ABSTRACT

Title of Thesis: IMPORTANCE OF CHANNEL NETWORKS ON NITRATE RETENTION IN FRESHWATER TIDAL WETLANDS, PATUXENT RIVER, MARYLAND

Emily Seldomridge, M.S., 2009

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Freshwater tidal marshes border stream channels near the upstream end of the tidal limit, and are likely to undergo significant changes in salinity, tidal inundation, and biogeochemical processes due to sea-level rise. Tidal channel networks enhance nutrient processing by delivering nitrate-rich water far into the marsh. The purpose of this study is to examine the geomorphological, hydrological, and biogeochemical processes that influence the delivery and processing of nutrient-rich waters into tidal marshes. In this study, field measurements were made to calculate water and nitrate flux for stream channels of varying order. These mass balance calculations indicate there is an exponential increase in net nitrate retention with channel order. This calculation could be compared with calculations of denitrification at different sites within the system to evaluate the role of these processes in total nitrate loss.

IMPORTANCE OF CHANNEL NETWORKS ON NITRATE RETENTION IN FRESHWATER TIDAL WETLANDS, PATUXENT RIVER, MARYLAND

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TABLE OF CONTENTS

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

1. INTRODUCTION

1.1.1 Importance of freshwater tidal wetlands

Freshwater tidal wetlands are diverse habitats that appear to play important roles in coastal nutrient budgets (Boynton et al., 2008). Hydrologic and ecological processes in tidal marsh systems are influenced by the dense networks of tidal channels that they often contain (Fig. 1.1). The Patuxent River is an example of a river system that is bordered by extensive channel network tidal wetlands in the freshwater segments of the river. Much of the freshwater tidal wetland area in the Upper Patuxent is in parkland (e.g. Jug Bay, Patuxent Wetland Park, and Patuxent River Park), which helps to limit human impacts to upstream modifications of the nutrient, sediment, and water fluxes into the Patuxent. Although tidal freshwater wetlands are areas for nutrient retention (e.g. Swarth and Peters, 1993; Vitousek et al., 1997), the importance of the tidal channel systems in nutrient retention processes has not been evaluated.

There have been few studies that quantify nitrogen retention within tidal freshwater wetlands (Greene, 2005*a*; Megonigal and Neubauer, 2009). Instead studies have focused on saltwater wetlands and terrestrial systems, or on one specific mechanism of loss from freshwater systems. There is also a lack of studies quantifying nitrogen loss *in situ* to ultimately characterize ecosystem processing. Previous research has, however, pointed to the idea that the majority of nitrogen processing occurs on the marsh surface area (Jenkins and Kemp, 1984; Joye and Paerl, 1994; Dong, 2000; Eriksson et al., 2003; Greene, 2005*b*), with additional sites including the near-channel groundwater (Phemister, 2006) and the channel itself (Seitzinger, 1988). These sites are particularly important to understand because they are likely to undergo significant hydrological and salinity changes associated with sea-level rise.

1.1.2 The tidal network and sea level rise

Rising sea level is affecting geomorphic, hydraulic, and ecosystem processes in tidal wetlands because as the wetlands are submerged there is a shift in wetland abundance and location (Kearny et al., 1988). Microtidal (<2 m tidal range) wetland systems, such as most freshwater tidal marshes, appear to be the most affected by sea level rise (Craft, et al. 2009; Stevenson and Kearney; in press). Wetland loss has great implications for ecosystem services because freshwater wetlands can sequester three times more nitrogen in the sediment by burial than can saltwater marshes (Craft, et al. 2009).

In tidal freshwater wetlands, sea level rise is causing wetland submergence, salt water intrusion, and inward habitat migration. Salt water intrusion affects coastal areas because as the water level increases, the barrier between fresh and salt water moves upstream, and once diverse freshwater habitats become less diverse salt water ecosystems. The Chesapeake Bay is a drowned river valley, and as such, the wetlands are migrating inland with sea level rise, which is approximated at 3 mm/year (Douglas, 2001). Tidal network marshes are being lost because sediment accretion isn’t occurring quickly enough to match the accelerated sea level rise, and these wetlands are becoming submerged. This trend is becoming evident in the Patuxent River wetland where the interior of the tidal channel network is beginning to be submerged.

Sea level rise is predicted to have negative impacts on the wetland ecosystems, but tidal freshwater wetlands may play an important role in nitrogen processing. The tidal channel network acts as a vehicle to transport nitrogen to the interior smaller order channels. Sea level rise will contribute a greater volume of water into this network. The greater volume of water will be forced into these smaller order channels, so that on a flooding tide a greater portion of the marsh is submerged. The greater area of marsh inundation may actually increase denitrification rates. Even though tidal freshwater marshes are ‘hot spots’ for denitrification and the rates may increase with sea level rise, if the wetlands can’t keep pace with increasing water levels, denitrification rates will be drastically reduced because marsh surface area will be reduced.

1.1.3 Tidal marsh terminology

The tidal channel network within this study is defined as the highly branching system of streams found within the tidal freshwater wetland (Fig. 1.1). The mainstem or main channel is the stream that passes adjacent to the marsh. Within this study, ‘channels’ and ‘streams’ are used interchangeably, and are defined as the body of water constrained by the surrounding wetlands. Interior channels are those found within the highly branching tidal network. Exterior channels are those that are located directly off of the main channel.

Several methods are used to define stream order; these methods generate different numerical values for stream orders larger than two. The ordering scheme developed by Horton (1945) indicates the degree of branching from the principal order stream (Fig. 1.1). A first order channel is the stream headwaters. A second order channel is the downstream channel of where two first order channels meet. A third order channel is the downstream channel where two second order channels meet, and so on. Order can be determined by aerial photos such as that pictured below, but the certainty in this method depends on the accuracy of the photo. Aerial photos often do not show all the first order channels, because they are very narrow and the channel can be hidden by vegetation (Lillibridge, 2009).

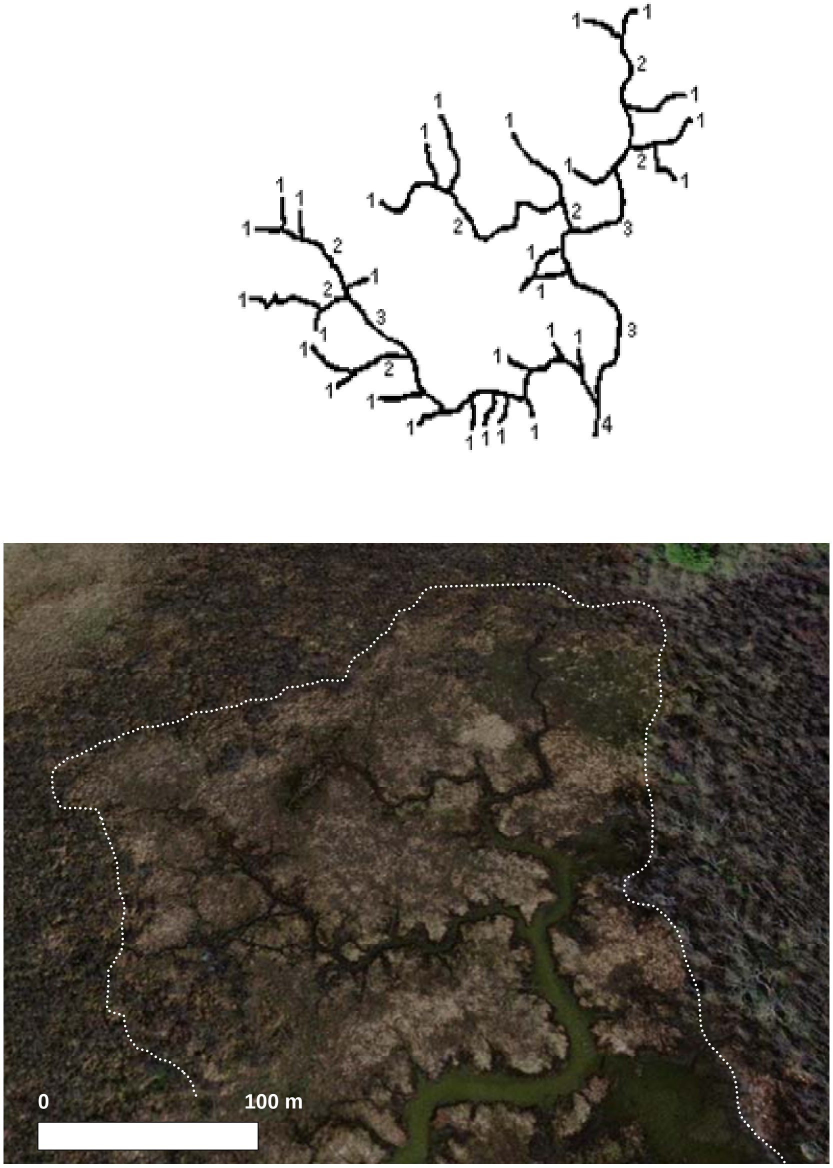


Figure 1.1. Example of the numbering of stream channel order (Smith-Hall, 2002) and an aerial photograph showing the complexity of tidal channel networks of the Upper Patuxent River. Image from U.S. Geological Survey photo, April 2005, obtained from Google Earth.

1.1.4 Influence of tidal network on nitrate retention

The tidal network is an important geomorphic factor that may exert controls on the locations and rates of ecologic processes within the wetland system. It has been suggested that tidal marshes can serve as sinks for nutrients (Valiela et al., 1973; Merrill and Cornwell, 2000). Within tidal marshes, water flux within the tidal channel network is the only vehicle that transports nutrients into smaller order channels, and ultimately floods into the surrounding marsh where nutrient removal is thought to occur. The geomorphic structure of the network determines the amount of water that enters the channel, the amount of overbank flooding that occurs, and the residence time of the water in the marsh system. Overall, little is known about the control that the channel geomorphic organization has on net nitrate retention within these tidal marsh systems.

1.1.5 Objectives

The overall objective of this study is to determine how the geomorphic and hydrologic organization of the tidal network influences net nitrate retention within tidal marsh systems. This study links together geomorphic, hydrologic, and biogeochemical investigations. The following hypotheses were examined:

1. Previous research suggests that tidal channel velocities are nearly constant through the network; therefore, water flux (and nitrate flux) into tidal marsh networks is primarily determined by channel cross sectional area.
2. Nitrate processing varies by type of site within the tidal marsh system, with marsh surface denitrification> groundwater denitrification > in-stream denitrification.
3. Marsh surface area, however, is extensive; therefore, net nitrate retention within a marsh system should increase at the same rate as the increase in marsh surface area when comparing marsh systems of varying size.

2. PREVIOUS WORK

The quality of coastal waters, such as the Chesapeake Bay, has been adversely affected by anthropogenic activities (Nixon, 1995). The most substantial anthropogenic alterations have occurred through land-use changes to agricultural and urban lands. Landuse change alters how the atmosphere interacts with the aquatic and terrestrial systems. This land-cover change has caused increased fluxes of particulates and nutrients, such as nitrogen (N) and phosphorus (P) (Vitousek et al. 1997; Galloway et al. 2008). Reduced water clarity and increased sediment loading have contributed to the losses of submerged aquatic vegetation. Increased sediment loading promotes turbidity and sedimentation, while increased N and P loading stimulates phytoplankton growth, both of which reduce water clarity

The combination of increased organic sediments and the decomposition of phytoplankton often lead to seasonal hypoxia or in extreme conditions anoxia, in the process known as eutrophication (Boynton et al., 1995). In the Mid-Atlantic region, landuse change has increased the rate of nitrogen deposition on the land and increased the delivery of nitrogen to bodies of water (Boyer et al., 2002), which causes many Chesapeake Bay systems to be eutrophic.

Resolving the issue of population-based eutrophication is imperative to improving the health of the Chesapeake Bay, but it is a daunting task. At one time, managers believed that reducing direct nutrient inputs into an ecosystem would allow the system to return to an idealized reference state. It is now known that even by removing direct human pressures such as nutrient inputs, ecosystems may not revert back to this idealized reference condition. Often times there are shifting baselines or the system may have reached a threshold that resulted in a drastic regime shift. This suggests that reversing eutrophication by nutrient removal alone isn't possible, and managers must now focus on restoring and preserving key ecosystem functions (Duarte et al., 2008).

To evaluate this problem, we must define the ecosystem function of nitrogen processing in various locations within the tidal wetlands, and determine how they are controlled by external factors, such as tidal network geomorphology and hydrology.

1.2.1 Geomorphic and hydrologic organization

Freshwater tidal wetlands include both fringing wetlands, and marshes that contain tidal channel networks that affect the movement of water and nutrients into the marsh ecosystem (Smith-Hall, 2002). These tidal network channels are hydraulically connected to the marsh groundwater (Nuttle, 1988); thus, nitrogen processing can take place *within the tidal channels, on the marsh surfaces, and in the near-channel groundwater*. The relative importance of these sites for net nitrate retention is not well understood.

Although the relative importance of the above mentioned sites is unknown, models infer that nitrogen is lost as water moves through the tidal channel networks, and tidal channels are influential on denitrification rates (Seitzinger et al., 2002). River networks can remove ~ 48% and as high as ~ 80% of nitrogen inputs while exporting only ~ 20-40% of the total nitrogen inputs downstream or to coastal systems. Low order streams (1st and 2nd order) receive the greatest proportion of direct watershed nitrogen loading, and can also remove the largest amount of this nitrogen before reaching larger orders. Smaller orders (1st to 4th) encompass 91% of the channel networks while larger orders (5th to 9th) only compose 9% of the networks. Models have predicted that the smaller orders remove less nitrogen than larger orders, but there is a greater extent of smaller orders than larger orders within a network, so that sum of smaller orders remove 60-70% of nitrogen while the sum of larger orders only removes 30-40% of nitrogen (Seitzinger et al., 2002). Additionally, Peterson et al. (2001) found that smaller streams with high nitrogen loads removed a proportionally larger amount of nitrogen because of the large surface area to volume ratio. Overall, the exact importance of the tidal network is still largely unknown.

To compare the importance of the components of the tidal network, the channels of the network must first be classified. Tidal marsh networks are not homogeneous; however, the channels have systematic geomorphic properties, such as relationships between stream order and stream length, that aid in characterizing the channels. First order channels are the most heterogeneous of all orders, and the degree of heterogeneity differs depending on whether the channel is located directly off of the mainstem (exterior channels) or within a highly branching network (interior channels). Although there is variability within smaller orders, tidal channel order characterizes channel width and channel length, which control the discharge and extent of marsh surface area (Myrick and Leopold, 1963; Williams and Zedler, 1999; Smith-Hall, 2002).

The complexity of the geomorphology of the wetland channel network is important because if nitrogen isn't processed in one region, it is transported by the tides to a different location within the system where it is then processed. Each individual channel order is therefore integral to the overall ecosystem function. The geomorphology of the tidal network is a significant controlling factor in denitrification because the channel geometry governs the hydrology of the network. The width and depth of the channel mouth can restrain the amount of water that can flux into and out of the channel since discharge is proportional to channel area and therefore channel width (Myrick and Leopold, 1963). Since the classic Myrick and Leopold (1963) paper was published, very little research has been conducted to evaluate the geomorphology of tidal freshwater wetlands, and how this controls ecosystem functioning.

1.2.1a Hydraulic geometry

Hydraulic geometry can be used to determine the relationship between channel forms and discharge (Myrick and Leopold, 1963). At-a-station hydraulic geometry relates the adjustment of hydraulic characteristics (such as width, depth, and velocity) to changing discharge at one cross-section location. At-a-station hydraulic geometry uses the continuity equation Q = w*d*v:

$$
\begin{gathered}
w \ \alpha \ Q^{b} \\
d \ \alpha \ Q^{f} \\
v \ \alpha \ Q^{m}
\end{gathered}
$$

where *Q* is the discharge, *w* is surface width, *d* is mean depth, *v* is mean velocity, and *b*, *f*, and *m* are exponents. The exponents add to equal one, $b + f + m = 1$. These values are related to the qausi-equilibrium state of the channel, or the equilibrium conditions necessary to transport the sediment and water of the system. Natural tidal freshwater wetlands are generally morphologically balanced, relatively low energy systems (Garofalo, 1980), and therefore annual stream channel migration is small. Channels naturally migrate laterally, but tidal freshwater wetlands only migrate about 1.04 feet per year (Garofalo, 1980). Characterizing channel networks is very important because the relationships can be used to predict other factors within the wetland system, such as nitrogen loss, the distribution of vegetation in wetland systems (Sanderson et al., 2000), or the composition of fish communities within varying channel orders (Visintainer et al. 2006). These relationships are critical for gaining an understanding of geomorphologic controls on the tidal network system; however, research describing tidal channel hydraulic geometry remains limited, and generally geomorphology literature examines streams or salt marsh systems.

1.2.2 Denitrification in the tidal channel network

Tidal freshwater marshes can serve as sinks for nutrients contributed by stream-flow and groundwater discharge from terrestrial ecosystems (Odum, 1980; Boesch, 2000). The role of sub-tidal sediments as a potential sink for nitrogen is well established (Jenkins and Kemp, 1984; Eriksson et al., 2003; Greene, 2005*b*). Surfaces of tidal marshes are additional sinks for nitrogen (Joye and Paerl, 1994; Dong, 2000). Sedimentation, plant assimilation, and denitrification are reported to be the most important sinks for nitrogen (Bowden, 1986). Denitrification can occur on marsh surfaces (Fig. 1.2; Joye and Paerl, 1994), in the shallow groundwater (Addy et al. 2002), and in the channels (Seitzinger, 1988). The proportion of nitrate that undergoes denitrification is controlled by the hydrology and geomorphology of the system (Seitzinger et al., 2006).

