.Text
PONsettle2 = PONSettling2TextBox.Text
PONsettle3 = PONSettling3TextBox.Text
'the litterfall decay rate, as determined by the user
PlantNdecay = DecayTextBox.Text / 24
'the diffusion coefficients, as determined by the user
SONdif = SONDiffusionTextBox.Text
NH4dif = NH4DiffusionTextBox.Text

```

```

N03dif = N03DiffusionTextBox.Text

ReDim PercPlant(layers)
PlantBioMass = 0
'initial flow rate of the system, as determined by the user or by the
automated algorithm initiated previously
InputRate = InletRateTextBox.Text
'the computational time step
dT = TimeStepTextBox.Text
pH = pHTextBox.Text
'the pK value controls the volatilization of ammonium
pK = 0.09018 + 2729.92 / (273.2 + Temp)
'the partitioncoefficient and the spectrate control the sorption of ammonium
to and from the soil
NH4PartitionCoeff = PartitionTextBox.Text
Spectrate = SpectrateTextBox.Text
'the half saturation constants, km, and the nitrogen demand, Ndemand, as
determined by the user
RootsKm = RootsKmTextBox.Text
LeavesKm = LeavesKmTextBox.Text
Ndemand = NdemandTextBox.Text
Catch ex As Exception
    MessageBox.Show("Sorry. Variable Initialization Error: " & ex.Message)
Exit Sub
End Try
End Sub

```

```

Public Sub RunFlume()
    'This variable determines if the flow through time has been reached yet
    Dim done As Boolean = False
    T = Tinit
    Try
        'Run the simulation until the user defined lenght and then until all the
        water has been allowed to flow through the system
        Do While T < Tmax + FlowThroughTime
            If T Mod 24 = 0 Then
                'Everyday the seasonally and temperature dependent variables are
                reassigned
                ReassignRates()
            End If
            'When residence time has expired, send water storages to next cell. For
            the first cell refill it with the input
            If T Mod RT = 0 And T > 0 Then
                If T > (Tinit + FlowThroughTime) Then
                    If done = False Then
                        For c = 0 To cells - 1
                            For z = 0 To layers
                                'Determine the initial amount of nitrogen in the
                                system for later analyses
                                TotalInitialNitrogen += Cell(c).PONstor(z) +
                                Cell(c).SONstor(z) + Cell(c).solNH4stor(z) +
                                Cell(c).sornh4stor(z) + Cell(c).No3stor(z)
                            Next
                        Next
                        done = True
                    End If
                End If
            End If
        End While
    End Try
End Sub

```

```

If T < Tmax Then
    'keep track of the amount of nitrogen loaded as well as that
    exported for each day
    TotalNitrogenLoaded += (NO3in + NH4in + SONin + PONin) * 1000
    * InputRate * RT * 60 * 60
    NitrogenInput_t = (NO3in + NH4in + SONin + PONin) * 1000 *
    InputRate * RT * 60 * 60
End If
NitrogenOutput += Cell(cells - 1).No3stor(0) + Cell(cells -
1).solNH4stor(0) + Cell(cells - 1).SONstor(0) + Cell(cells -
1).PONstor(0)
NitrogenOutput_t = Cell(cells - 1).No3stor(0) + Cell(cells -
1).solNH4stor(0) + Cell(cells - 1).SONstor(0) + Cell(cells -
1).PONstor(0)
End If
'transfer the contents of the upstream cells to that of the
downstream cells
For c = CInt(cells - 1) To 1 Step -1
    Cell(c).No3stor(0) = Cell(c - 1).No3stor(0)
    Cell(c).solNH4stor(0) = Cell(c - 1).solNH4stor(0)
    Cell(c).sornh4stor(0) = Cell(c - 1).sornh4stor(0)
    Cell(c).SONstor(0) = Cell(c - 1).SONstor(0)
    Cell(c).PONstor(0) = Cell(c - 1).PONstor(0)
Next
If T > Tmax Then
    Cell(0).No3stor(0) = 0
    Cell(0).solNH4stor(0) = 0
    Cell(0).sornh4stor(0) = 0
    Cell(0).SONstor(0) = 0
    Cell(0).PONstor(0) = 0
Else
    Cell(0).No3stor(0) = NO3in * 1000 * InputRate * (RT * 60 * 60)
    Cell(0).solNH4stor(0) = NH4in * 1000 * InputRate * (RT * 60 * 60)
    Cell(0).sornh4stor(0) = 0 * 1000 * InputRate * (RT * 60 * 60)
    Cell(0).SONstor(0) = SONin * 1000 * InputRate * (RT * 60 * 60)
    Cell(0).PONstor(0) = PONin * 1000 * InputRate * (RT * 60 * 60)
End If
End If

'For each cell in the system, run the model
For c = 0 To CInt(cells) - 1
    With Cell(c)
        z = 0 'water layer
        'Rates act on concentrations but the storages are counted as
        masses, so conversions are necessary
        'decay is a first order rate equation that converts the
        litterfall to PON
        .Decay(z) = (DifferentialEquations.RK4_FirstOrder(AddressOf
        FirstOrder, Litterfall / .layervolume(z), PlantNdecay, dT)) *
        .layervolume(z)
        'enzyme hydrolysis is a first order rate that converts PON to SON
        .enzymehydrolysis(z) =
        (DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
        .PONstor(z) / .layervolume(z), PONtoSON_(z), dT)) *
        .layervolume(z)
        'PON settles out from the surface water to the aerobic layer
    End With

```