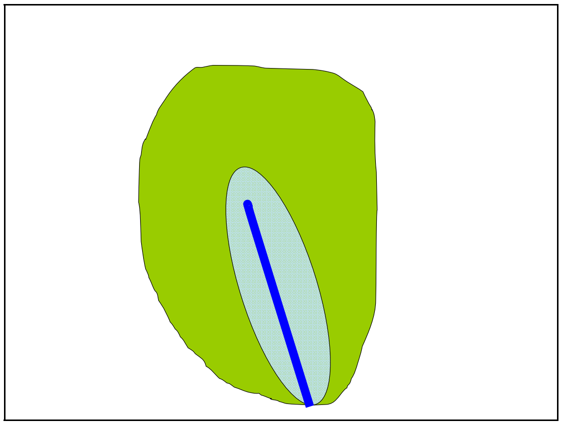


Figure 1.2. Conceptual diagram of locations of nitrogen processing within a tidal freshwater wetland channel. The green is the marsh surface area, light blue is near channel groundwater, and the dark blue is in-stream.

Tidal networks are critical for denitrification because they increase the amount of marsh surface area per volume of channel water, and in some freshwater tidal streams, marsh area exceeds the river bottom area. In tidal channel ecosystems, nitrate-rich water infiltrates into the marsh system, and then drains back into the channels in regions within 20 m of a tidal channel (Harvey et al., 1987; Nuttle, 1988; Phemister, 2006). Groundwater denitrification rates, in general, are limited by amount of this exchange (Lowrance et al., 1984; Cooper, 1990; Hedin et al., 1998). In Jug Bay, groundwater fluxes from the marsh to the channel are a function of channel depth, stream length, and hydraulic parameters (hydraulic conductivity, K, and gradient). These parameters (K and gradient) don’t change much due to stream order; therefore, total stream channel length and channel depth are the major controls on groundwater flux, and groundwater processing may be a major source of nitrogen loss (Phemister, 2006).

In-stream denitrification has been examined for both tidal and terrestrial stream channels, and in both cases, denitrification is highest where water flow is the slowest, and where there is the largest interaction between water and sediment. In general, water column denitrification is highest in shallow, low order streams (Seitzinger, 1988); however, the overall greatest denitrification rates are in the sediments, and in-stream denitrification is thought to be minimal in comparison.

1.2.2a Approaches to quantifying denitrification

Selected previous work on denitrification rates within different locations in freshwater tidal wetlands is summarized in table 1.I; a comprehensive review can be found in Greene (2005*a*). Although previous research suggests that denitrification, burial, and assimilation are important loss pathways for nitrogen, the role of denitrification may be overemphasized. Current research has pointed to the idea that alternative microbial pathways may play an integral role in net nitrogen retention in freshwater ecosystems (Burgin and Hamilton, 2007). This idea has been exemplified through nitrogen loading experiments conducted in aquatic sediments where denitrification accounted for less than half of the total nitrate disappearance (Seitzinger, 1988). Although previous research has separately quantified loss pathways, little research has taken a mass balance approach to determine the ultimate importance of denitrification. Studies have separately quantified nitrogen burial (Table 1.I; Eriksson et al., 2003; Greene, 2005*b*), groundwater inputs (Taniguchi, 2008), and benthic microbial processing (Joye and Paerl, 1994; Arango et al., 2007), but have failed to link these processes to the organization or geomorphology of the freshwater tidal network.

Table 1.I. Selected denitrification rates measured during the growing season for various types of freshwater marsh systems (including natural and constructed wetlands) using acetylene inhibition, core incubation, ^{15}N tracer, N$_2$ flux, and mass balance calculations

Denitrification Rate	**Location of Study**	**Technique**	**Source**
Measurements from Soil Surface and Subsurface (0-15cm)-Localized Area of Study			
46 ± 15 to 107 ± 31 μmol N m^{-2} h^{-1} April	Ponded freshwater marsh, Davis Pond Diversion Structure, LA (created)	Acetylene inhibition	DeLaune et al., 2005
Max rate: 450 μmol N m^{-2} h^{-1} Sept.	Northern portion of the Barataria Basin Estuary receiving water from Davis Pond Diversion, LA (created system)	^{15}N labeling; N$_2$:N$_2$0 gas sampling	Yu et al., 2006
3.3 to 57.1 μmol N m^{-2} h^{-1} March-July	Intertidal region of freshwater tributary Tomales Bay, CA	Acetylene inhibition	Joye and Paerl, 1994
28 (fall) to 178 (spring) μmol N m^{-2} h^{-1}	Tidal freshwater wetland, Patuxent River, MD	Core incubation N$_2$:Ar	Merrill and Cornwell, 2000
≤ 20 to 260 μmol N m^{-2} h^{-1} Summer	Freshwater riparian wetlands, NJ/PA	Core incubation N$_2$:Ar	Seitzinger, 1994
0 ± 1 to 99 ± 5 μmol N m^{-2} h^{-1}	Vilhemsborg sø, Denmark	Acetylene inhibition	Setizinger et al., 1993
77 to 290 μmol N m^{-2} h^{-1}		^{15}N tracer	
395 ± 45 to 490 ± 120 μmol N m^{-2} h^{-1} September		N$_2$ flux	
0 to 330 μmol N m^{-2} h^{-1}	Literature review of 52 freshwater wetlands	Various	Greene, 2005*a*
Max rate in spring: 500 μmol N m^{-2} h^{-1} Annual average: 110 μmol N m^{-2} h^{-1}	Tidal freshwater marsh, Patuxent River, MD	Core incubations N$_2$:Ar	Boynton et al., 2008
Measurements from Soil Surface and Water Column-Whole Ecosystem Approach			
65 to 881 ± 162 μmol (NO$_2$+ NO$_3$) m^{-2} tide^{-1} July-August	Intertidal freshwater emergent marsh, Upper Cooper River, SC	Tidal mass balance calculation	McKellar et al., 2007
54 to 278 μmol N m^{-2} h^{-1} April and July	Created freshwater wetland, Lake Waco Wetland, TX (created)	Core incubations (N$_2$:Ar) and chemical analysis of water column nutrients	Scott et al., 2008

There is a large variability within the above reported rates because each experiment has a different area of study, not only by location within the wetland, but also by type of wetland (i.e. restored wetlands, or wetlands experiencing controlled hydrologic releases compared to natural wetlands such as those studied by Merrill and Cornwell, 2000). The researchers may have overestimated *in situ* rates because the acetylene inhibition and core incubations measure potential denitrification rates. These overestimations are then used to extrapolate ecosystem denitrification rates with a synergistic effect of overestimation. Since wetlands have high spatio-temporal variability, the entire ecosystem functioning is still unknown. The variability documented within the above table suggests that researchers may have inaccurately estimated denitrification on a large scale.

It is difficult to measure denitrification over a large spatial scale, so researchers target denitrification 'hot spots.' It is well known that denitrification occurs within the marsh soils of the marsh surface/subsurface, the near-channel groundwater (within 20 meters of the channel), and the channel itself (Fig 1.2). In an effort to encompass the variability of denitrification, researchers often compartmentalize the ecosystem to describe the processing (i.e. Boynton et al., 2008). Again, conceptual models can be powerful tools, but within the Chesapeake Bay, the estuary is divided by salinity regions such as Upper, Mid, and Lower regions, and the geomorphology of the system is often overlooked.

This study will link together the geomorphology (by characterizing channel geometry by order), hydrology (by measuring total volume of water fluxes into and out of the channel order), and biogeochemistry (by measuring nitrogen concentrations over a tidal cycle) to characterize the ecosystem function of net nitrogen retention within the tidal channel network, and determine if geomorphology alone can be used to predict net nitrate retention.

3. EXPERIMENTAL APPROACH

1.3.1 Study site

The freshwater tidal wetlands investigated for this study receive streamflow inputs from the tidal Patuxent River. The Patuxent River watershed is located between Washington, D.C. and Baltimore and is 2,260 km^2 in area. The land-use in the basin is dominated by forest (63.5%), followed by agriculture (20.3), urban (15.7%), and intertidal wetlands (0.4%). Agriculture land-uses have decreased in the 20th century as the basin underwent reforestation and suburbanization, and much of the agriculture land was lost as the population expanded. The population has increased 10 fold since 1950. The population density for this basin is 262 no. km^{-2} with a sewage flow of 235×10^6 L d^{-1} (Fisher et al., 2006).

The research site (Fig. 1.3) is located within Patuxent Wetland Park in Anne Arundel County (38°48'42"N 76°42'35"W). The area is a tidal freshwater environment, and generally experiences salinities less than 0.2 ppt. Tides in the Park are semi-diurnal and generally range 0.6 meters (NERRS, 2004). The Patuxent Wetland Park has many heterogeneous tidal channels ranging in order from 0 to greater than 5 (Smith-Hall, 2002). There is a mobile home park development on the banks of the Patuxent including a wastewater treatment plant that discharges directly into the waterway.

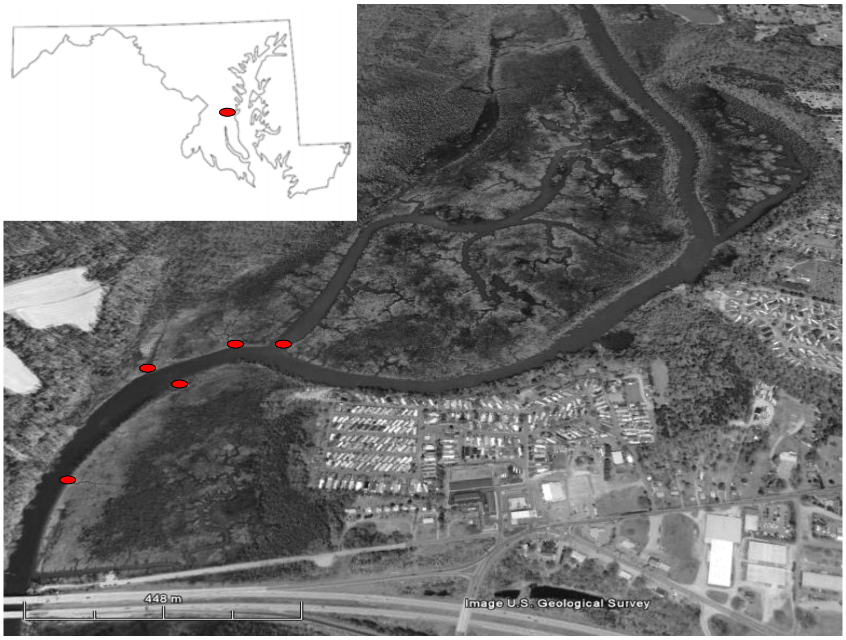


Figure 1.3. Aerial map of research site showing channel network complexity and heterogeneity of tidal channels.

The study site is a naturally meandering channel with a variety of orders of branching tributaries. The branching tributaries, ranging from 1st-5th order, were used in this study. The lower marsh of both sites is dominated by *Nuphar advena/luteum, Peltandra virginica*, *Polygonum sagittatum*, *Pontederia cordata,* and *Zizania aquatica*. The river bed is seasonally dominated by invasive *Elodea* species, which affect water velocities and flows.

1.3.2 Geomorphologic and hydrologic measurements of tidal channels

Relationships among stream order, marsh area, and stream length for the region have been developed for the Jug Bay marshes (Smith-Hall, 2002; Phemister, 2006). Ultimately, relationships of channel order, width, length, cross-sectional area, and discharge were derived. Tidal network characteristics provide a structure for predicting hydraulic characteristics (channel area, discharge), and provide a framework for sampling hydrological and geochemical fluxes within these systems.

Tidal duration, height, maximum velocity, and discharge were measured to calculate the water flux for each measured tidal cycle. Tidal duration and height was determined from the Maryland Department of Natural Resources Tide Finder (Appendix A). Tidal height was also measured in the field using a staff gauge. The tidal discharge was determined by measuring the cross-section and mean velocity at every sampling point. The mean velocity was determined by factoring in the vegetation roughness height. The roughness height was estimated using velocity profiles. Cross-sectional profiles of the channel were measured at bankfull condition (defined as the average high tide water line was at the vegetation).

Hydraulic geometry relationships were determined using the collected field data of discharge, width, depth, and velocity. Channel width was determined as a function of gauge height drop and cross-sectional area change. Channel depth was derived by dividing the cross-sectional area by the channel width. Relationships were determined by fitting a power function to each data set.

1.3.3 Geochemical sampling locations

Synoptic sampling was used to measure the spatial variability of denitrification within the tidal network. Sampling was completed within the system at designated sites to evaluate fluxes as a function of stream order. Sample sites were representative of the tidal network. A total of five sites were sampled; 2 first order streams, 1 third order, 1 fourth order, and 1 fifth order (Fig. 1.3). Samples were collected beginning an hour before high tide at half hour intervals for a minimum of three hours into the falling tide and an average of six hours until low tide.

By measuring the incoming and outgoing nitrogen concentrations of the channel water, the samples encompass the spatial diversity and extent (such as vegetation types and elevation variation with distance from the channel) of each channel order.

1.3.4 Analytical methods to determine water chemistry for flux measurements

Water chemistry was sampled in concert with measurements of gauge height and velocity. Samples were taken one hour prior to high tide and over the entire falling tide at each location in half hour intervals.

Samples were filtered in the field using a syringe and a 0.45 micron glass-fiber filter (for ammonium) or 0.20 micron glass-fiber filter (for nitrite and nitrate), and then frozen until analysis. All samples were run within a month of collection to avoid sample degradation.

Water samples were analyzed for nitrite and nitrate using an ion chromatograph. The detection level for the nitrite and nitrate analyses was 2 μM.

Water samples were analyzed for ammonium using the phenolhypochlorite method adapted from Solorzano (1969). After reagent addition, the samples were set in the dark for a minimum of two hours and a maximum of 24 hours to develop. The detection level for ammonium is 0.5 μM. All analyses outlined in the above methods were performed at Horn Point Laboratory, University of Maryland Center for Environmental Sciences under the supervision of Dr. Jeff Cornwell and Mike Owens.

1.3.5 Nitrate retention

Nutrient flux measurements were first calculated by multiplying nitrate concentrations by discharge. Nitrate was the most soluble form of nitrogen, and therefore was used for further calculations. Nitrate loss was then determined by incorporating the nutrient removal process into the equation. Nitrate retention was determined by finding the difference between the nitrate concentrations on the flooding and ebbing tide, and factoring in discharge:

$$NR = Q_t * (N_i - N_t)$$

Where NR = nitrate retention in μmoles s^{-1}

Q_t = discharge in L s^{-1} at time (t)

N_i = initial [NO_3-N] of tidally introduced water

N_t = [NO_3-N] of draining tidal channel water at time (t)

The net nitrate retention was determined by integrating to calculate the area under the curve for the nitrate retention over time.

1.3.6 Sites of nitrogen processing

To target the location of nitrate retention, further experiments were conducted to determine the impact of each site of processing.

1.3.6a Net in-stream nitrate retention

To examine in-stream net nitrate retention, an additional study site was used. The study site is a 5th order channel located directly off of the boat launch (Fig 1.4). This study site was chosen to measure in-stream nitrate flux over a reach because the channel was manually altered, and consequently has no meander bends. To determine in-stream nitrate retention rates, sampling sites were chosen along the manually altered stream segment directly off of the boat launch because that portion of the river no longer has meander bends and few tributaries. Both a 50 and 100 meter reach were tested on an outgoing low tide to determine the influence of distance on nitrogen flux. As mentioned previously, the site is seasonally dominated by *Elodea* species, so this sampling site was only used when growth of the macrophytes was minimal.

Figure 1.4. Map showing sample collection points for in-stream denitrification experiment over a 100 meter reach with no meanders. The 50 meter reach was from site B to 50 meters between the markers.

1.3.6b Groundwater processing

Seeping groundwater was collected from a draining 3rd order channel to determine the contribution of groundwater. A simplifying assumption was made that the water recharging the near-channel groundwater originated from nitrate-rich, tidally introduced main stem water. The difference in nitrate concentrations in relation to volume of groundwater flux determined the amount of groundwater processing. Piezometers weren't installed to measure groundwater because Phemister (2006) extensively characterized groundwater processing.

To determine the rate of denitrification, water samples were collected and analyzed for excess nitrogen gas by quantifying the change in the ratio of N_2:Ar using Membrane Inlet Mass Spectrometry (MIMS). Water samples (5 mL) were collected in the field in glass vials and preserved with $HgCl_2$. Care was taken to fill the vials completely to minimize the formation of air bubbles. The vials were stored at the same temperature as collected, and submerged in water to prevent air entry or degassing. Although samples collected from the water column or seeping groundwater are considered to come from an open system, if ratios are high enough over ambient conditions, determination of denitrification is still possible.

1.3.6c Marsh surface denitrification: Core incubation using Membrane Inlet Mass Spectrometry (MIMS)

The dissolved gas concentrations (N_2, O_2, and Ar) were measured using the MIMS Dissolved Gas Analyzer (Kana et al., 1994). Water samples were pumped through a semi-permeable silicon membrane under high vacuum into the attached mass spectrometer to measure dissolved gas concentrations. Data were corrected for instrument drift and background, and sample temperature and salinity. Using the dissolved gas concentration ratios over time, sediment-water N_2 and O_2 fluxes were calculated using the following equation:

$$F = S*h*k$$

Where F = the net analyte flux in µmoles m^{-2} h^{-1},

s = the slope of the best fit line from linear regressions of concentration change over time in µmoles L^{-1} h^{-1},

h = is the height of the water column in cm for a given core

k = a constant of 10 derived from the equation conversion of 1 L to 1000 cm^3

and 10,000 cm^2 to $1m^2$

Any samples with regression value of <0.90 were designated as not interpretable and single outliers were removed before analysis.

Marsh cores were analyzed for nitrogen flux of the marsh surface and subsurface. Samples were taken along a transect at distances of <1, 20.5, and 33.4 m from the marsh creek using 30 cm long (6.5 cm inner diameter) PVC cores to a depth of approximately 10-15 cm. Cores were transported on ice and stored in a temperature controlled room, which was maintained at the temperature of the river water collected that day. Once at the lab, the cores were placed under water that was collected from the river, and bubbled overnight to equilibrate. The cores were equilibrated in a dark, temperature-controlled chamber for approximately 18 hours to allow background N_2 levels to decrease to approximately 1% by using overlying water and a headspace flushed with air. The cores were then sealed with polycarbonate lids outfitted with a magnetic stir bar and sampling ports with only water in the headspace. The cores were arranged around a central magnet, which turned the lid magnetic stir bars at ~ 40 rpm. Cores were incubated in this manner for a minimum of 4 hours (when water temperature was above 12^oC), and a maximum of 7 hours (when water temperature was $<12^oC$). Initial samples (30 mL for nutrient analyses and duplicate 5 mL samples for N_2 and O_2 analyses) were drawn from the headspace of each core and then approximately every 1.5 hours thereafter for the duration of the incubation. The 5 mL gas samples were killed with $HgCl_2$ and stored under water in the temperature controlled room. The nutrient samples were filtered using a 0.2 micron filter and frozen until analysis. Care was taken to draw only the necessary volume of water for analyses. Water drawn for the samples was replaced with additional river water that was fed into the cores as water was sampled. Triplicate cores were run, as well as a control core without sediment.

Air bubbles formed under the lids of three of the cores during incubation. The time of appearance and size were noted. The source of the bubbles appeared to be from air pockets in the sediment or from anaerobic metabolism, and not from a leaking seal on the lid of the core. Cores with bubbles weren't disregarded. The collected samples were then analyzed for dissolved gases within two weeks of the experiment using MIMS. The samples collected for nutrient analyses (NH_4-N, NO_2-N, and NO_3-N) were immediately analyzed as outlined below.

4. Implications

This experimental design represents a novel approach to determining ecosystem functioning based on geomorphic parameters. The approach considers the constraints of geomorphology and hydrology of the tidal freshwater wetland system to characterize nitrate retention. Previously, practitioners and scientists have often overlooked or underestimated the importance of these two factors in ecosystem processing. When characterizing nitrate retention or denitrification on a large scale, a small scale experiment is conducted, and the results are scaled up to the ecosystem level without taking into account spatial variability. By linking together the geomorphology, hydrology, and biogeochemistry of the ecosystem, the net nitrate retention can be more accurately estimated.

CHAPTER 2

1. Geomorphic and hydrologic organization of freshwater tidal marshes

2.1.1 Morphologic characteristics of the tidal network

The freshwater tidal marshes along the Patuxent River contain highly organized channel networks that serve to convey water into the marshes that border the river (Fig. 2.1). This study was conducted in the upstream boundary of the freshwater tidal wetlands. Incoming tides push water into tidal channels that border the channel, these channel systems considerably extend the tidal marshes into regions where levels along the channel would otherwise prevent overbank flooding of the channels during high tides.

Figure 2.1. Tidal marshes showing levees along main channel, tidal network marsh (outlined), interior tidal channels, exterior tidal channels. Image from U.S. Geological Survey, April 2006.

Relationships among channel order, channel width, channel length, and marsh area were explored to characterize channel and marsh organization. These relationships for the study area (north of Jug Bay) have been previously examined by Smith-Hall (2002) and Phemister (2006). Smith-Hall (2002) noticed that the smaller order channels located within extensive channel networks (interior channels) have somewhat different characteristics than channels that come directly from the main channel (exterior channels). Therefore, the relationships developed for interior channels by Smith-Hall (2002) and Phemister (2006) were compiled and compared with those obtained for exterior channels, which are the focus of this study. Compiled data are found in the appendix along with additional data collected for this study (Appendices B and C). Both Smith-Hall (2002) and Phemister (2006) examined relationships between stream length and stream order, and tidal marsh area and stream length. Stream length is one of the easiest morphological variables to measure, since data can be obtained from aerial photos and other images. These relationships for the Upper Patuxent are shown in figures 2.2 and 2.3. The reported error is +/- 1 standard deviation.

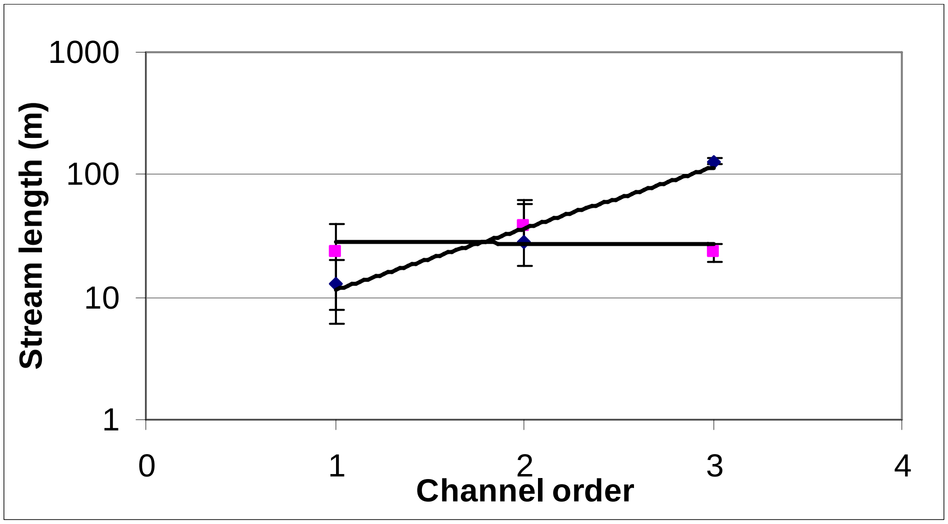


Figure 2.2. Relationship between stream length and stream order. For interior channels, stream length = 3.6729e $^{1.1461*\text{channel order}}$, no relationship was found for exterior channels. Blue points are for interior channels (n=40) and purple points are for exterior channels (n=18). Reported data from Smith-Hall (2002). Note that the 3rd order stream lengths for exterior channels are shorter.

These data indicate that for channels within a highly branched network (interior channels), stream length increases exponentially with channel order. This relationship is similar to that of terrestrial stream channels, although the stream lengths are much shorter. For exterior channels, there is not a systematic increase in stream length with stream order. This suggests that either these channels can not grow headward easily (due to low velocities and high resistance), or that the channels are truncated by processes occurring along the main channel.

The inundated marsh area can also be related to stream order or stream length (Fig. 2.3). If systematic relationships between marsh area and stream length can be determined, then stream length can be used to estimate marsh area for unmeasured parts of the system. The marsh basin area and stream length were closely correlated for both interior ($r^2 = 0.96$) and exterior channels ($r^2 = 0.98$). Again, there is large variability for the reported measurements because smaller order channels are more variable than larger order channels.

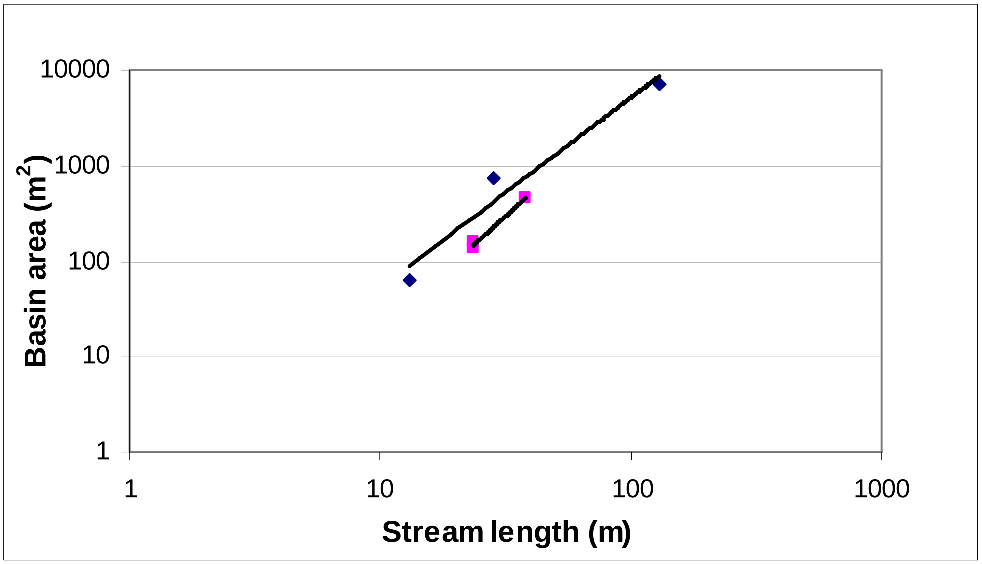
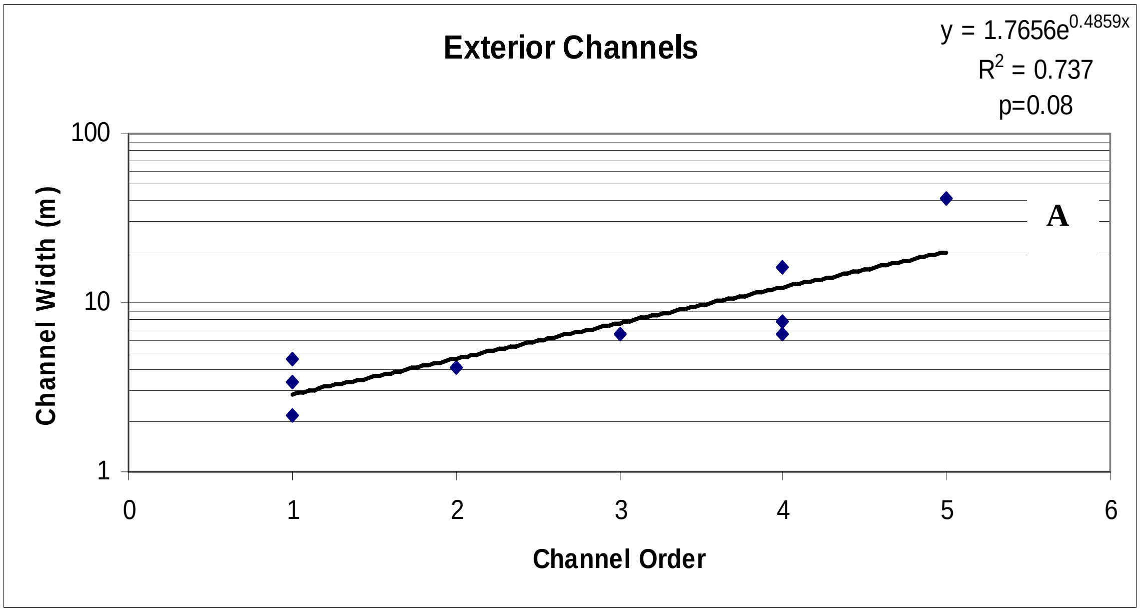


Figure 2.3. Relationship of channel length to channel area for average 1-3rd order interior (blue, n=40) and exterior (purple, n=18) streams (Smith-Hall, 2002). For interior streams, basin area = 0.5516*stream length $^{1.9844}$, and for exterior streams, basin area = 0.0846*stream length$^{2.3603}$.

Channel size and shape also exhibit systematic organization within tidal marsh channel networks. The size of the channel mouth constrains the amount of water fluxes into the tidal network; therefore, the relationship of channel width and cross-sectional area to stream order were also examined (Fig. 2.4). The channel width and cross-sectional area increase exponentially with increased channel order. These morphologic relationships are crucial because they create a framework to estimate channel dimensions and water fluxes for unmeasured channels. Channel width can easily be obtained from aerial photos, and if other channel parameters can be estimated from channel width measurements, then perhaps channel area and water flux can also be estimated.



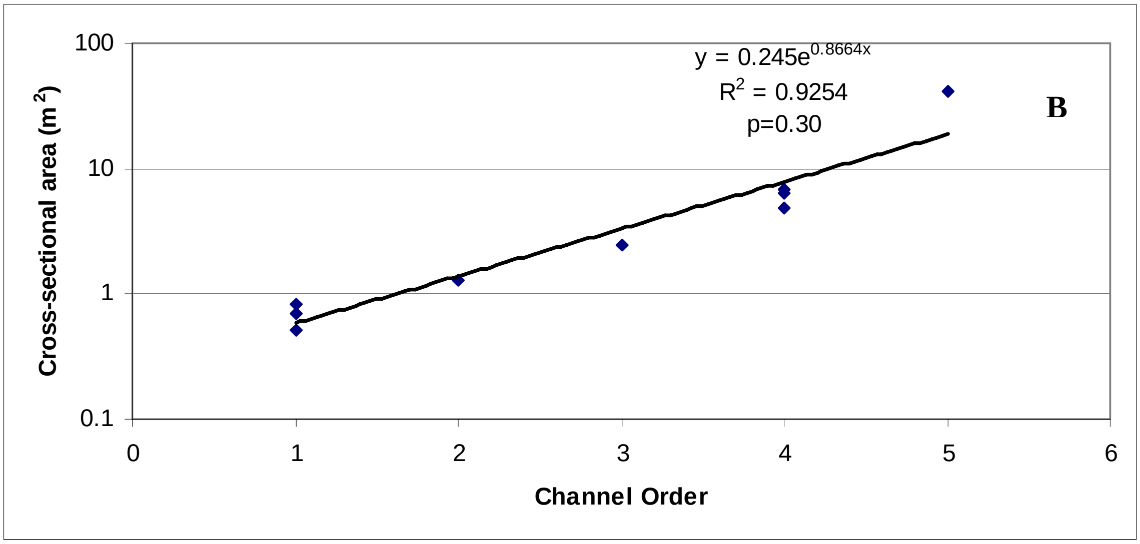
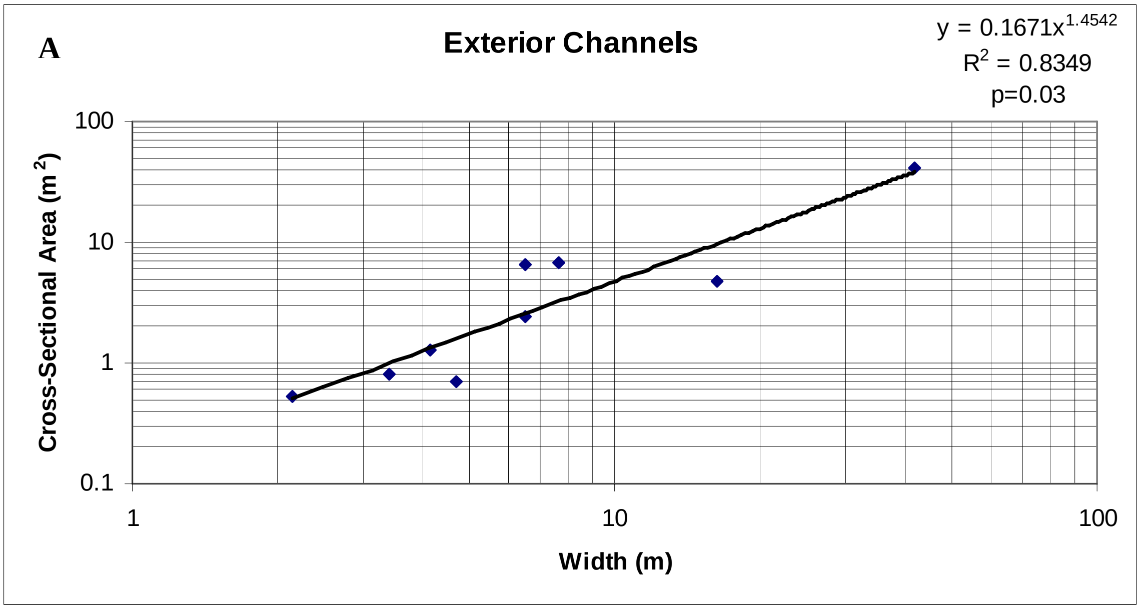


Figure 2.4.a-b. Relationship of channel order and channel mouth width (a), and channel order and cross-sectional area (b) for exterior channels. The channel width increases in an exponential manner as channel order increases incrementally.

To determine relationships between channel width and other channel morphological variables, channel cross sections were measured at the mouth exterior stream channels of order 1-5 (Appendix B; Fig. 2.5). These data were compared with other channel data measured on interior channels by Phemister (2006). Channel cross-sectional area was calculated from these measurements. Average channel depth was determined by dividing total channel area by surface width. The relationship between channel width and cross-sectional area is more closely correlated for interior channels ($r^2 = 0.98$, $p < 0.01$) than exterior channels ($r^2 = 0.83$, $p = 0.03$). The small p-values for the width relationships for exterior channels (width and channel order, $p = 0.08$; and cross-sectional area and width, $p = 0.03$) indicate that width can be used to predict channel order and cross-sectional area, which can be used to estimate discharge. In general, smaller order channels exhibit more morphological variability than higher order channels. Although cross-sectional area increased logarithmically with increased channel order, the majority of channels measured were less than 17 meters wide. The cross-sectional area is an essential morphologic measurement because the values can be used to calculate discharge.



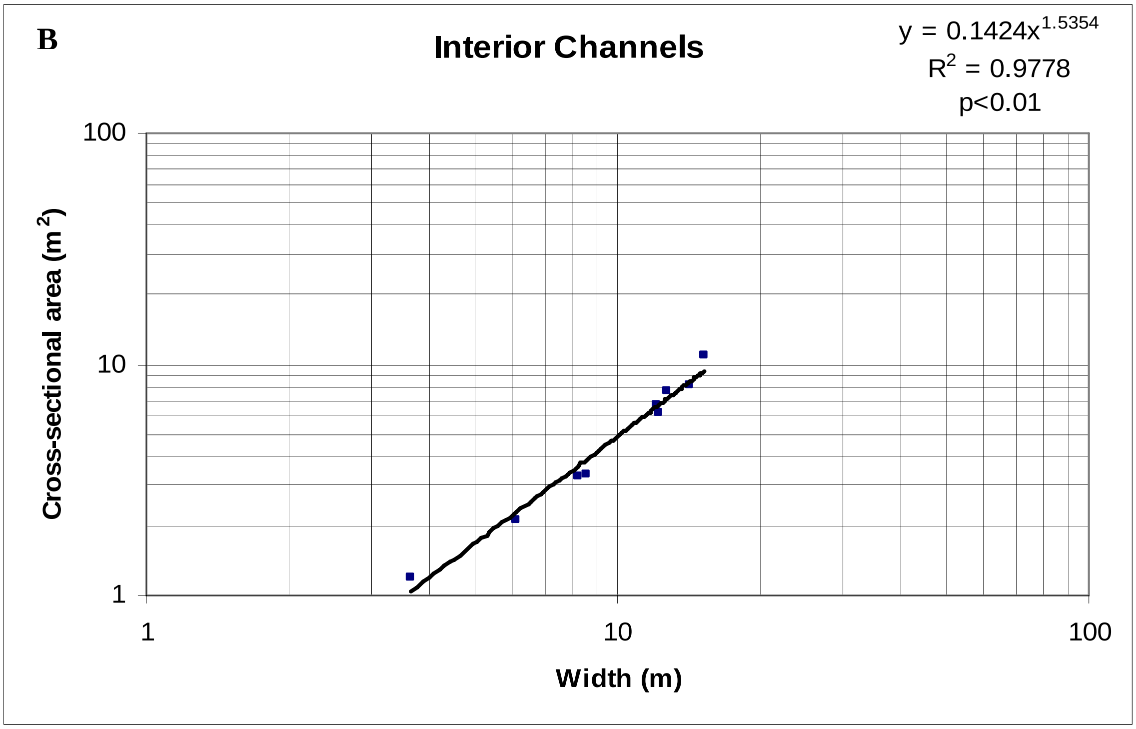


Figure 2.5.a-b. Morphologic relationship between channel width and channel mouth cross-sectional area for (a) exterior channels and (b) interior channels. The relationship was more closely correlated for interior channels, which are more homogenous. Data for interior channels are from Phemister (2006).