```

.Settling(z) = (DifferentialEquations.RK4_FirstOrder(AddressOf
FirstOrder, .PONstor(z) / .layervolume(z), PONsettle1, dT)) *
.layervolume(z)
'SON diffuses between layers according to Ficks law
.SONDiffusion(z) = (DifferentialEquations.RK4_Diffusion(AddressOf
DiffusionWater, .SONstor(z) / .layervolume(z), .SONstor(z + 1) /
.layervolume(z + 1), .depth(z), .depth(z + 1), SONdif, dT)) *
CellArea(c)
'Ammonium can be volatilized from the surface water only
.volatilization(z) =
(DifferentialEquations.RK4_volatilization(AddressOf
Volatilization, (.solNH4stor(z) * 14 / 1000000) / CellArea(c),
pH, pK, dT)) * (CellArea(c) * 1000000 / 14)
'mineralization of SON to NH4
.mineralization(z) =
(DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
.SONstor(z) / .layervolume(z), SONtoNH4_(z), dT)) *
.layervolume(z)
'nitrification of NH4 to NO3 is an aerobic process
.nitrification(z) =
(DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
.solNH4stor(z) / .layervolume(z), NH4toNO3_(z), dT)) *
.layervolume(z)
'NH4 diffuses between layers according to Ficks law
.NH4Diffusion(z) = (DifferentialEquations.RK4_Diffusion(AddressOf
DiffusionWater, .solNH4stor(z) / .layervolume(z), .solNH4stor(z +
1) / .layervolume(z + 1), .depth(z), .depth(z + 1), NH4dif, dT))
* CellArea(c)
'DNRA is an anaerobic process but will still occur if the user
defines a rate > 0
.DNRA(z) = (DifferentialEquations.RK4_FirstOrder(AddressOf
FirstOrder, .No3stor(z) / .layervolume(z), NO3toNH4_(z), dT)) *
.layervolume(z)
'NO3 diffuses between layers according to Ficks law
.NO3Diffusion(z) = (DifferentialEquations.RK4_Diffusion(AddressOf
DiffusionWater, .No3stor(z) / .layervolume(z), .No3stor(z + 1) /
.layervolume(z + 1), .depth(z), .depth(z + 1), NO3dif, dT)) *
CellArea(c)
'denitrification is an anaerobic process but will still occur if
the user defines a rate > 0
.denitrification(z) =
(DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
.No3stor(z) / .layervolume(z), NO3toN2_(z), dT)) *
.layervolume(z)
'vegetation may assimilate nitrogen from the surface water
.NH4PlantUptake(z) = (DifferentialEquations.RK4_veg(AddressOf
VegUptake, .solNH4stor(z) / .layervolume(z), .No3stor(z) /
.layervolume(z), LeavesKm * 1000, Ndemand,
PercentAboveGroundTextBox.Text * (RootDepth / .depth(z)),
.depth(z), dT)) * CellArea(c)
.NO3PlantUptake(z) = (DifferentialEquations.RK4_veg(AddressOf
VegUptake, .No3stor(z) / .layervolume(z), .solNH4stor(z) /
.layervolume(z), (LeavesKm * 1000), Ndemand,
PercentAboveGroundTextBox.Text * (RootDepth / .depth(z)),
.depth(z), dT)) * CellArea(c)
'the changes in each storage, for each layer depend on the
processes that act on them
.delpon(z) = (.Decay(z) - .enzymehydrolysis(z) - .Settling(z))

```



```

.delson(z) = (.SONDiffusion(z) + .enzymehydrolysis(z) -
.mineralization(z))
.delnh4(z) = (.mineralization(z) + .NH4Diffusion(z) -
.nitrification(z) - .volatilization(z) + .DNRA(z) -
.NH4PlantUptake(z))
.delno3(z) = (.nitrification(z) + .NO3Diffusion(z) -
.denitrification(z) - .DNRA(z) - .NO3PlantUptake(z))
.delveg(z) = .NO3PlantUptake(z) + .NH4PlantUptake(z)
'Litterfall is counted as a system wide variable, with no
separate cell storages
Litterfall += -.Decay(z)

'For the Aerobic Layer
z = 1
CurrentDepth += .depth(z)
.enzymehydrolysis(z) =
(DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
.PONstor(z) / .layervolume(z), PONtoSON_(z), dT)) *
.layervolume(z)
.Settling(z) = (DifferentialEquations.RK4_FirstOrder(AddressOf
FirstOrder, .PONstor(z) / .layervolume(z), PONSettle2, dT)) *
.layervolume(z)
.SONDiffusion(z) = (DifferentialEquations.RK4_Diffusion(AddressOf
Diffusion, .SONstor(z) / .layervolume(z), .SONstor(z + 1) /
.layervolume(z + 1), .depth(z), .depth(z + 1), SONdif, dT)) *
CellArea(c)
.mineralization(z) =
(DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
.SONstor(z) / .layervolume(z), SONtoNH4_(z), dT)) *
.layervolume(z)
.nitrification(z) =
(DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
.solNH4stor(z) / .layervolume(z), NH4toNO3_(z), dT)) *
.layervolume(z)
.NH4Diffusion(z) = (DifferentialEquations.RK4_Diffusion(AddressOf
Diffusion, .solNH4stor(z) / .layervolume(z), .solNH4stor(z + 1) /
.layervolume(z + 1), .depth(z), .depth(z + 1), NH4dif, dT)) *
CellArea(c)
.DNRA(z) = (DifferentialEquations.RK4_FirstOrder(AddressOf
FirstOrder, .No3stor(z) / .layervolume(z), NO3toNH4_(z), dT)) *
.layervolume(z)
.partition(z) = (DifferentialEquations.RK4_Partitioning(AddressOf
Partitioning, .sornh4stor(z) / .layervolume(z), .solNH4stor(z) /
.layervolume(z), dT)) * .layervolume(z)
.NH4PlantUptake(z) = (DifferentialEquations.RK4_veg(AddressOf
VegUptake, .solNH4stor(z) / .layervolume(z), .No3stor(z) /
.layervolume(z), RootsKm * 1000, Ndemand,
PercentBelowGroundTextBox.Text, .depth(z), dT)) * CellArea(c)
.NO3PlantUptake(z) = (DifferentialEquations.RK4_veg(AddressOf
VegUptake, .No3stor(z) / .layervolume(z), .solNH4stor(z) /
.layervolume(z), (RootsKm * 1000), Ndemand,
PercentBelowGroundTextBox.Text, .depth(z), dT)) * CellArea(c)
.NO3Diffusion(z) = (DifferentialEquations.RK4_Diffusion(AddressOf
Diffusion, .No3stor(z) / .layervolume(z), .No3stor(z + 1) /
.layervolume(z + 1), .depth(z), .depth(z + 1), NO3dif, dT)) *
CellArea(c)
.denitrification(z) =
(DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,

```

```

.No3stor(z) / .layervolume(z), NO3toN2_(z), dT)) *
.layervolume(z)
.volatilization(z) = 0
.delpon(z) = (.Decay(z) - .enzymehydrolysis(z) - .Settling(z) +
    .Settling(z - 1))
.delson(z) = (.SONDiffusion(z) - .SONDiffusion(z - 1) +
    .enzymehydrolysis(z) - .mineralization(z))
.delnh4(z) = (.mineralization(z) + .NH4Diffusion(z) -
    .NH4Diffusion(z - 1) - .nitrification(z) + .partition(z) -
    .NH4PlantUptake(z) + .DNRA(z))
.delshn4(z) = (-.partition(z))
.delno3(z) = (.nitrification(z) + .NO3Diffusion(z) -
    .NO3Diffusion(z - 1) - .NO3PlantUptake(z) - .denitrification(z) -
    .DNRA(z))
.delveg(z) = .NO3PlantUptake(z) + .NH4PlantUptake(z)

'For the Anaerobic layers
For z = 2 To layers - 1
    CurrentDepth += .depth(z)
    .enzymehydrolysis(z) =
        (DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
        .PONstor(z) / .layervolume(z), PONtoSON_(z), dT)) *
        .layervolume(z)
    .Settling(z) =
        (DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
        .PONstor(z) / .layervolume(z), PONSettle2, dT)) *
        .layervolume(z)
    .SONDiffusion(z) =
        (DifferentialEquations.RK4_Diffusion(AddressOf Diffusion,
        .SONstor(z) / .layervolume(z), .SONstor(z + 1) /
        .layervolume(z + 1), .depth(z), .depth(z + 1), SONdif, dT)) *
        CellArea(c)
    .mineralization(z) =
        (DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
        .SONstor(z) / .layervolume(z), SONtoNH4_(z), dT)) *
        .layervolume(z)
    .nitrification(z) =
        (DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
        .solNH4stor(z) / .layervolume(z), NH4toNO3_(z), dT)) *
        .layervolume(z)
    .NH4Diffusion(z) =
        (DifferentialEquations.RK4_Diffusion(AddressOf Diffusion,
        .solNH4stor(z) / .layervolume(z), .solNH4stor(z + 1) /
        .layervolume(z + 1), .depth(z), .depth(z + 1), NH4dif, dT)) *
        CellArea(c)
    .partition(z) =
        (DifferentialEquations.RK4_Partitioning(AddressOf
        Partitioning, .sornh4stor(z) / .layervolume(z),
        .solNH4stor(z) / .layervolume(z), dT)) * .layervolume(z)
    'if the current depth is greater than the extent of the
    roots, than veg uptake does not occur
    If CurrentDepth > RootDepth Then
        .NO3PlantUptake(z) = 0
        .NH4PlantUptake(z) = 0
    Else
        .NH4PlantUptake(z) =
            (DifferentialEquations.RK4_veg(AddressOf VegUptake,
            .solNH4stor(z) / .layervolume(z), .No3stor(z) /

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```

        .layervolume(z), RootsKm * 1000, Ndemand,
        PercentBelowGroundTextBox.Text, .depth(z), dT)) *
        CellArea(c)
        .NO3PlantUptake(z) =
        (DifferentialEquations.RK4_veg(AddressOf VegUptake,
        .No3stor(z) / .layervolume(z), .solNH4stor(z) /
        .layervolume(z), (RootsKm * 1000), Ndemand,
        PercentBelowGroundTextBox.Text, .depth(z), dT)) *
        CellArea(c)
    End If
    .NO3Diffusion(z) =
    (DifferentialEquations.RK4_Diffusion(AddressOf Diffusion,
    .No3stor(z) / .layervolume(z), .No3stor(z + 1) /
    .layervolume(z + 1), .depth(z), .depth(z + 1), NO3dif, dT)) *
    CellArea(c)
    .DNRA(z) = (DifferentialEquations.RK4_FirstOrder(AddressOf
    FirstOrder, .No3stor(z) / .layervolume(z), NO3toNH4_(z), dT))
    * .layervolume(z)
    .denitrification(z) =
    (DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
    .No3stor(z) / .layervolume(z), NO3toN2_(z), dT)) *
    .layervolume(z)
    .delpon(z) = (-.enzymehydrolysis(z) - .Settling(z) +
    .Settling(z - 1))
    .delson(z) = (.SONDiffusion(z) - .SONDiffusion(z - 1) +
    .enzymehydrolysis(z) - .mineralization(z))
    .delnh4(z) = (.mineralization(z) + .NH4Diffusion(z) -
    .NH4Diffusion(z - 1) - .nitrification(z) + .partition(z) -
    .NH4PlantUptake(z) + .DNRA(z))
    .delsnh4(z) = (-.partition(z))
    .delno3(z) = (.nitrification(z) + .NO3Diffusion(z) -
    .NO3Diffusion(z - 1) - .NO3PlantUptake(z) -
    .denitrification(z) - .DNRA(z))
    .delveg(z) = .NO3PlantUptake(z) + .NH4PlantUptake(z)