Width to depth ratios were examined (Fig. 2.6; Appendix B), which characterize the channels as being relatively shallow and wide. This geomorphologic characteristic can be used to aid in predicting sediment type and transport. The data set isn't large enough to make any conclusions about width to depth ratios within the system because the low order channels are highly variable, especially for exterior channels. Also, the measurements were taken within one position of the network, and not along the length of the network system. As a comparison, relationships drawn by Myrick and Leopold (1963) from the neighboring Potomac River range from 4.4 to 32.4; however, that study didn't encompass enough data to draw relationships either. Also, the smallest channel measured in that study was a 4th order.

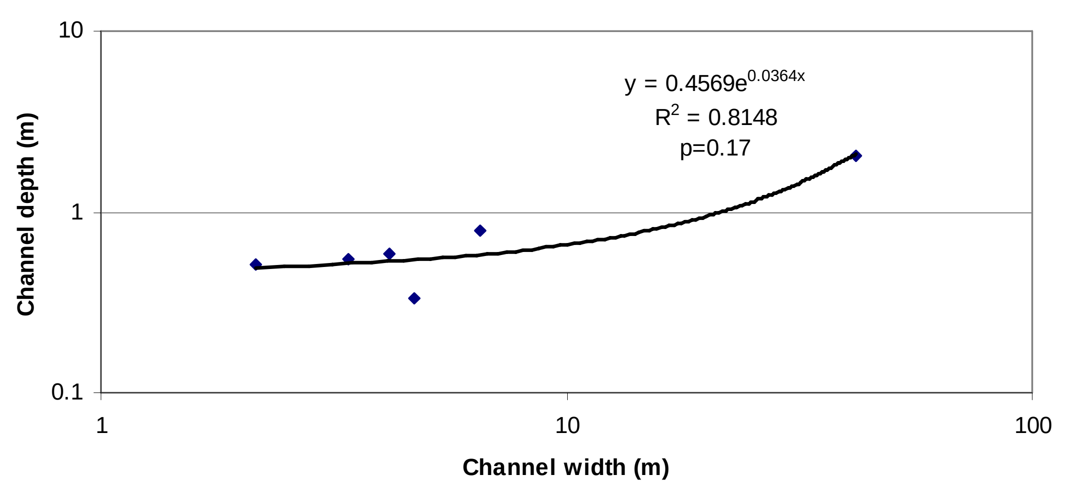


Figure 2.6. Relationship between channel width and depth determined from field data. Using the width to depth ratio, channels of the Patuxent River tidal network were characterized as being relatively shallow and wide.

Morphologic relationships for both the marsh (marsh area vs. stream length; stream length vs. stream order) and the tidal channels can be excellent tools for estimating marsh hydraulics or fluxes over large areas of tidal marsh, which would be difficult to measure for every portion of channel or marsh within a network. Aerial photos, other remotely sensed data, and high resolution Lidar topographic data can be used to measure channel width and channel length. From these measurements, estimates of marsh surface area and channel characteristics can be made. Although field measurements provide the most accurate data, use of aerial photographs on Google Earth to measure channel widths for the study site resulted in an error of less than 2% (Lillibridge, 2009).

2.1.2 Hydrologic characteristics of the tidal network: Discharge

The goal of this study was to determine the flux of water and nitrogen into and out of tidal channels, and to determine the amount of nitrogen retention within the marsh system; therefore, the ability to accurately measure and estimate discharge is essential.

Water discharge is defined as volume divided by time. At any instant in time, discharge can be measured by knowing the channel cross sectional area and the average velocity of the channel:

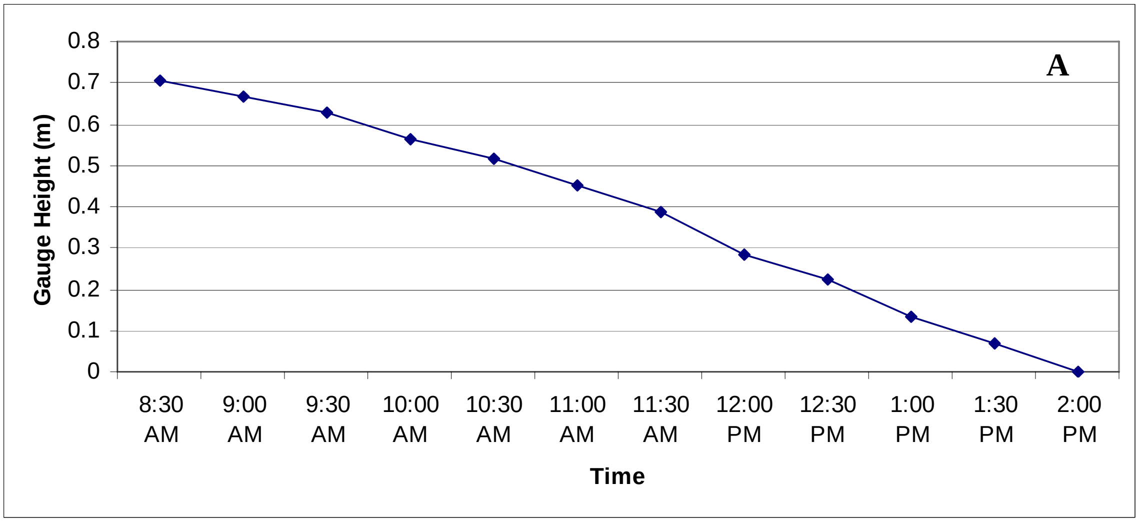
$$Q = A*v$$

Where Q = discharge in $m^3\ s^{-1}$

A = channel cross-sectional area in m^2

v = mean velocity in $m\ s^{-1}$

For tidal channels, it is very difficult to measure either channel cross sectional area or velocity as the tide is changing with flooding or ebbing conditions. The channel cross sectional area can easily be measured at high tide, when the velocity goes to zero. Once the maximum channel cross sectional area is measured, the channel cross sectional area for the falling stage can be determined by monitoring gauge height and calculating the cross sectional area for that stage. Average channel velocity is usually obtained from measurements across the channel, which are used to determined discharge and average velocity (Q/area). For tidal channels, however, the stage and velocity change too rapidly for this to be effective. Therefore, velocity profiles across half of the channel, and at selected vertical profiles are collected to determine velocity structure, and the relationship between the average velocity and the maximum velocity in the cross section. Discharge was determined using instantaneous measurements of maximum velocity over the tidal cycle. The total volume of discharge was determined by integrating the area under the curve over half a tidal cycle (either flooding or ebbing tide). Discharge was calculated every time water chemistry samples were collected. A graphical example is given in figure 2.7, but complete measurements are in Appendix D.


A
Gauge Height (m)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
8:30 AM
9:00 AM
9:30 AM
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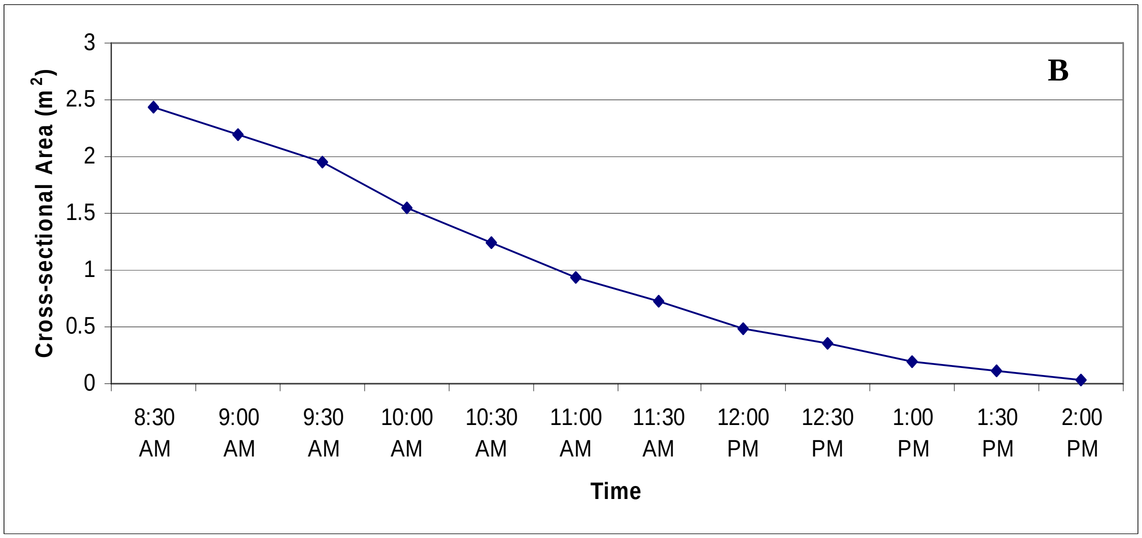
Time


B
Cross-sectional Area (m²)
3
2.5
2
1.5
1
0.5
0
8:30 AM
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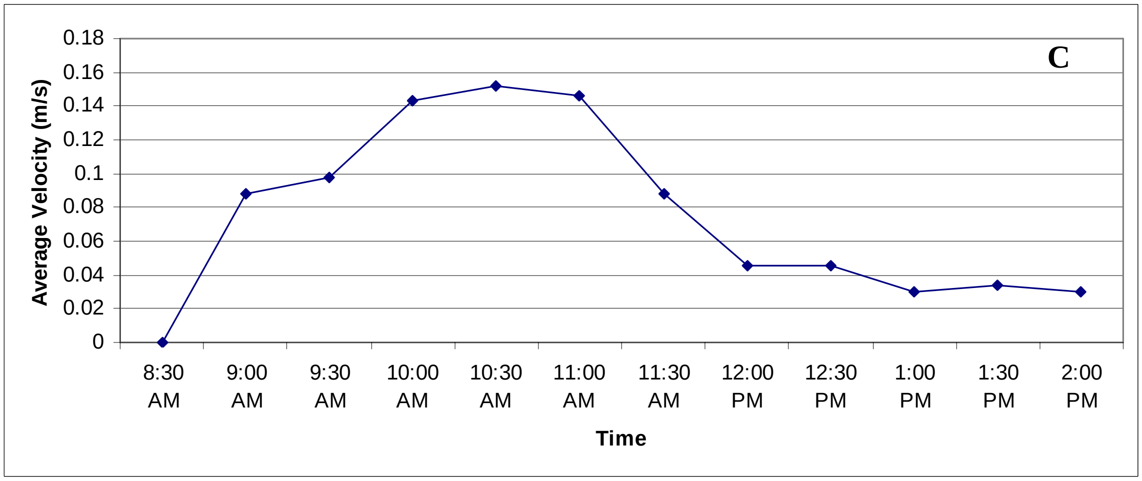
Time


C
Average Velocity (m/s)
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
8:30 AM
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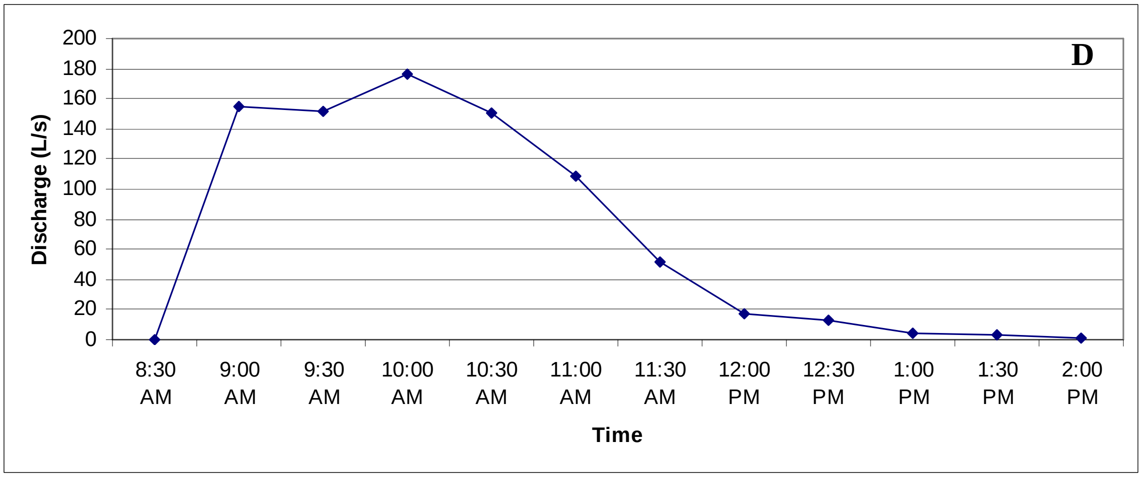

Figure 2.7.a-d. Measurements used to determined discharge for a 3rd order channel: (a) gauge height, (b) cross-sectional area, (c) average velocity, and (d) discharge. Data were collected 10/1/08.

The maximum discharge was calculated for each site using the parameters at the bankfull condition (Fig. 2.8). The maximum discharge was slightly greater for the spring measurements (collected on 5/29/09); however, the area experienced heavy rain in the week prior to measurement. The fall measurements were collected on 9/24/08 and 10/1/08. Both the fall and spring discharge were closely correlated with channel order ($r^2 = 0.99$). Discharge increased exponentially with channel order, similar to the trend found for width and channel order; therefore, channel width controls the channel discharge.

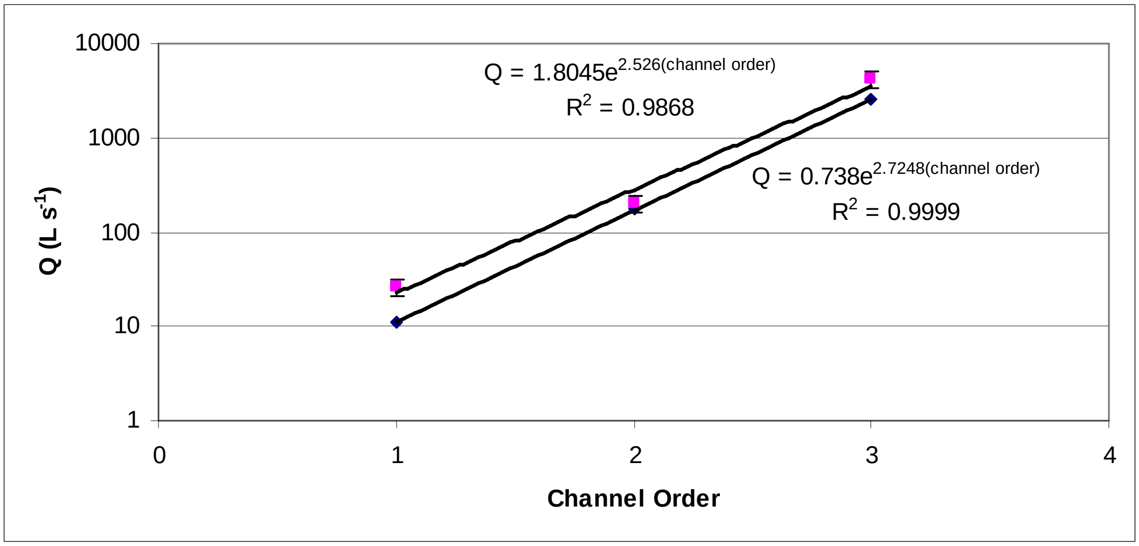

Figure 2.8. Comparison of maximum discharge and channel order for fall (blue) and spring (purple) sampling periods for exterior channels only (p=0.19 for both seasons). Fall sampling was conducted on 9/24/08 and 10/1/08, and spring sampling was conducted on 5/29/09.

An important note must be made that interior and exterior channel discharge was markedly different because of variations in velocity. An example of exterior channel discharge can be found in figure 2.7.d. The velocity of the channel water wasn't conservative, and mimicked the mainstem velocities more so than interior channels. Exterior channels are also greatly affected by the wind. On one occasion, the wind on the Patuxent River was strong enough to force the smaller exterior channels to stay at near bankfull condition while the mainstem was draining.

In making velocity measurements, an assumption was made that the maximum velocity was being measured; however, velocity profiles weren't measured for each site. The maximum surface velocity for the smaller order channels was determined using markers on the surfaces to determine the area of fastest flow. The velocity was then measured at that point. The velocity was assumed to be accurate for smaller orders because the flow was contained in a small area. Since the exterior channels were mostly devoid of vegetation on the channel bed, the roughness height was not a complicating factor. Future research will refine the discharge measurements and draw relationships such that discharge can be estimated based on tidal stage.

An additional assumption was made that the discharge was completely contained within the channel on a flooding tide. The marsh surface experienced overbank flooding at times, but depended on the magnitude of the tidal stage. With this assumption, the uncertainty lies within the smaller order channels. Larger order channels fully contain the tidal flow, and less frequently experience marsh surface inundation compared to smaller order channels. Smaller orders were more susceptible to overbank flooding. Also, interior channels flood to a differing extent than exterior channels that are influenced by the levees.

2. Hydraulic geometry characteristics of the tidal network

The at-a-station hydraulic geometry was determined for each site (Appendix D). Examples of the hydraulic geometry relationships for tidal channels are shown in figure 2.9. These relationships indicate that the increase in discharge with tidal stage is accommodated for this 3rd order channel primarily by an increase in width and velocity. For the higher order channel, width does not increase significantly with stage, but velocity increases significantly. The hydraulic geometry relationships for exterior channels are reported in table 2.I.

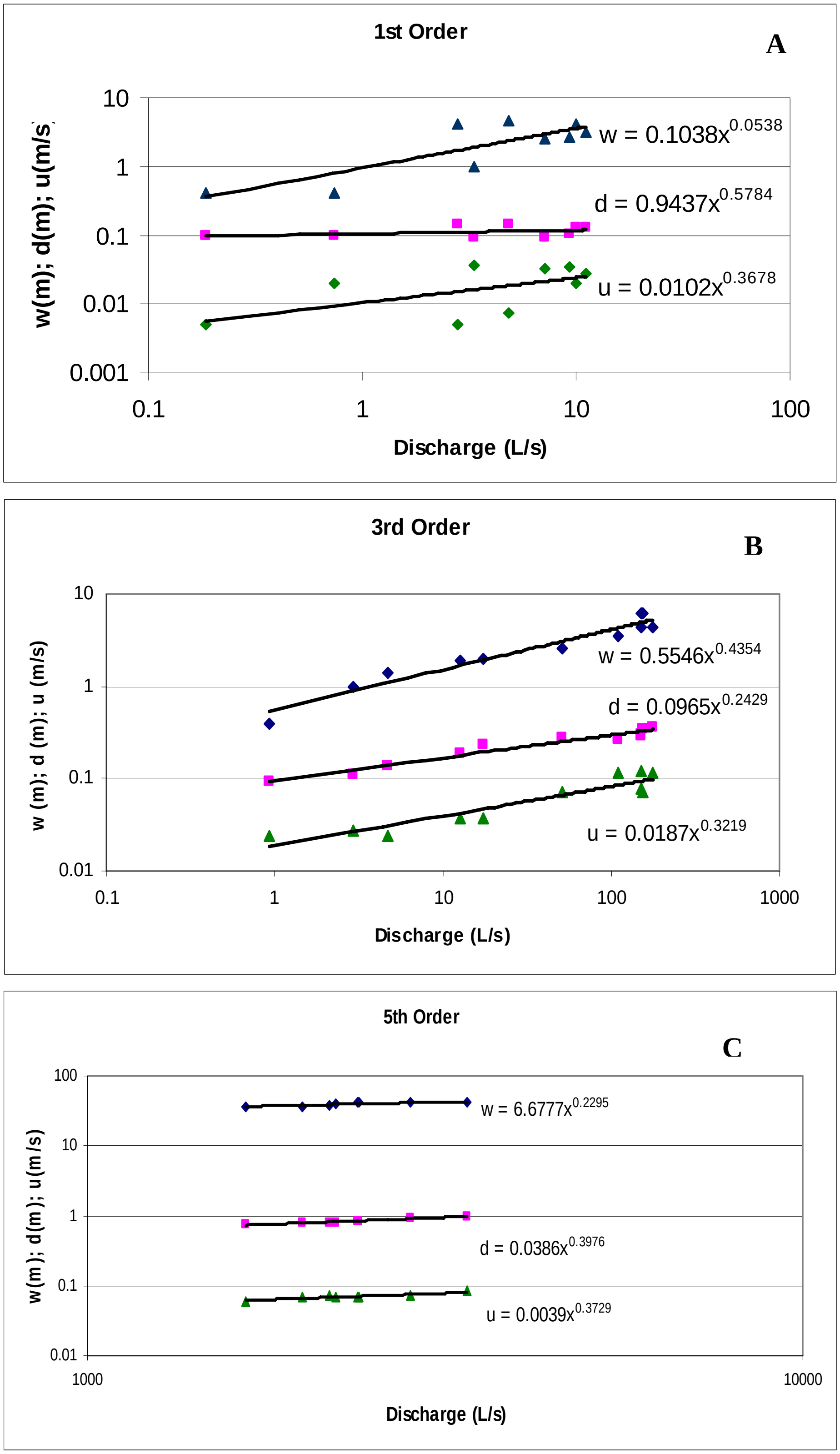

Figure 2.9.a-c: Hydraulic geometry relationships determined for a 1st order (a), 3rd order (b), and 5th order (c) channel. Relationships determined from data collected on 9/24/08, 10/1/08, and 7/7/09 respectively.

Table 2.I. At-a-station hydraulic geometry relationships

	Width (m) *b*	Depth (m) *f*	Velocity (m/s) *m*
1st order:9/24/08[a]	0.054	0.578	0.368
3rd order: 10/1/08	0.435	0.243	0.322
5th order: 7/7/09	0.229	0.378	0.373
Myrick and Leopold (1963)	0.04	0.18	0.78

a-Reported relationships were determined using data from a flooding tide. All other relationships were determined using data from an ebbing tide.

Tidal channel hydraulic geometry presented in table 2.I is based on data collected from July through the fall, when submerged aquatic vegetation (SAV) was at its peak. The freshwater tidal channels are covered with dense growths of *Elodea* sp., which greatly increases the flow resistance and decreases velocity of these channels. Therefore, based on the fall data set (Table 2.I), the 1st order channel experienced a relatively small change in channel width (b = 0.054) over the tidal cycle, and a large change in channel depth (f = 0.578). The external smaller order channels aren't very wide, but they respond significantly in depth due to their proximity to the main channel. The 3rd order channel experienced the opposite because the change in channel width was large (b = 0.4354) compared to the change in channel depth (f = 0.2409). The velocity was less variable between the two sites, and *m* for the 1st order was 0.3678, and for the 3rd order was 0.3219. The largest tidal channel measured shows a small exponent for width b = 0.229 and a larger exponent for velocity. Due to the large increase in width with increasing stream order, the larger order channels convey significantly larger flow into the system and flow depths are significantly large so that the flow goes over the SAV.

A comparison of the above measurements with other studies is difficult because there are few other data on at-a-station hydraulic geometry for tidal channels. Myrick and Leopold (1963) made pioneering measurements in the Chesapeake Bay system, on the freshwater tidal Potomac River, but little other data exists. They present the following average at-a-station hydraulic geometry: $b = 0.04$, $f = 0.18$, and $m = 0.78$. The high exponent for velocity in their study might relate to differences in SAV, higher order channel, and proximity to the Potomac River, a much larger and higher velocity river than the Patuxent River. For comparison, terrestrial at-a-station hydraulic geometry average the following (Leopold and Maddock, 1953): $b = 0.26$, $f = 0.40$, and $m = 0.34$.

The measurements of discharge and hydraulic geometry indicate that the relationship between velocity and gauge height (and thus discharge and gauge height) can vary significantly by season, likely from the growth of SAV in the channels. The hydraulic geometry relationships indicate that width and depth are important variables in the at-a-station hydraulic geometry for small order channels (that often completely drain during the tidal cycle), but that velocity is an important parameter for the higher order channels.

3. Implications

2.3.1 Implications for geomorphology

The geomorphic relationships outlined above can be used to quantify hydrologic fluxes within the tidal network systems. The reported data were compiled using data from both interior and exterior channels. Although complete data sets weren’t reported for all relationships for both types of channels, a clear trend was shown within and between the systems. Exterior marsh channel networks are less extensive than interior channels and usually do not extend to orders higher than 3. Exterior channels drain completely on an ebbing tide whereas interior channels don't completely drain. Interior channel velocity was much more conservative than exterior channel velocity, which more closely followed mainstem discharge. Finally, the interior channel beds were completely vegetated with SAV, which affects flow velocities, whereas exterior channels due to their drainage characteristics aren't vegetated. This vegetation significantly affects roughness height and flow velocities for interior channels. Overall, quantifying the hydrologic fluxes within the individual channel orders led to many unanswered questions.

The geomorphology and hydrology of a system are vital components of an ecosystem that are often overlooked when scientists are trying to determine large scale denitrification or nitrogen retention. This study worked toward quantifying the hydrology of the system, but in drawing the relationships, a difference between interior and exterior channels became evident. These differences will be explored in future work.

2.3.2 Implications for water fluxes

The hydrology of the various channel orders is a fundamental component in describing ecosystem denitrification. The tidal channel network functions as a vehicle to transport water into the smaller order channels within the network. This nitrate-rich tidal water then interacts with the marsh surface and hyporheic zone where denitrification occurs. As shown by the discharge data, the amount of water fluxing into and out of the channel is controlled by the stream width and channel order. There is an exponential relationship between discharge and channel order, and between marsh surface area and channel order; therefore, an exponential relationship can be expected for net nitrate retention and channel order.

CHAPTER 3

1. Nitrogen flux and retention in tidal marsh networks

In this chapter, data are presented on the retention of nitrogen in the tidal marshes as a function of stream order. These data were determined from direct measurements of hydrologic fluxes and nitrogen (nitrate, nitrite, and ammonium) concentrations in tidal channel water. The experimental design for determining nitrogen fluxes and net nitrate retention was previously outlined in chapter 1, but the approach was refined after hydraulic data were collected and analyzed. A significant amount of data is required to determine nitrogen flux and retention. These analyses are streamlined with a few simplifying assumptions, which are outlined and tested in the next section.

3.1.1 Assumptions

The first assumption is that the nitrogen in the water in the tidal channel network is introduced into the channels from the flooding tide. This assumption was tested by sampling both the mainstem and channel waters over time on a flooding tide (Fig. 3.1). The nitrate concentrations from both sites were within the reported error, so that the samples were not significantly different. In addition, after the tide reversed, the first slug of water draining from the tidal channel was similar in nitrate concentration to that which was just introduced into the channel from the flooding mainstem water. There was variability within the mainstem samples. Samples were taken from the middle of the main channel and were meant to represent maximum concentrations, but field work can be unpredictable. Variability was probably caused by the drifting of the kayak into the stream of water leaving the 5th order channel. Samples should be sampled upstream of the site, so as not to sample the draining channel water. Note that the maximum values remained relatively constant for the mainstem over time; the few dips in concentration were similar to values measured near the mouth of the 5th order channel.

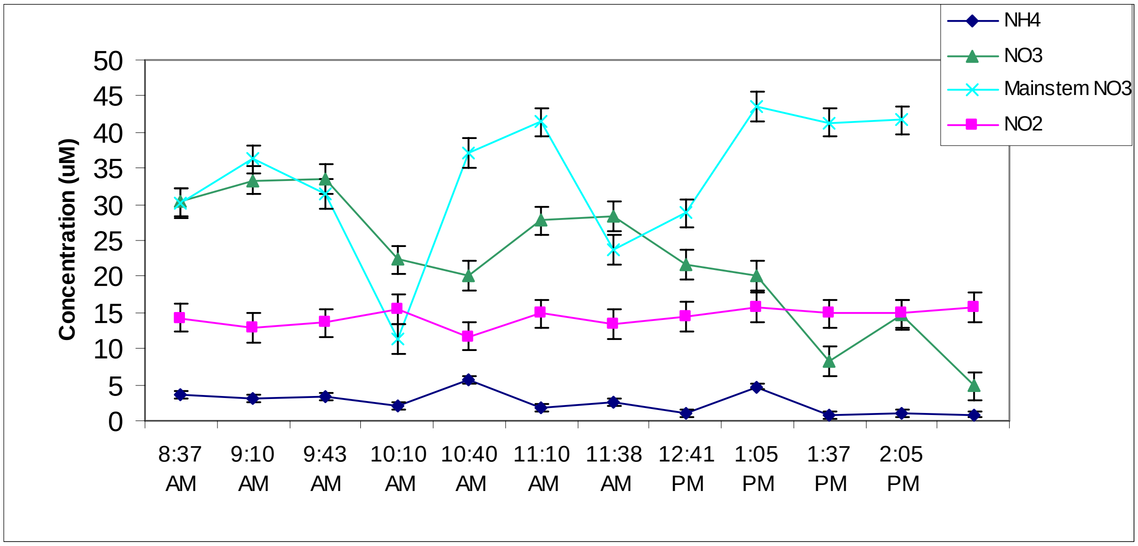

Figure 3.1. Nitrogen concentrations for the 5th order channel. The mainstem concentrations are drawn in light blue. Data were collected on 10/1/08.

The next major assumption is that the nitrogen concentrations introduced from the mainstem into a tributary channel remain constant over time on a flooding tide. This assumption was tested by measuring the nitrogen concentrations at the mouth of a 1st order channel for 3 hours on a flooding tide (Fig. 3.2). Nitrogen concentrations remained fairly constant over the 3 hour period; there was a range of 6 μmol L^{-1} NO_3-N. Due to the validation of this assumption with field measurements, the experimental approach was modified to include only an hour of the flooding tide prior to the reversal of flow direction. The 3-4 nitrogen concentration measurements made during this hour of the flooding tide can be used to characterize the incoming nitrate concentration data. This significantly reduces the amount of time required for data collection and analysis. Nitrogen retention measurements can be made within this 1-hour of incoming tide concentration data plus the complete data for the outgoing tide.

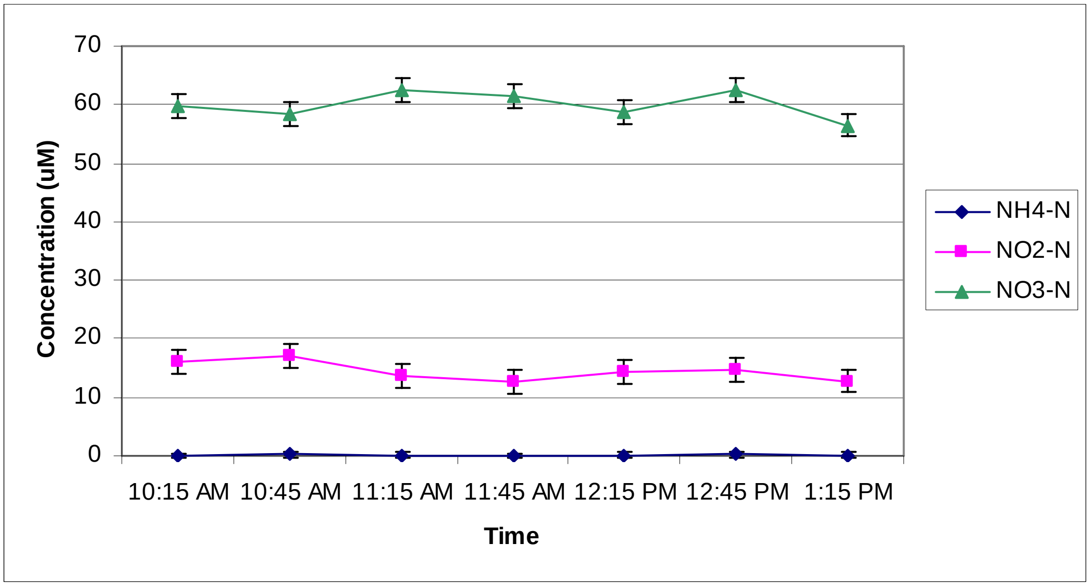

Figure 3.2. Nitrogen concentrations over time for a 1st order channel on a flooding tide. These data support the assumption that mainstem nitrogen concentrations were conservative over time.

The third assumption based on the data in figure 3.1 was made in reference to the fate of the nitrate-rich tidally introduced water. As seen in figure 3.1, the nitrate-rich water was processed within the tidal channel, and when the tide continued to fall, the nitrate-depleted water was returned to the channel causing the nitrate concentrations to drop close to zero (<5 µM). This led to the third assumption that there was net nitrate retention within the tidal channel network, and that the majority of nitrate was processed within the tidal marsh system between the maximum stage of the flooding tide and ebbing tide. An independent experiment by Swarth and Peters (1993) documented that nitrate concentrations at Jug Bay were continually greater on flooding tides, and appreciably lower on ebbing tides pointing to the significance of the tidal marsh network for nitrate processing.

A final assumption is that nitrate is the most abundant, soluble, and mobile form of nitrogen found within the tidal network; for that reason, nitrate is the only form that shows significant variation over the tidal cycle. This is illustrated with nitrogen flux data from a 5th order channel (Fig. 3.3). Nitrate fluxes were of the greatest magnitude followed by nitrite and ammonium. The area created by the flux curve for each nitrogen species was considered the net nitrogen retention. Nitrate retention was by far the greatest, nitrite and ammonium were nominal in comparison; therefore, nitrate fluxes and loss were the focus of this study.

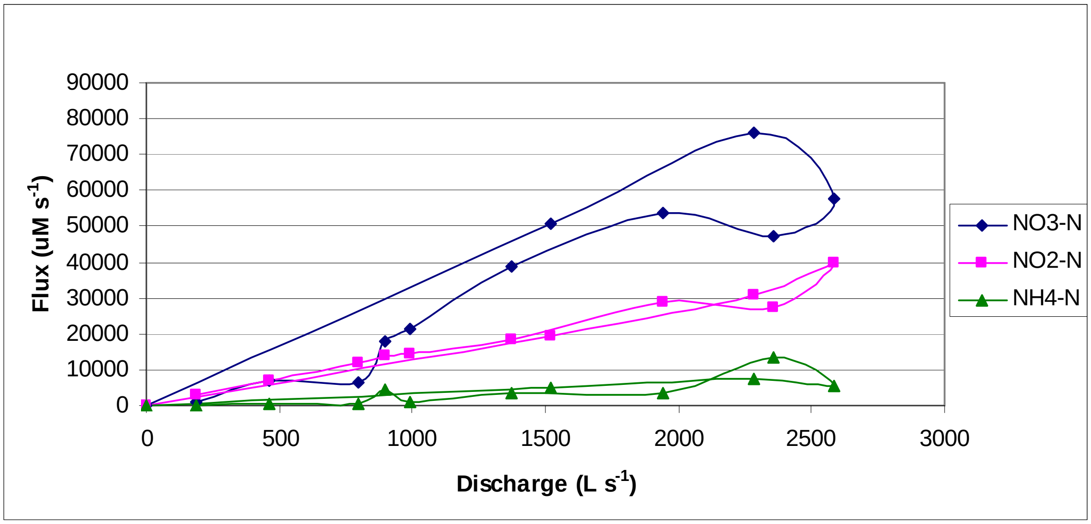

Figure 3.3. Nitrogen fluxes for the 5th order channel calculated based on nitrogen concentrations presented in Figure 3.1. Nitrogen was the most abundant and mobile form of nitrogen within the tidal network.