Next z
'The final layer cannot diffuse mass any lower
z = layers
CurrentDepth += .depth(z)
.denitrification(z) =
(DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
.No3stor(z) / .layervolume(z), NO3toN2_(z), dT)) *
.layervolume(z)
.partition(z) = (DifferentialEquations.RK4_Partitioning(AddressOf
Partitioning, .sornh4stor(z) / .layervolume(z), .solNH4stor(z) /
.layervolume(z), dT)) * .layervolume(z)
.mineralization(z) =
(DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
.SONstor(z) / .layervolume(z), SONtoNH4_(z), dT)) *
.layervolume(z)
.enzymehydrolysis(z) =
(DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
.PONstor(z) / .layervolume(z), PONtoSON_(z), dT)) *
.layervolume(z)
.Settling(z) = (DifferentialEquations.RK4_FirstOrder(AddressOf
FirstOrder, .PONstor(z) / .layervolume(z), PONSettle3, dT)) *
.layervolume(z)

```

```

.DNRA(z) = (DifferentialEquations.RK4_FirstOrder(AddressOf
FirstOrder, .No3stor(z) / .layervolume(z), NO3toNH4_(z), dT)) *
.layervolume(z)
.delnh4(z) = (-.NH4Diffusion(z - 1) + .partition(z) +
.mineralization(z) + .DNRA(z))
.delsnh4(z) = -.partition(z)
.delno3(z) = (-.NO3Diffusion(z - 1) - .denitrification(z) -
.DNRA(z))
.delson(z) = (-.mineralization(z) - .SONDiffusion(z - 1) +
.enzymehydrolysis(z))
.delpon(z) = (.Settling(z - 1) - .Settling(z) -
.enzymehydrolysis(z))
.Peat += (.Settling(z))

'reset then current depth to 0
CurrentDepth = 0
'for each layer, reset the masses according to the calculated
changes
For z = 0 To layers
.PONstor(z) = .PONstor(z) + .delpon(z)
If .PONstor(z) < 0 Then
.PONstor(z) = 0
End If
.SONstor(z) = .SONstor(z) + .delson(z)
If .SONstor(z) < 0 Then
.SONstor(z) = 0
End If
.solNH4stor(z) = .solNH4stor(z) + .delnh4(z)
If .solNH4stor(z) < 0 Then
.solNH4stor(z) = 0
End If
.sornh4stor(z) = .sornh4stor(z) + .delsnh4(z)
If .sornh4stor(z) < 0 Then
.sornh4stor(z) = 0
End If
.No3stor(z) = .No3stor(z) + .delno3(z)
If .No3stor(z) < 0 Then
.No3stor(z) = 0
End If
PlantBioMass += .delveg(z)
'Each day, make calculations for plotting and database
storage
If T Mod 24 = 0 Then
If Not z = 0 Then
SoilStorage_t += .PONstor(z) + .SONstor(z) +
.solNH4stor(z) + .sornh4stor(z) + .No3stor(z)
Else
WaterStorage_t += .PONstor(z) + .SONstor(z) +
.solNH4stor(z) + .No3stor(z)
End If
Denitrification_t += .denitrification(z)
Nitrification_t += .nitrification(z)
DNRA_t += .DNRA(z)
decay_t += .Decay(z)
uptake_t += .NO3PlantUptake(z) + .NH4PlantUptake(z)
If z = 0 Then
volatilization_t += .volatilization(z)
End If

```

```

End If
'convert some of the storages to uM for plotting purposes
.No3stor_uM(z) = (.No3stor(z) / (.layervolume(z)) / 1000) 'uM
.NH4stor_uM(z) = (.solNH4stor(z) / (.layervolume(z)) / 1000)
'uM
.sorbNH4stor_uM(z) = (.sornh4stor(z) / (.layervolume(z)) /
1000) 'uM
'If the water has been allowed to flow through the entire
system, begin keeping track of the rates for layer analyses
If T > Tinit + FlowThroughTime Then
    If z = 0 Then
        TotalVolatilized += .volatilization(z)
        DailyNitrogenRemoved += .volatilization(z)
    End If
    ConversionFromDNRA(c, z) += .DNRA(z)
    RemovalFromDenitrification(c, z) += .denitrification(z)
    TotalDenitrified += .denitrification(z)
    ConversionFromNitrification(c, z) += .nitrification(z)
    DailyNitrogenRemoved += .denitrification(z)
End If
Next z
SoilStorage_t += .Peat
If T Mod 24 = 0 Then
    .NO3_t += .No3stor_uM(0)
    .NH4_t += .NH4stor_uM(0)
    WaterNO3stor_uM = (.No3stor(0) / (CellArea(c) * .depth(0))) /
    1000 'uM
    WatersolNH4stor_uM = (.solNH4stor(0) / (CellArea(c) *
    .depth(0))) / 1000 'uM
End If
End With
Next c