It is important to note that nitrite concentrations were consistently high throughout this study. This may likely be because of the wastewater discharge into the system. A wastewater plant with the enhanced nutrient removal technology discharges into the study area. The wastewater plant may not completely oxidize the ammonium, or may partially reduce the nitrate, which may attribute to the high levels of nitrite.

3.1.2 Framework for determination of net nitrate retention

Using the simplifying assumptions discussed above, hydraulic measurements and nitrogen concentration measurements were made at each sampling site to provide the necessary data for calculation of net nitrate retention (Appendices D and E; Fig. 3.3-3.6). Measurements were made at the mouths of 2nd, 3rd, 4th and 5th order channels to determine net nitrate retention within each of these systems. For each site, gauge height and velocity were measured in the field at the same time that water samples were collected (these samples were filtered in the field and then frozen until analysis). These measurements were used to calculate discharge (velocity*area), and nitrate fluxes (concentration* discharge) as outlined in Chapter 1. These data were used to determine net nitrate retention as a function of stream order.

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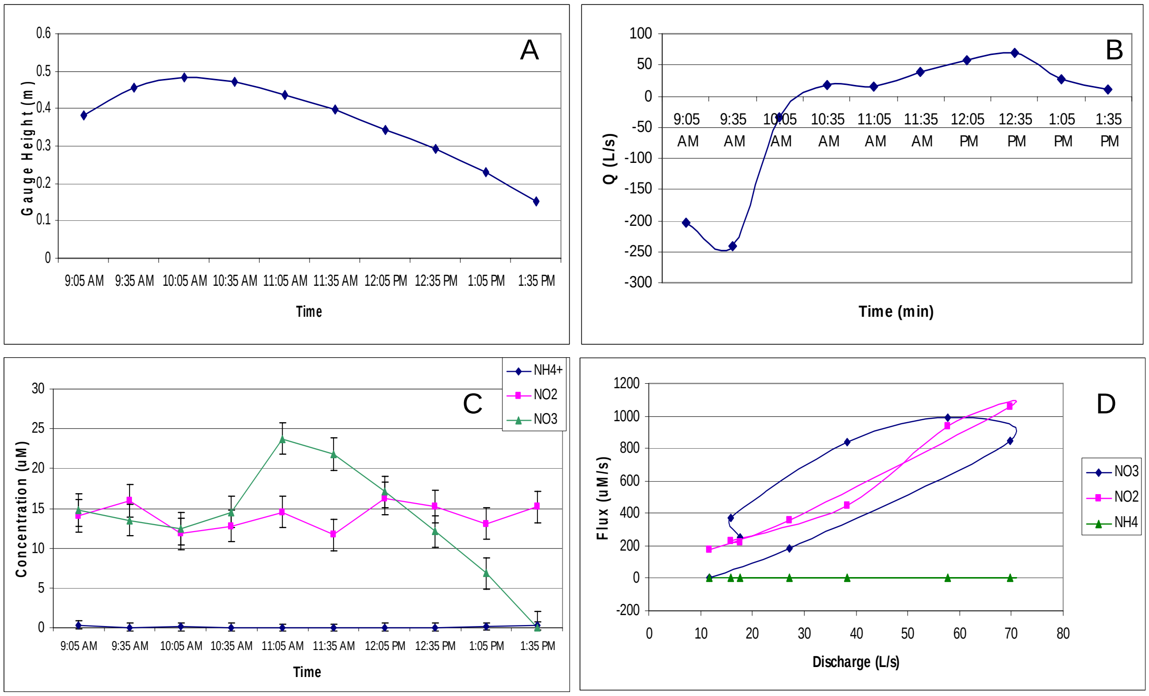

Figure 3.4. Framework for calculation of net nitrate retention for a 2nd order channel: (a) gauge height over time (b) discharge over time (c) nitrogen concentrations sampled over the tidal cycle (d) nitrogen fluxes calculated by incorporating discharge. Data were collected 9/20/08. Negative discharge values denote direction of flow into the channel. Flux measurements were only reported for ebbing tide.

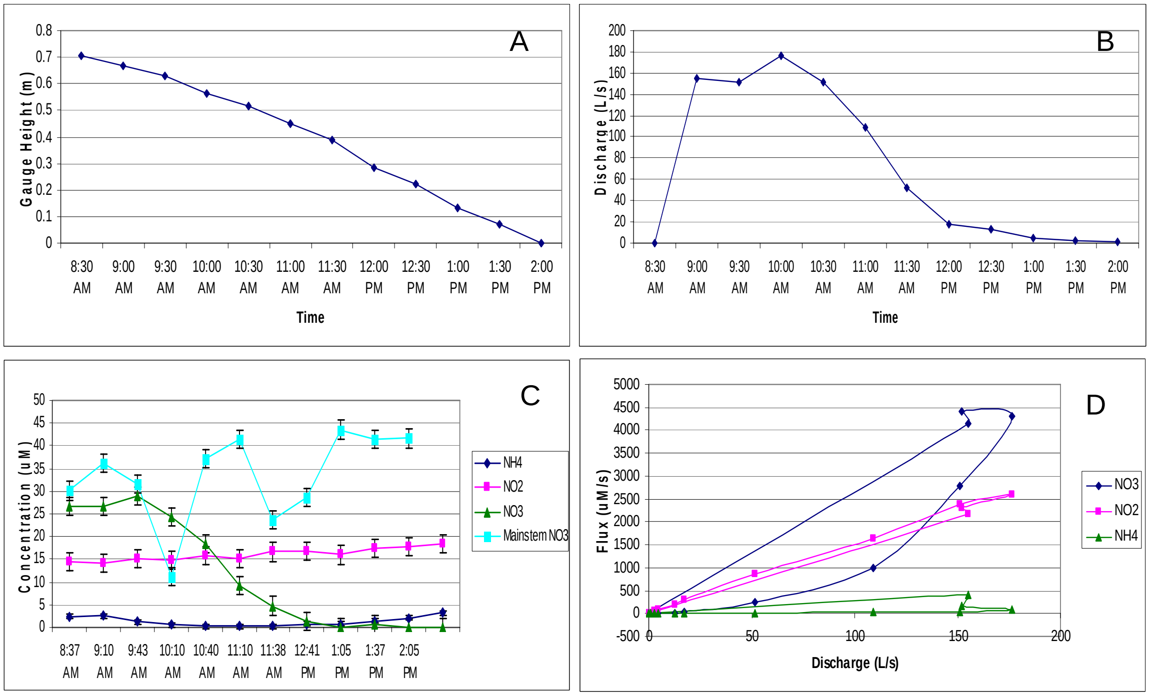

Figure 3.5. Framework for calculation of net nitrate retention for a 3rd order channel: (a) gauge height over time (b) discharge over time (c) nitrogen concentrations sampled over the tidal cycle (d) nitrogen fluxes calculated by incorporating discharge. Data were collected 10/1/08.

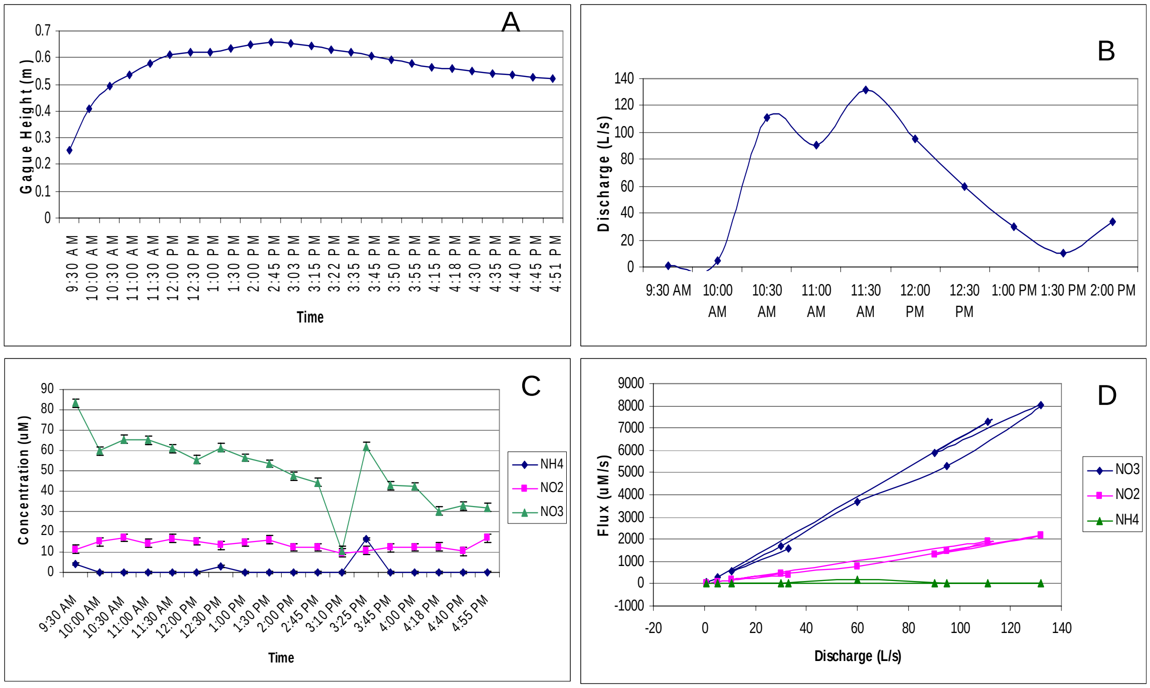

Figure 3.6. Framework for calculation of net nitrate retention for a 4th order channel: (a) gauge height over time (b) discharge over time (c) nitrogen concentrations sampled over the tidal cycle (d) nitrogen fluxes calculated by incorporating discharge. Data were collected 9/24/08.

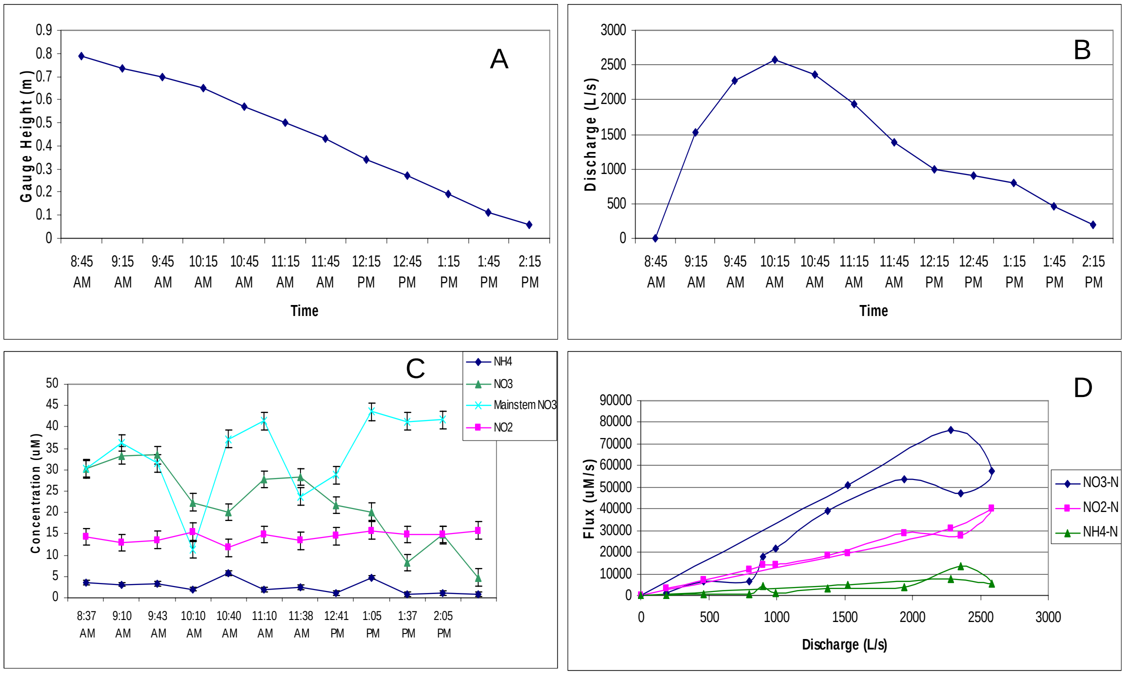

Figure 3.7. Framework for calculation of net nitrate retention for a 5th order channel: (a) gauge height over time (b) discharge over time (c) nitrogen concentrations sampled over the tidal cycle (d) nitrogen fluxes calculated by incorporating discharge. Data were collected 10/1/08.

2. Net nitrate retention

3.2.1 Calculation of net nitrate retention

Net nitrate retention was determined by incorporating the magnitude of discharge into the loss equation. The following equation was used to determine net nitrate retention (see Chapter 1 for detailed methods):

$$\text{Nitrate retention} = Q_t * (N_i - N_t)$$

Where Q_t = discharge in L s^{-1} at time (t)

N_i = initial [NO_3-N] of tidally introduced water

N_t = [NO_3-N] of draining tidal channel water at time (t)

Net nitrate retention was then calculated by integrating the area under the curve of nitrate loss over time.

3.2.2 Net nitrate retention

The maximum rate of nitrate retention and the net nitrate retention were determined for a 2nd, 3rd, and 5th order channel (Fig. 3.8-3.10; Table 3.I). The 4th order channel isn't included in this portion of the study because the measurements were taken on an extraordinarily windy day. As previously mentioned on windy days, the channels are kept from properly draining (as seen by the hydrograph in Fig. 3.6), so that data weren't representative of the channel. A 2nd order channel processed at a maximum rate of 814 μM s^{-1} of nitrate, 3rd order channel processed 2,160 μM s^{-1} of nitrate, and a 5th order channel processed 31,390 μM s^{-1} of nitrate.

To determine the net nitrate retention, the time for processing was factored into the equation. As seen in the above framework, the nitrate concentrations dropped to zero before the completion of the tidal cycle. Since nitrate depletion occurred rapidly, the time periods for retention varied. The net nitrate retention for the 2nd order was 3.4 moles NO_3-N over a 2.5 hour sampling period, as determined by integrating the area under the curve. The net nitrate retention for the 3rd order was 13.2 moles NO_3-N, and the 5th order was 240.3 moles NO_3-N, both values determined over a 5.5 hour sampling period. The greatest error within these data is probably due to the discharge calculations, which may contain up to a 10% error due to the measurement of discharge. Even with factoring in a 10% error, net nitrate retention increases exponentially with stream order (Fig. 3.11)

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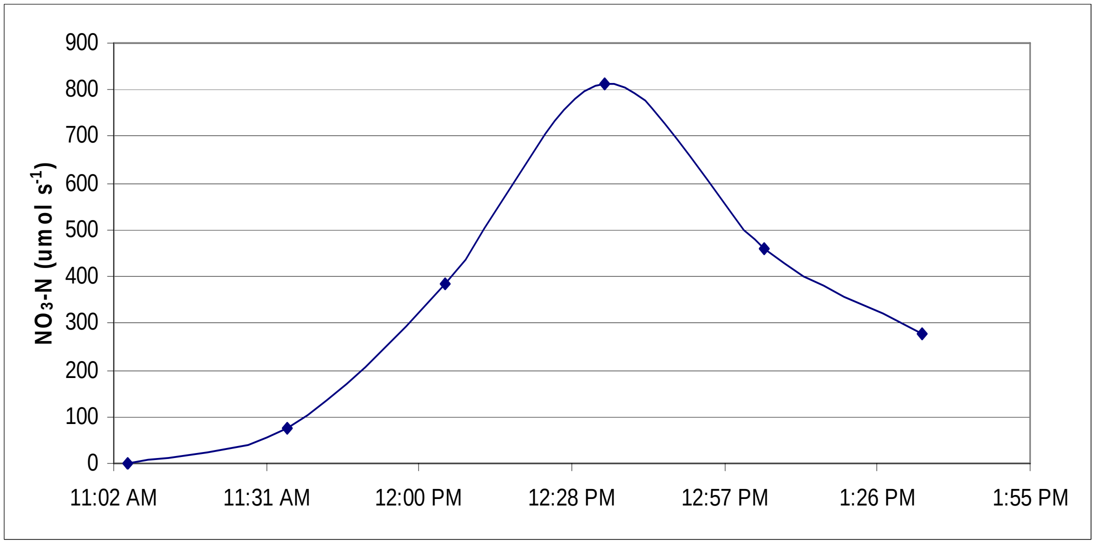


Figure 3.8. Net nitrate retention for a 2nd order stream. The maximum rate of nitrate processing was 814 µmol s^{-1} for a total loss of 3.4 moles NO_3-N over the 2.5 hour sampling period. Data collection was in the Fall on 9/20/2008.

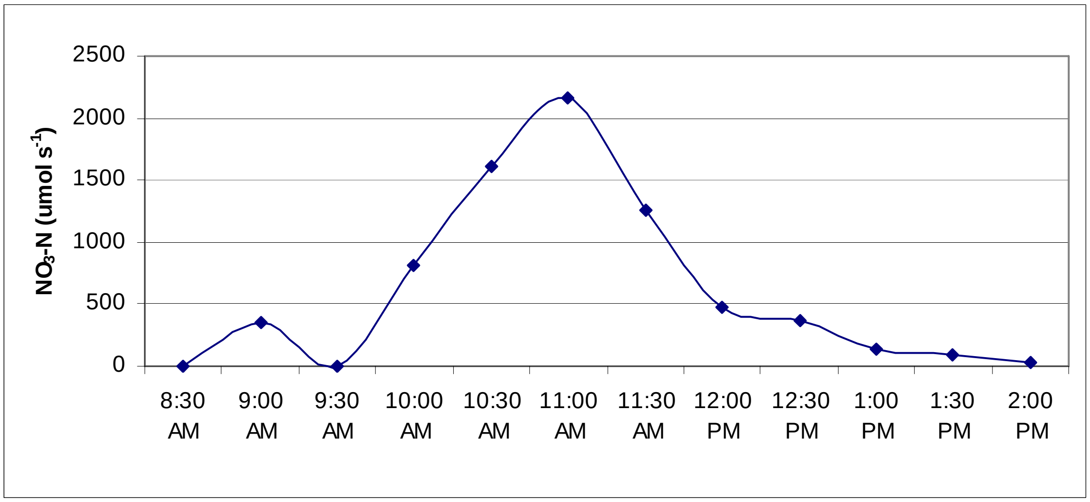


Figure 3.9. Net nitrate retention for a 3rd order stream. The maximum rate of nitrate processing was 2,160 µmol s^{-1} for a total loss of 13.2 moles NO_3-N over the 5.5 hour sampling period. Data collection was in the Fall on 10/1/2008.

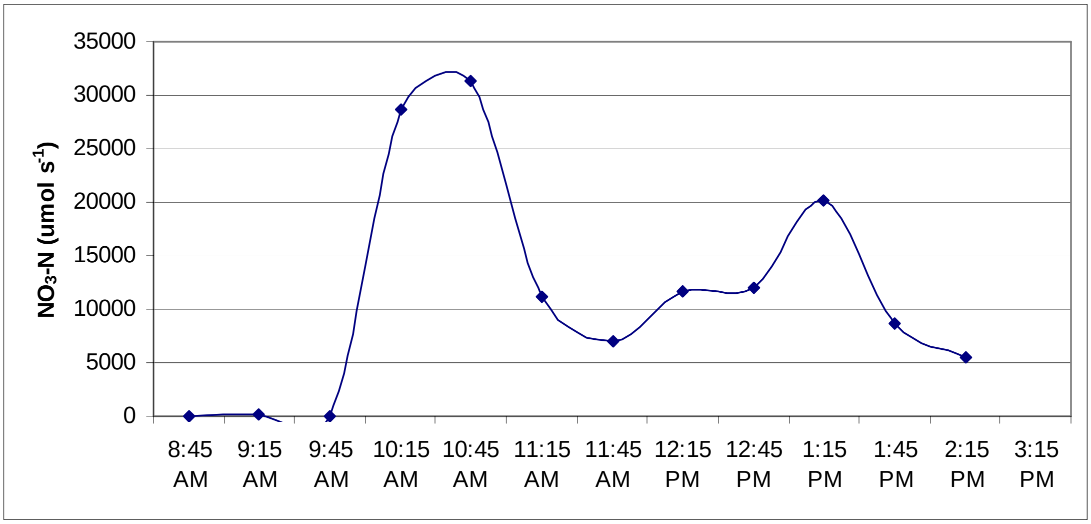


Figure 3.10. Nitrate loss for a 5th order stream. The maximum rate of nitrate processing was 31,390 µmol s^{-1} for a total nitrate loss of 240.3 moles in the 5.5 hour sampling period. Data collection was in the Fall on 10/1/2008.

These results indicate that tidal channels deliver nitrate into the smaller order channels on a flooding tide and ultimately onto the marsh surface. The concentrations of nitrate in water draining out of the channels on the ebbing tide were close to zero. The greatest nitrate retention occurred in higher order channels that have the greatest marsh surface area. The 5th order channel processed an order of magnitude greater amount of nitrate than the 3rd order channel. The significance of processing changes depending on the type of comparison. When estimating processing per unit marsh surface area, the 3rd order had a greater amount of processing. This may be due to the fact that the marsh of the smaller 3rd order channels entirely drains on an ebbing tide, while higher order channels, such as a 5th order, aren't completely flushed of stream water.

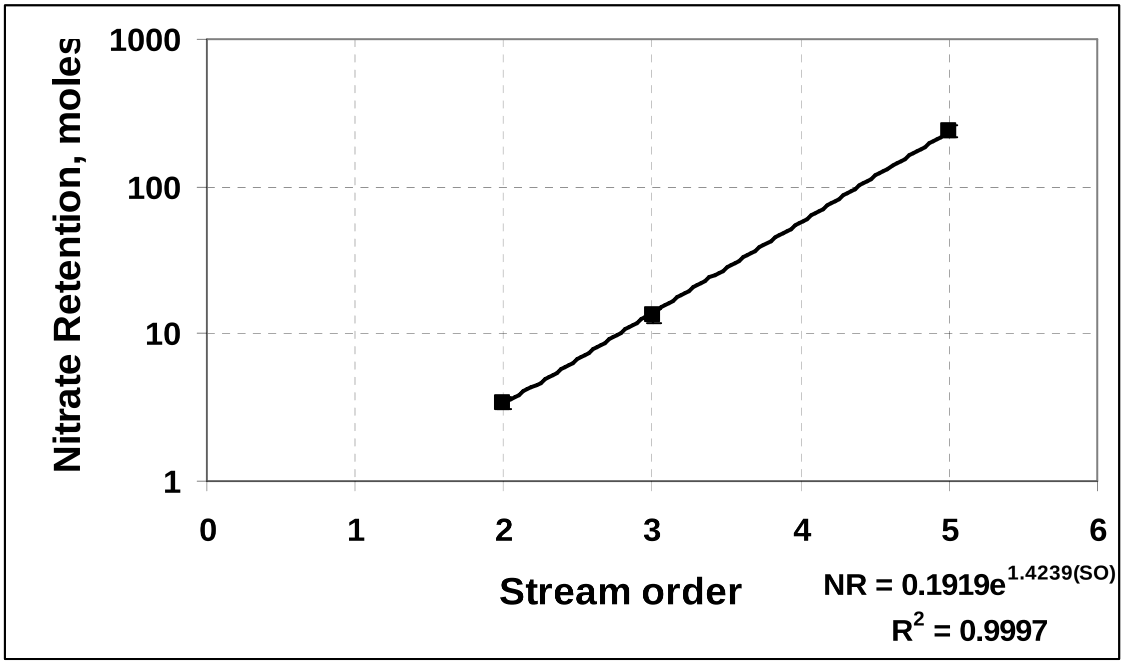


Figure 3.11. Net nitrate retention as a function of stream order. Size of data point incorporates 10% error calculation.

Since marsh surface area seems to be a controlling factor in net nitrate loss, additional relationships of net nitrate loss per unit area were explored (Table 3.I). When the marsh area was factored into the loss equation, the greatest loss was within the 2nd order channel, indicating the importance of surface area for processing. The smaller orders generally have a greater surface area for processing per volume discharge. When viewing the loss process in context of discharge, the 3rd order had the greatest amount of retention. Possibly, the 5th order doesn't retain more nitrate because the velocities are much lower in the larger orders, so that a smaller volume of water is conveyed into the interior networks. The 2nd order didn't have the greatest retention because the hydrologic fluxes were too small overall for comparison within the smallest orders.

The scope of this study wasn't large enough to measure residence times or the ultimate fate of nitrate on the flooding tide; however, the longer residence time of water within the higher order channels may increase net nitrate retention over time. Residence times will be explored in future work.

Table 3.I. Comparison of channel order and nitrate retention characteristics.

Channel order	Net nitrate retention (moles)	Net nitrate retention per unit area (moles m^{-2})[c]	Max rate of nitrate loss (μmol s^{-1})	Max rate of nitrate loss as a function of discharge (μM)
2	3.4[a]	5.07×10^{-3}	814	11.7
3	13.2[b]	2.26×10^{-3}	2160	19.8
5	240.3[b]	5.43×10^{-4}	31390	13.3

a- Loss occurred over a period of 2.5 hours

b- Loss occurred over a period of 5.5 hours

c- Marsh area was determined using the geomorphic relationships outlined in Chap. 2

3. Implications

Previous studies indicate that denitrification rates are not uniform in space or time (McClain et al., 2003). In this study, nitrate retention within tidal marsh systems was determined by measuring the water flux and chemistry of nitrate-rich, tidally-introduced waters flooding into tidal channels and continuing the measurements into the ebbing tide. From these data, the spatial variability of net nitrate retention within the tidal marsh systems of varying size and stream order was determined. This study quantified nitrate processing *in situ* within tidal channel networks of varying size, but the specific sites of maximum nitrogen retention or loss pathways were not determined.

3.3.1 Net nitrate retention

In this study, nitrate retention was determined for exterior channel systems of varying stream order. The 5th order channel had the greatest net nitrate retention when sampled as an exterior channel; however, the 5th order is composed of numerous smaller order interior channels that are integral to the nitrate retention. The individual interior channels weren't sampled and compared with the overall nitrogen processing of the 5th order, but the results of this section lead to the idea that nitrate processing may vary with location in the marsh and by interior or exterior channel type.

3.3.2 Tidal marsh systems act as nitrogen sinks

The results of this section support the idea that tidal freshwater wetlands are sinks for nitrogen. There has been a long-standing controversy regarding the issue of wetlands being sources or sinks of nitrogen. Tidal freshwater wetlands are generally viewed as sinks for nitrogen (e.g. Vitousek et al., 1997); however, moving down the continuum into the saline environment reverses this phenomenon and oligohaline wetlands may be sources of nitrogen (e.g. Heinle and Flemer, 1976). Although the mechanism of nitrate loss isn't known, these results indicate that the tidal channel and marsh network are an integral component to the overall ecosystem denitrification, and must be considered when delineating boundaries for conceptual models of denitrification.

CHAPTER 4

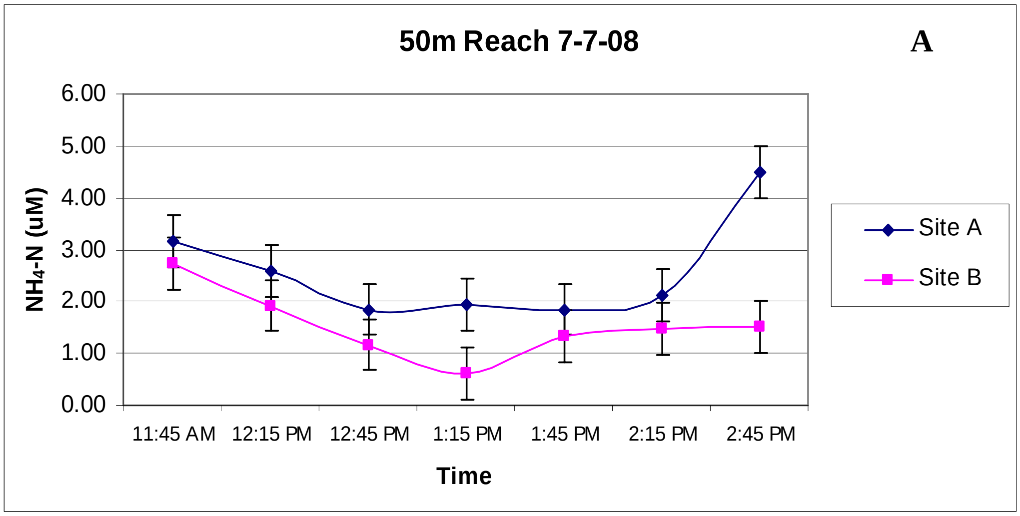
1. Sites of nitrate processing within the marsh

In Chapter 3, nitrate retention in tidal network marshes of different sizes was examined. The size of a tidal marsh network can be portrayed as stream order, marsh area, or discharge. This analysis indicated that nitrogen retention increased exponentially as a function of tidal marsh stream order. Previous work indicates that freshwater tidal wetlands can serve as sinks for both sediment and nutrients introduced into wetlands by stream-flow (Seitzinger, 1988; Comin et al., 1997). In this chapter, potential sites of nitrate loss within the marsh system are examined.

Nitrate processing can occur in the channels (Seitzinger, 1988), in the groundwater (Addy et al., 2002), and on the marsh surface (Jenkins and Kemp, 1984; Joye and Paerl, 1994; Dong, 2000; Eriksson et al., 2003; Greene, 2005*b*). Burial and recycling are two additional sinks for nitrogen, but they are evaluated by measuring marsh surface processing through the seasons, and by evaluation of annual or seasonal changes in nitrogen content of the biomass. In this portion of the study, nitrate processing that occurs on the temporal scale of a tidal cycle was measured by conducting experiments at different sites within the wetland: in-stream, marsh groundwater, and marsh surface. The approach is described in Chapter 1, but the methods are reviewed briefly in the next section.

4.1.1 In-stream nitrogen processing

In-stream denitrification rates were determined from measurements of the nitrogen concentrations in parcels of water (n = 7 trials) that were tracked and sampled over reaches 50- and 100-meter in length. Channel cross sectional area was measured in a straight, uniform reach at distances of 0 (beginning point), 50, and 100 meters. The tidal channel at this location had an average width of x, and an average depth of y (Appendix B). The parcels of water sampled were identified by surface drogues (miniature marshmallows). Nitrogen concentrations (ammonium, nitrite, and nitrate) were measured over a span of at least 3 hours beginning at high tide into a falling tide for both the 50- and 100-m reaches (Appendix F). No significant difference in nitrogen concentration between the two stations was identified (Fig. 4.1). These data suggest that in-stream nitrogen loss was not measurable at the time of measurement in July 2008, and therefore in-stream processing is a minor process in channels similar to the measured one.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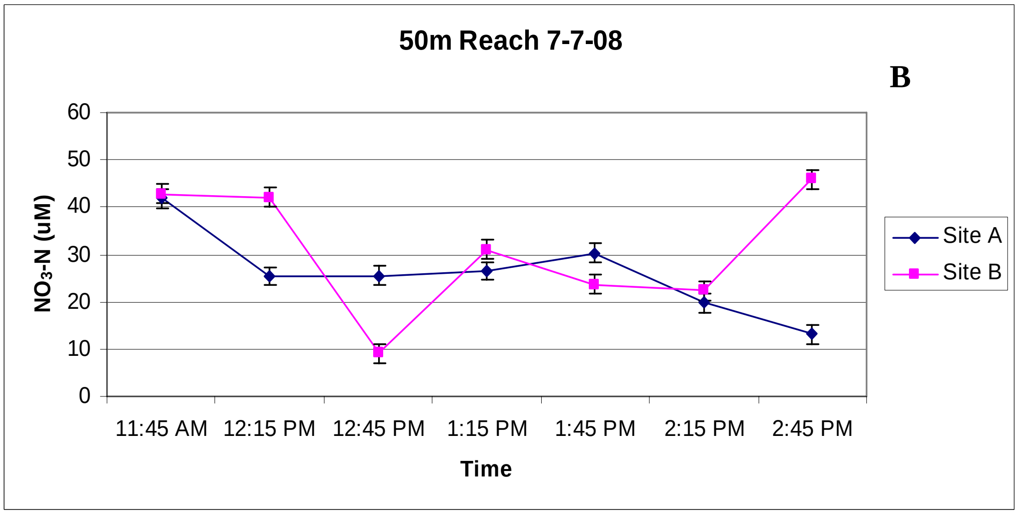
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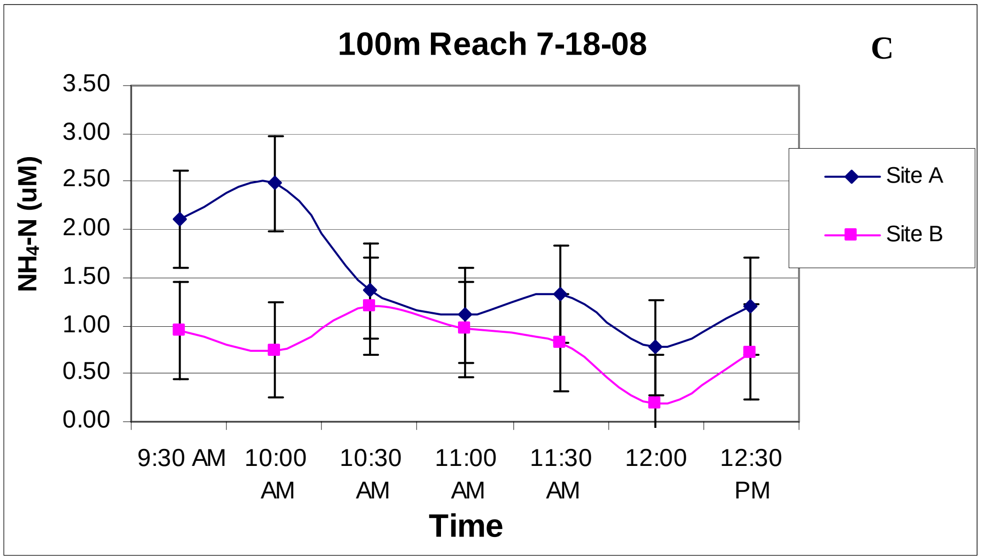