If T Mod 24 = 0 Then
    'each day, keep track of certain variables in a database and make
    statistical calculations
    FillTable(T, Denitrification_t /
    (DataGridView1.Rows(CellNumberTextBox.Text).Cells(6).Value * dT),
    Nitrification_t /
    (DataGridView1.Rows(CellNumberTextBox.Text).Cells(6).Value * dT),
    DNRA_t / (DataGridView1.Rows(CellNumberTextBox.Text).Cells(6).Value
    * dT), volatilization_t /
    (DataGridView1.Rows(CellNumberTextBox.Text).Cells(6).Value * dT),
    uptake_t / DataGridView1.Rows(CellNumberTextBox.Text).Cells(6).Value
    * dT), PlantBioMass / TotalWaterSurfaceArea, NitrogenOutput_t,
    NitrogenInput_t, 100 * NitrogenOutput_t / NitrogenInput_t, RT,
    TotalWaterSurfaceArea, CellWaterVolume, Temp, DailyNitrogenLoaded,
    100 * (SoilStorage_t + PlantBioMass) / (SoilStorage_t +
    WaterStorage_t + PlantBioMass + Litterfall))

    PlantBioMass += -litterfall_t
    SumT += T
    SumNO3Conc += WaterNO3stor_uM 'uM
    SumNH4Conc += WatersolNH4stor_uM 'uM
    SumTimeNO3Conc += T * WaterNO3stor_uM 'uMh
    SumTimeNH4Conc += T * WatersolNH4stor_uM 'uMh
    SumTT += T ^ 2

```

```

NO3slope = (days * SumTimeNO3Conc - SumT * SumNO3Conc) / (days *
SumTT - (SumT ^ 2)) 'uM/h
NO3intercept = (SumNO3Conc - NO3slope * SumT) / days 'uM
NH4Slope = (days * SumTimeNH4Conc - SumT * SumNH4Conc) / (days *
SumTT - (SumT ^ 2)) 'uM/h
NH4intercept = (SumNH4Conc - NH4Slope * SumT) / days 'uM
days += 1
'chart variables of interest for quick observation when the run is
complete
Form2.Chart5.Series("Denitrification").Points.AddXY(T / 24 /
30.41667, Denitrification_t /
(DataGridView1.Rows(CellNumberTextBox.Text).Cells(6).Value * dT))
Form2.Chart5.Series("Nitrification").Points.AddXY(T / 24 / 30.41667,
Nitrification_t /
(DataGridView1.Rows(CellNumberTextBox.Text).Cells(6).Value * dT))
Form2.Chart5.Series("DNRA").Points.AddXY(T / 24 / 30.41667, DNRA_t /
(DataGridView1.Rows(CellNumberTextBox.Text).Cells(6).Value * dT))
Form2.Chart5.Series("Volatilization").Points.AddXY(T / 24 / 30.41667,
volatilization_t /
(DataGridView1.Rows(CellNumberTextBox.Text).Cells(6).Value * dT))
Form2.Chart5.Series("Uptake").Points.AddXY(T / 24 / 30.41667,
uptake_t / (DataGridView1.Rows(CellNumberTextBox.Text).Cells(6).Value
* dT))
Form2.VegChart.Series("Series1").Points.AddXY(T / 30.41667,
PlantBioMass / TotalWaterSurfaceArea)
Form2.VegChart.Series("Series2").Points.AddXY(T / 30.41667,
Litterfall / TotalWaterSurfaceArea)
Form2.Chart2.Series("Series1").Points.AddXY(T / 24, RT * cells)
Form2.Chart1.Series("Cell 1 NO3").Points.AddXY((T / 24),
Cell(0).No3stor(0) / 1000 / CellWaterVolume)
'reset the daily accumulated values for the next day
volatilization_t = 0
Denitrification_t = 0
Nitrification_t = 0
litterfall_t = 0
DNRA_t = 0
decay_t = 0
uptake_t = 0
SoilStorage_t = 0
WaterStorage_t = 0
Form2.EfficiencyChart.Series("Series1").Points.AddXY(T / 24, 100 *
NitrogenOutput_t / NitrogenInput_t)
If T > Tinit + FlowThroughTime Then
    Form2.Chart6.Series("Series1").Points.AddXY(RT, 100 *
    NitrogenOutput_t / NitrogenInput_t)
End If
DailyNitrogenRemoved = 0
End If
If T = Tmax - 120 Then
    'chart the final soil cocentration profile for NO3 and NH4
    ChartSoilProfile(Cell)
End If
T = T + dT
Loop
Form2.SurfaceNO3Chart.Series("Surface Water Nitrate").Points.AddXY(0, NO3in)
Form2.SurfaceNH4Chart.Series("Surface Water Ammonium").Points.AddXY(0, NH4in)
For c = 0 To CInt(cells) - 1

```

```

        Form2.SurfaceNO3Chart.Series("Surface Water
        Nitrate").Points.AddXY(CInt(DataGridView1.Rows(c).Cells(2).Value +
        DataGridView1.Rows(c).Cells(1).Value / 2), (Cell(c).NO3_t / ((Tmax -
        Tinit) / 24)))
        Form2.SurfaceNH4Chart.Series("Surface Water
        Ammonium").Points.AddXY(CInt(DataGridView1.Rows(c).Cells(2).Value +
        DataGridView1.Rows(c).Cells(1).Value / 2), (Cell(c).NH4_t / ((Tmax -
        Tinit) / 24)))
    Next
    'chart the final fluxes
    ChartFluxes(NO3slope, NH4Slope, TotalDenitrified, CellWaterVolume,
    TotalWaterSurfaceArea)
Catch ex As Exception
    MessageBox.Show("Sorry. Flume Run Error: " & ex.Message & "At Time " & T)
Exit Sub
End Try
End Sub

Private Function FirstOrder(ByRef Storage, ByRef Rate) As Single
    'the first order rate equation
    FirstOrder = Storage * Rate
End Function

Private Function Diffusion(ByRef C1, ByRef C2, ByRef Depth1, ByRef Depth2, ByRef Rate) As
Single
    'diffusion of mass between layers other than the water layer
    Diffusion = -Rate * (C1 - C2) / ((Depth1 + Depth2) / 2)
End Function

Private Function DiffusionWater(ByRef C1, ByRef C2, ByRef Depth1, ByRef Depth2, ByRef
Rate) As Single
    'diffusion of mass to and from the water layer
    DiffusionWater = -Rate * (C1 - C2) / (Depth2 / 2)
End Function

Private Function VegUptake(ByRef Storage1, ByRef Storage2, ByRef Sat, ByRef Vmax, ByRef
Percent, ByRef Depth) As Single
    'Vegetation uptake of mass according to Michaelis Menten kinetics and the amount
of vegetation in a given layer
    If Storage1 = 0 Or Storage2 = 0 Then
        VegUptake = 0
    Else
        VegUptake = Vmax * Percent * (Depth / RootDepth) * (Storage1 / (Storage1 +
        Sat)) * (Storage1 / (Storage1 + Storage2))
    End If
End Function

Private Function Partitioning(ByRef sorNH4stor, ByRef solNH4stor) As Single
    'sorbtion and desorbtion of ammonium to and from the soil
    Partitioning = ((NH4PartitionCoeff * sorNH4stor) - solNH4stor) * Spectrate
End Function

Private Function Volatilization(ByRef AmmoniumStorage, ByRef pH, ByRef pk) As Single
    'volatilization of ammonium from the surface water
    Volatilization = AmmoniumStorage / (1 + (10 ^ (pk - pH)))

```

End Function

```
Private Function VolumePolynomial(ByVal Length, ByVal a, ByVal b)
    Return a * (Length ^ 2) + b * Length
End Function
```

```
Private Function LengthQuadratic(ByVal CumLength, ByVal Cumvolume, ByVal a, ByVal b)
    Dim BigA, BigB, BigC As Single
    BigA = a
    BigB = b + (2 * CumLength * a)
    BigC = -Cumvolume + (b) * CumLength + a * (CumLength ^ 2)
    Return (-BigB + Math.Sqrt((BigB ^ 2) - (4 * BigA * BigC))) / (2 * BigA)
End Function
```

```
Private Sub Quadric(ByVal WaterElevation, ByVal Length)
    Dim Depth, CumulativeDepth, AverageDepth As Single
    ReDim CellArea(CellNumberTextBox.Text)
    TotalWaterSurfaceArea = 0
    Dim z As Single
    Dim n As Integer
    Dim start, finish As Integer
    start = 0
    finish = Math.Round(Length(1))
    For c = 1 To Length.length - 1
        n = 0
        CumulativeDepth = 0
        For y = start To finish
            For x = -400 To 400
                'If x = 4600 Then Stop
                z = 0.000005 * x ^ 2 + -0.00022 * y + 0.12
                'z = 0.00000004 * x ^ 2 + 0.00000001 * y ^ 2 - 0.00022 * y + 0.12
                If z > WaterElevation Then
                    Else
                        CellArea(c) += 1
                        Depth = WaterElevation - z
                        CumulativeDepth += Depth
                        n += 1
                    End If
                Next
            Next
            AverageDepth = CumulativeDepth / n
            If c = Length.length - 1 Then
                DataGridView1.Rows(c - 1).Cells(5).Value = AverageDepth
            Else
                DataGridView1.Rows(c - 1).Cells(5).Value = AverageDepth
                start = finish
                finish = start + Math.Round(Length(c + 1))
            End If
            TotalWaterSurfaceArea += CellArea(c)
            DataGridView1.Rows(c - 1).Cells(6).Value = CellArea(c)
        Next c
        DataGridView1.Rows(CellNumberTextBox.Text).Cells(6).Value = TotalWaterSurfaceArea
    End Sub
```

```
Private Sub ReassignRates()
    If SeasonalAmmoniumCheckBox.Checked = True Then
```



```

    NH4in = Seasonal(T / 24, AmmoniumEquationTextBox)
End If
If SeasonalNitrateCheckBox.Checked = True Then
    NO3in = Seasonal(T / 24, NitrateEquationTextBox)
End If
If SeasonalTemperatureCheckBox.Checked = True Then
    Temp = Seasonal(T / 24, TemperatureEquationTextBox)
Else
    Temp = TemperatureTextBox.Text
End If
If SeasonalNdemandCheckBox.Checked = True Then
    Ndemand = NitDemand(T / 24, SeasonalNdemandTextBox)
    If Ndemand < 0 Then
        Ndemand = 0
    End If
End If
If DependentDecayCheckBox.Checked = True Then
    If 0 < Temp And Temp < 28 Then
        PlantNdecay = DecayTextBox.Text * TemperatureRates(Temp,
            DecayEquationTextBox1) / 24
    ElseIf 28 <= Temp Then
        PlantNdecay = DecayTextBox.Text * TemperatureRates(Temp,
            DecayEquationTextBox2) / 24
    End If
End If
If EnzymeHydrolysisCheckBox.Checked = True Then
    For z = 0 To 6
        PONtoSON_(z) = TemperatureRates(Temp, EnzymeHydrolysisTemperatureTextBox)
        * TabPage4.Controls.Item("PONtoSONTextBox" & z).Text()
    Next
    For z = 7 To layers
        PONtoSON_(z) = PONtoSON_(z - 1)
    Next
End If
If MineralizationCheckBox.Checked = True Then
    For z = 0 To 6
        SONtoNH4_(z) = TemperatureRates(Temp, MineralizationTemperatureTextBox) *
        TabPage4.Controls.Item("SONtoNH4TextBox" & z).Text()
    Next
    For z = 7 To layers
        SONtoNH4_(z) = SONtoNH4_(z - 1)
    Next
End If
If NitrificationCheckBox.Checked = True Then
    For z = 0 To 6
        If Temp >= 0 And Temp <= 35 Then
            NH4toNO3_(z) = TemperatureRates(Temp,
                NitrificationTemperatureTextBox1) *
            TabPage4.Controls.Item("NH4toNO3TextBox" & z).Text()
        Else
            NH4toNO3_(z) = TemperatureRates(Temp,
                NitrificationTemperatureTextBox2) *
            TabPage4.Controls.Item("NH4toNO3TextBox" & z).Text()
        End If
    Next
    For z = 7 To layers
        NH4toNO3_(z) = NH4toNO3_(z - 1)
    Next

```

```

End If
If DenitrificationCheckBox.Checked = True Then
    For z = 0 To 6
        If Temp >= 0 And Temp <= 10 Then
            NO3toN2_(z) = TemperatureRates(Temp,
            DenitrificationTemperatureTextBox1) *
            TabPage4.Controls.Item("NO3toN2TextBox" & z).Text()
        ElseIf Temp > 10 And Temp <= 20 Then
            NO3toN2_(z) = TemperatureRates(Temp,
            DenitrificationTemperatureTextBox2) *
            TabPage4.Controls.Item("NO3toN2TextBox" & z).Text()
        Else
            NO3toN2_(z) = TemperatureRates(Temp,
            DenitrificationTemperatureTextBox3) *
            TabPage4.Controls.Item("NO3toN2TextBox" & z).Text()
        End If
    Next
    For z = 7 To layers
        NO3toN2_(z) = NO3toN2_(z - 1)
    Next
End If
If DNRACheckBox.Checked = True Then
    For z = 0 To 6
        NO3toNH4_(z) = TemperatureRates(Temp, DNRATemperatureTextBox) *
        TabPage4.Controls.Item("NO3toNH4TextBox" & z).Text()
    Next
    For z = 7 To layers
        NO3toNH4_(z) = NO3toNH4_(z - 1)
    Next
End If
If SeasonalMortalityCheckBox.Checked = True Then
    If T / 24 < 122 Then
        Litterfall = 0
    Else
        Litterfall += Mortality(T / 24, SeasonalMortalityTextBox) * PlantBioMass
        'umolN
        litterfall_t = Mortality(T / 24, SeasonalMortalityTextBox) * PlantBioMass
        'Litterfall = (DifferentialEquations.RK4_FirstOrder(AddressOf FirstOrder,
        PlantBioMass / .layervolume(z), PlantNdecay, dT)) * .layervolume(z)
    End If
Else
    End If
pK = 0.09018 + 2729.92 / (273.2 + Temp)

If SeasonalElevationCheckBox.Checked = True Then
    If T >= 0 And T < 214 Then
        WaterElevation = Seasonal(T / 24, ElevationEquationTextBox1)
    Else
        WaterElevation = Seasonal(T / 24, ElevationEquationTextBox2)
    End If
Else
    WaterElevation = WaterElevationTextBox.Text
End If

If DependentFlowCheckBox.Checked = True Then
    WaterElevationTextBox.Text = WaterElevation
    Button2_Click(Nothing, Nothing)

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CellWaterVolume = DataGridView1.Rows(1).Cells(3).Value
For c = 0 To cells - 1
    Cell(c).depth(0) = DataGridView1.Rows(c).Cells(5).Value
    CellLength(c) = CInt(DataGridView1.Rows(c).Cells(1).Value)
    CellArea(c) = DataGridView1.Rows(c).Cells(6).Value
    Cell(c).layervolume(0) = CellWaterVolume
Next
InletRateTextBox.Text = Flow(WaterElevation, FlowEquationTextBox)

RT = Math.Round((1 / InletRateTextBox.Text) * CellWaterVolume / (60 * 60), 2)
InputRate = InletRateTextBox.Text
Else

    WaterElevation = WaterElevationTextBox.Text
    RT = Math.Round((1 / InletRateTextBox.Text) * CellWaterVolume / (60 * 60), 2)
End If
DailyNITrogenLoaded = (NH4in + NO3in + SONin + PONin) * (InputRate * 1000) * (60
    * 60 * 24) * (14 / (1000000 * 1000)) / (TotalWaterSurfaceArea * 0.0001)
Form2.LoadingRateChart.Series("Loading Rate").Points.AddXY(T / 24,
DailyNITrogenLoaded)
Form2.LoadingRateChart.Series("Flow Rate").Points.AddXY(T / 24, InputRate)
End Sub

Public Class DifferentialEquations

    Public Delegate Function FirstOrder(ByRef y1 As Single, ByRef R As Single) As Single
    Public Delegate Function Diffusion(ByRef y1 As Single, ByRef y2 As Single, ByRef D1
        As Single, ByRef D2 As Single, ByRef R As Single) As Single
    Public Delegate Function Partitioning(ByRef y1 As Single, ByRef y2 As Single) As
Single
    Public Delegate Function Veg(ByRef y1 As Single, ByRef y2 As Single, ByRef K As
        Single, ByRef V As Single, ByRef V As Single, ByRef D1 As
        Single) As Single
    Public Delegate Function vegstor(ByRef y1 As Single, ByRef y2 As Single, ByRef D1 As
Single) As Single
    Public Delegate Function volatilization(ByRef y1 As Single, ByRef ph As Single, ByRef
pk As Single) As Single

    Public Shared Function RK4_FirstOrder(ByRef F As FirstOrder, ByRef y1 As Single, ByRef R
        As Single, ByRef dT As Single) As Single
        Dim k1 As Double = dT * F(y1, R)
        Dim k2 As Double = dT * F(y1 + k1 / 2, R)
        Dim k3 As Double = dT * F(y1 + k2 / 2, R)
        Dim k4 As Double = dT * F(y1 + k3, R)
        'MessageBox.Show(k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
        Return (k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
    End Function

    Public Shared Function RK4_Diffusion(ByRef F As Diffusion, ByRef y1 As Single, ByRef y2
        As Single, ByRef D1 As Single, ByRef D2 As Single,
        ByRef R As Single, ByRef dT As Single) As Single
        Dim k1 As Double = dT * F(y1, y2, D1, D2, R)
        Dim k2 As Double = dT * F(y1 + k1 / 2, y2 + k1 / 2, D1, D2, R)
        Dim k3 As Double = dT * F(y1 + k2 / 2, y2 + k2 / 2, D1, D2, R)
        Dim k4 As Double = dT * F(y1 + k3, y2 + k3, D1, D2, R)
        'MessageBox.Show(k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
        Return (k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
    End Function

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```

Public Shared Function RK4_Partitioning(ByRef F As Partitioning, ByRef y1 As Single,
                                       ByRef y2 As Single, ByRef dT As Single) As Single
    Dim k1 As Double = dT * F(y1, y2)
    Dim k2 As Double = dT * F(y1 + k1 / 2, y2 + k1 / 2)
    Dim k3 As Double = dT * F(y1 + k2 / 2, y2 + k2 / 2)
    Dim k4 As Double = dT * F(y1 + k3, y2 + k3)
    'MessageBox.Show(k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
    Return (k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
End Function

Public Shared Function RK4_veg(ByRef F As Veg, ByRef y1 As Single, ByRef y2 As Single,
                               ByRef K As Single, ByRef V As Single, ByRef P As Single,
                               ByRef D1 As Single, ByRef dT As Single) As Single
    Dim k1 As Double = dT * F(y1, y2, K, V, P, D1)
    Dim k2 As Double = dT * F(y1 + k1 / 2, y2 + k1 / 2, K, V, P, D1)
    Dim k3 As Double = dT * F(y1 + k2 / 2, y2 + k2 / 2, K, V, P, D1)
    Dim k4 As Double = dT * F(y1 + k3, y2 + k3, K, V, P, D1)
    'MessageBox.Show(k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
    Return (k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
End Function

Public Shared Function RK4_vegstor(ByRef F As vegstor, ByRef y1 As Single, ByRef y2 As
                                   Single, ByRef D1 As Single, ByRef dT As Single) As
                                   Single
    Dim k1 As Double = dT * F(y1, y2, D1)
    Dim k2 As Double = dT * F(y1 + k1 / 2, y2 + k1 / 2, D1)
    Dim k3 As Double = dT * F(y1 + k2 / 2, y2 + k2 / 2, D1)
    Dim k4 As Double = dT * F(y1 + k3, y2 + k3, D1)
    'MessageBox.Show(k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
    Return (k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
End Function

Public Shared Function RK4_volatilization(ByRef F As volatilization, ByRef y1 As Single,
                                           ByRef ph As Single, ByRef pk As Single, ByRef dT
                                           As Single) As Single
    Dim k1 As Double = dT * F(y1, ph, pk)
    Dim k2 As Double = dT * F(y1 + k1 / 2, ph, pk)
    Dim k3 As Double = dT * F(y1 + k2 / 2, ph, pk)
    Dim k4 As Double = dT * F(y1 + k3, ph, pk)
    'MessageBox.Show(k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
    Return (k1 / 6 + k2 / 3 + k3 / 3 + k4 / 6)
End Function
End Class

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VITA

Benjamin Lee Branoff was born in Daytona Beach, Florida. He attended Seabreeze Senior High School and graduated in 2003. He then immediately enrolled in the University of Florida, although it would be four years until he officially enrolled in the Environmental Engineering Sciences program, in which he received his bachelor's degree in 2009. As part of his undergraduate experience, Ben enrolled in two separate study abroad programs in Africa. The first, as part of the University of Florida's study abroad program, took place during the spring semester of 2007 at the University of Dar es Salaam, Tanzania. The second was awarded as a National Science Foundation's Research Experience for Undergraduates at the University of Cape Coast, Ghana. For six weeks, Ben served as the student director of this program while studying rocky shore intertidal ecology along the Ghanaian coast. Ben also worked as an aquatic toxicology laboratory technician at a local environmental consulting firm in Gainesville, FL during his undergraduate time. Immediately after graduation, Ben began a five month trek of the Pacific Crest Trail, in which he hiked 2,000 miles from the Canadian border with Washington State to Kennedy Meadows at the southern terminus of the Sierra Mountains in California. Before enrolling in the Master of Science program within the Department of Oceanography and Coastal Sciences at Louisiana State University in August of 2010, he worked as an environmental and marine science educator in the Florida Keys, where he earned his rescue diver certification. While enrolled at Louisiana State University, Ben served as the president of the Coast and Environment Graduate Organization. He developed a local environmental science radio program called, "Louisiology", which aired on a community radio station and is available as a podcast online. Along with Dr. Victor Rivera-Monroy, Ben also co-wrote the nitrogen spatial statistical model for the 2012 Louisiana Master Plan for a Sustainable Coast, in

collaboration with the Louisiana Coastal Protection and Restoration Authority as well as various modelers from around the state. He is expected to graduate in December of 2012 with a Master of Science in Oceanography and Coastal Sciences and a 4.0 GPA.