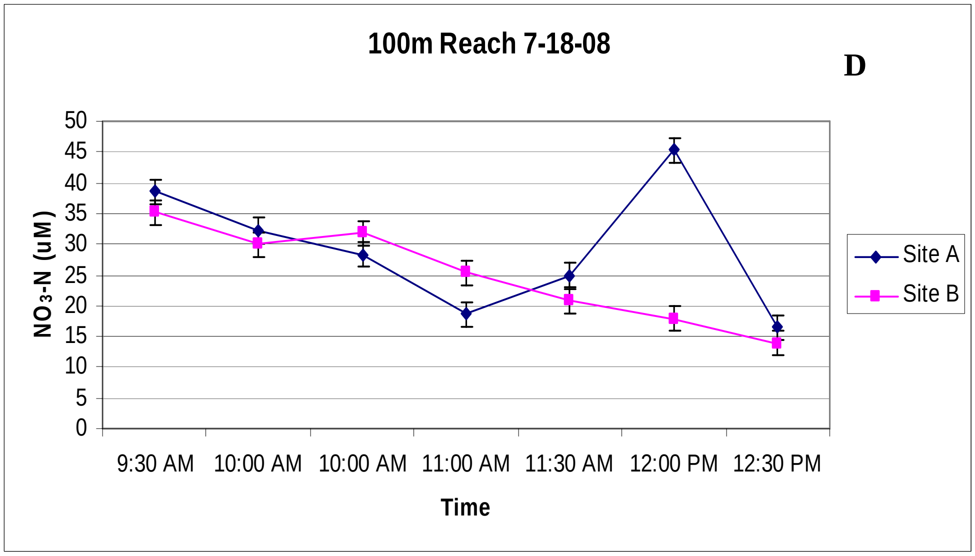
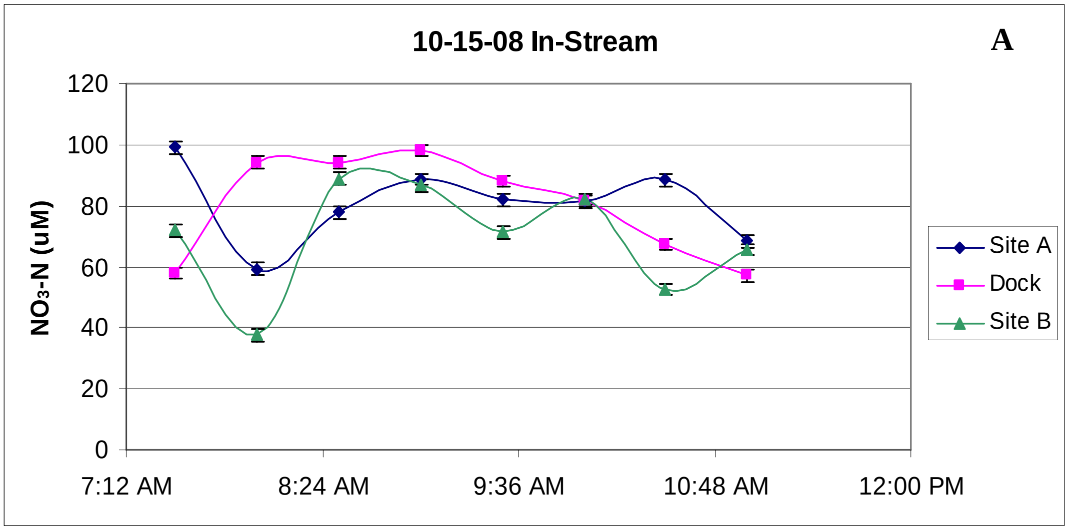
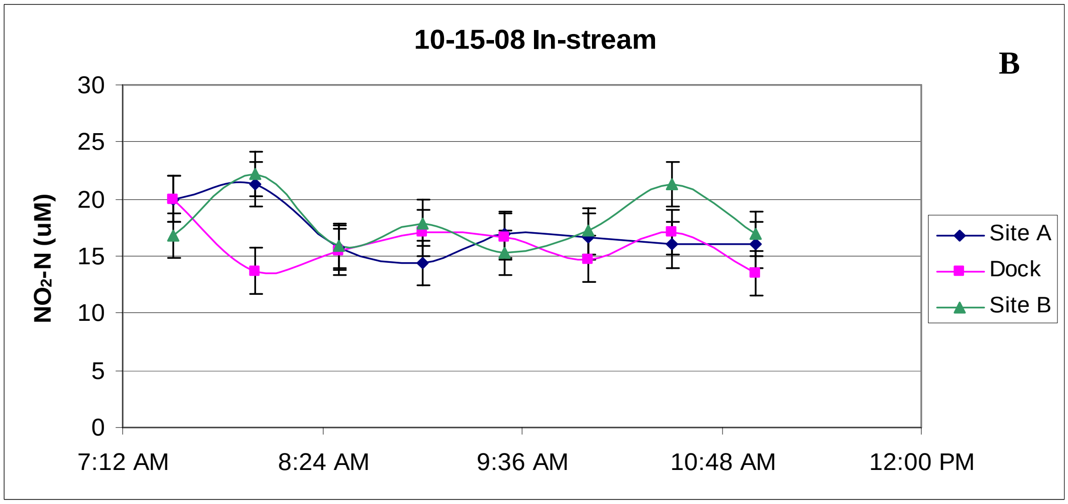


Figure 4.1. a-d. Ammonium (a) and nitrate concentrations (b) for 7/7/08 over a 50-m reach, which indicate no statistical difference in nitrate and ammonium concentrations between the two stations. The lower diagrams indicate ammonium (c) and nitrate (d) concentrations for 7/18/08 over a 100-m reach on an ebbing tide. Again, there is no statistical difference in nitrate concentration between the two stations, but the decrease in nitrate concentrations resulting from up-marsh processes is evident.

The same experiment was repeated on 10/15/08 (n = 8 trials). Similar results were found; no statistically significant changes in nitrogen species concentrations were observed in the samples (Fig. 4.2). In the data collected in October, nitrate, nitrite, and ammonium concentrations were almost double the concentrations of the summer. Nitrate concentrations in October ranged from 37.7 to 99.1 µM NO_3-N, nitrite ranged from 13.5-22.2 µM NO_2-N, and ammonium ranged from 0 to 8.4 µM NH_4-N. For the summer data, nitrate concentrations ranged from 9.1 to 46.0 µM NO_3-N and ammonium ranged from 1.1 to 5.4 µM NH_4-N. The increased concentrations reflect the seasonal variations in water column nitrogen availability.





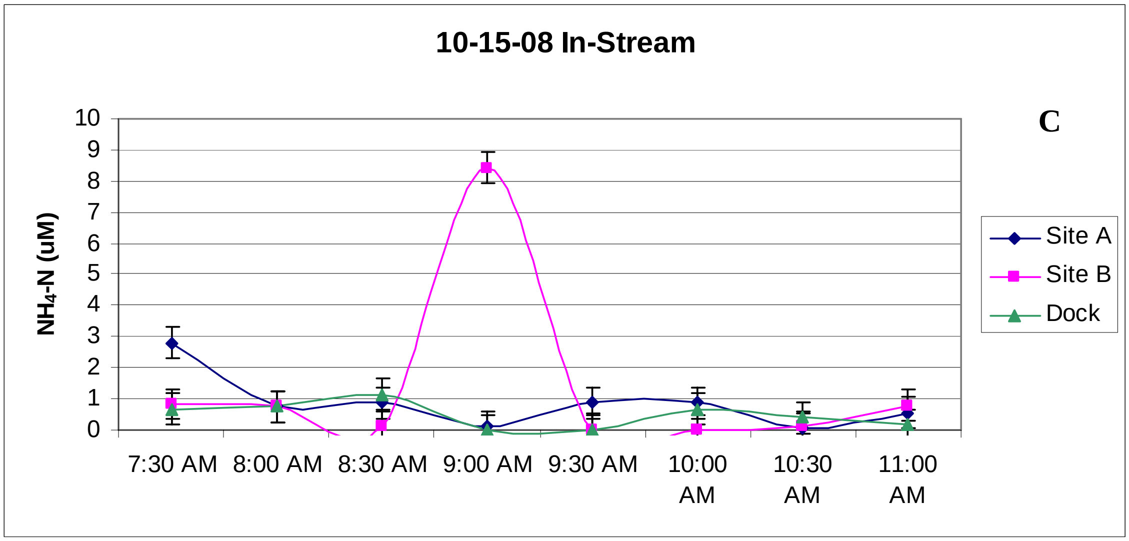


Figure 4.2 a-c. Nitrate (a), nitrite (b), and ammonium (c) concentrations measured on 10/15/2008 over a 50- and 100-m reach. Samples were collected beginning at Site A (upstream), at Site B (50-m downstream), and at the dock/boat launch (100-m downstream) on an ebbing tide.

The small tributaries feeding from the marsh into the measured reaches may have complicated the trend. This is inferred because of the spikes in ammonium concentrations that were sampled in both measurements. Within the system, there are no straight reaches of any distance without these small tributaries; I chose the straightest reach possible with the smallest number of tributary inputs to conduct these in-stream denitrification/nitrogen uptake experiments. These experiments should be repeated in early spring, when rapid growth of SAV might affect nitrogen concentrations.

4.1.2 Groundwater nitrogen processing

Seeping groundwater was collected on 11/18/08 at low tide (Table 4.I). Since the water was collected from an open system, the data were difficult to examine. The temperature of the water at the time of collection ranged from 4.5°C to 14.4°C. The samples were stored and run at 5°C. At 5°C, the ambient N_2:Ar is 37.263, and when converted into N_2 concentration over ambient argon levels is 725.69 µM. All ratios were above ambient levels of 37.263, and range from 37.919 to 38.612. Although the ratios were above ambient conditions, ambient N_2:Ar varies slightly with temperature and salinity and the data were therefore corrected for these variations. When calculating the nitrogen gas concentrations, the data don't support the same trend. Concentrations varied from 627.7039 to 745.6222 μM N_2-N. It is therefore difficult to determine a trend in the data of an open system. Based on the uncorrected N_2:Ar data, denitrification was occurring, but the magnitude of processing is unclear once the data are corrected for temperature. It is possible to infer that the measured water was already denitrified at time and location of collection because N_2:Ar ratio wasn't greatly higher than ambient conditions, and the MIMS technology allows accuracy of ± 0.02%.

Another way to evaluate the possible role of groundwater denitrification is to measure the nitrate concentrations of the seeping groundwater. Groundwater seepage from the marsh into the channel is most significant during low tide when horizontal groundwater gradients adjacent to the channel are the steepest. Under these conditions, groundwater is the greatest contributor of baseflow on an ebb tide. During these low ebb tide conditions, tidal channel nitrate concentrations fell to zero at some of the sites, which indicates that the seeping groundwater was not bringing nitrate into the channel. It is probable that denitrification was occurring within the groundwater, since the water recharging groundwater originates from infiltration of nitrate-rich tidal water during the flooding intervals in the tidal cycle. Previous work shows that the total amount of groundwater entering the tidal channels is small (Phemister 2006), and therefore the extent of groundwater contributions to total flux in the tidal channel networks is small compared to the return flow from the tidal marshes or from tidal channel drainage.

Table 4.I. N_2:Ar ratios for seeping groundwater collected on 11/18/08 used to determine whether denitrification was the dominant process. All ratios are above atmospheric levels of 37.263 at 5°C.

Time	N_2:Ar	N_2-N (µM)
11:15 AM	37.919	745.6222
11:45 AM	38.009	699.8356
12:45 PM	38.081	679.3477
1:00 PM	38.021	627.7039
1:15 PM	38.039	693.0992
1:45 PM	37.965	704.1689

4.1.3 Marsh surfaces nitrogen processing- Core incubations: Nutrient fluxes and ambient N_2 and O_2 fluxes

Marsh sediment cores (10-15 cm of surface sediment) were collected in Spring and Summer 2009 to determine marsh surface and subsurface (to a depth of ~15 cm) processing. Cores were equilibrated overnight, and then sealed and incubated with overlying water for approximately 6 hours. Water samples were collected over time to determine the amount of denitrification.

Core incubation experiments provided rates of nitrogen gas and oxygen gas fluxes (measured with N_2:Ar) from samples of the tidal marsh soils when incubated with water obtained from the adjacent channels on the incoming tide. These rates were examined for several different times of year (Spring and Summer), and at different locations from a tidal channel. Rates of N_2 fluxes (Appendix G) ranged from 7.3 (in March) to 227.2 (in June) µmol N_2-N m^{-2} hr^{-1} indicating a net flux into the water column from the tidal marsh (Fig. 4.3). The production of N_2 over time was strongly correlated (r^2 values ranged from 0.95 to 0.99). The average N_2 production for the March measurements was 56 µmol N_2-N m^{-2} $hr^{-1}$and in June the average was 154.6 µmol N_2-N m^{-2} hr^{-1}. Previously in Patuxent

River wetlands, Greene (2005*b*) measured an average N_2 flux of 120 μmol N_2-N m^{-2} hr^{-1}, and a range of -156 to 846 μmol N_2-N m^{-2} hr^{-1}, with a range of 10 to 200 μmol N_2-N m^{-2} hr^{-1}.

The data on spatial production of nitrogen gas for the March data indicate that the greatest production of N_2 was at the edge of the bank, at the site <1 meter from the marsh creek. This spatial pattern was not repeated for the June sampling period. In June, maximum nitrogen gas production was obtained from samples of the upper marsh over 30 meters from the marsh creek.

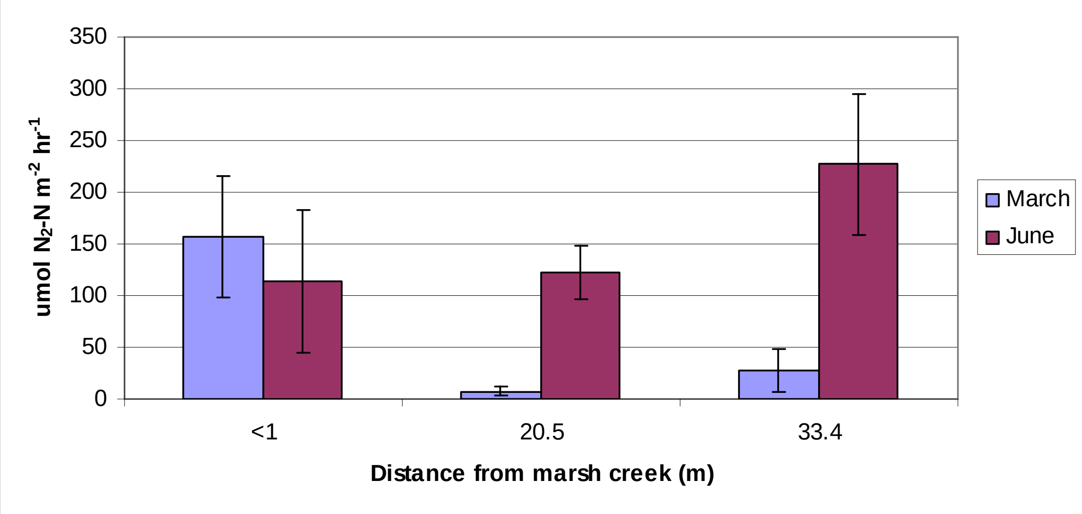


Figure 4.3. Production of N_2 during core incubations for samples measured along a 35 meter transect. Cores sampled on 3/19/08 and 6/9/09.

The O_2 fluxes ranged from – 1138 to – 1601 μmol O_2 m^{-2} hr^{-1} indicating a net flux into the sediment (Fig 4.4). The reduction of O_2 over time was strongly correlated for the sites sampled <1 and 33.4 meters from the channel (all r^2 values >0.99), but were not as strongly correlated for the 20.5 meter sample (all r^2 values were much less than 0.99, the largest value was 0.18) measured in March. No data were reported for the site 20.5 meters from the channel, but there was still a trend of net flux into the sediment.

Comparison between sites isn't possible because the sites were not statistically different. The average O_2 loss into the sediment for the March measurements was -1210 µmol O_2 m^{-2} $hr^{-1}$and June was -1358.6 µmol O_2 m^{-2} hr^{-1}. Previously in Patuxent River wetlands, Greene (2005*b*) measured a range of O_2 fluxes from 470 to 5293 µmol O_2 m^{-2} hr^{-1} with the flux directed into the sediment.

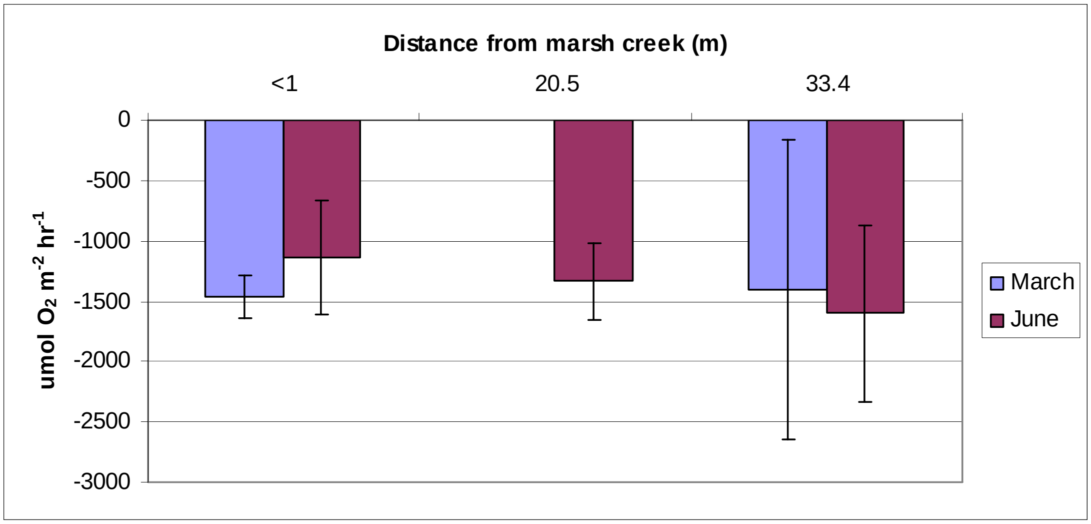


Figure 4.4. Flux of O_2 measured during core incubations for samples along a 35 meter transect. Cores sampled 3/19/08 and 6/9/09. No data were reported for the core taken at 20.5 meters on 3/19/08 because the trend in the data was not interpretable.

There is a general correlation between O_2 flux into the sediment, and N_2 flux into the water column ($r^2 = 0.41$; Greene, 2005*b*) for numerous marsh surface cores. The trend was not reported here because there were not enough data to determine a trend.

Net fluxes of nitrate, NO_3-N, were only reported for March samples because samples were incomplete for the June sampling. Fluxes ranged from 11 to – 123 µmol NO_3-N m^{-2} hr^{-1} with fluxes largely directed into the sediment (Fig. 4.5). Only one value was positive and was measured in one of the replicate samples <1 meter from the marsh creek indicating flux into the water column. This result supports the notion that nitrification and denitrification are coupled in the Bay sediments. The reduction of NO_3 over time was strongly correlated for the sites sampled (r^2 values ranged from 0.88 to 0.98). Error is large for all sites, so no comparisons can be drawn between sites. The average NO_3-N for the March measurements was -105 µmol NO_3-N m^{-2} hr^{-1}. Previously in Patuxent River wetlands, Greene (2005*b*) measured a range of NO_3–N fluxes from -276 to 84 µmol NO_3-N m^{-2} hr^{-1} with a range of -1 to -100 µmol NO_3-N m^{-2} hr^{-1} most commonly observed.

Specifically, Greene (2005*b*) measured a range of 8 to -155 µmol NO_3-N m^{-2} hr^{-1} in the mid marsh surface of Jug Bay in April. These rates are comparable to the rates measured in this study for the March samples (11 to – 123 µmol NO_3-N m^{-2} hr^{-1}). Since the study sites of both experiments are in close proximity to each other, and data are comparable, data from Greene (2005*b*) were used to estimate seasonal denitrification rates.

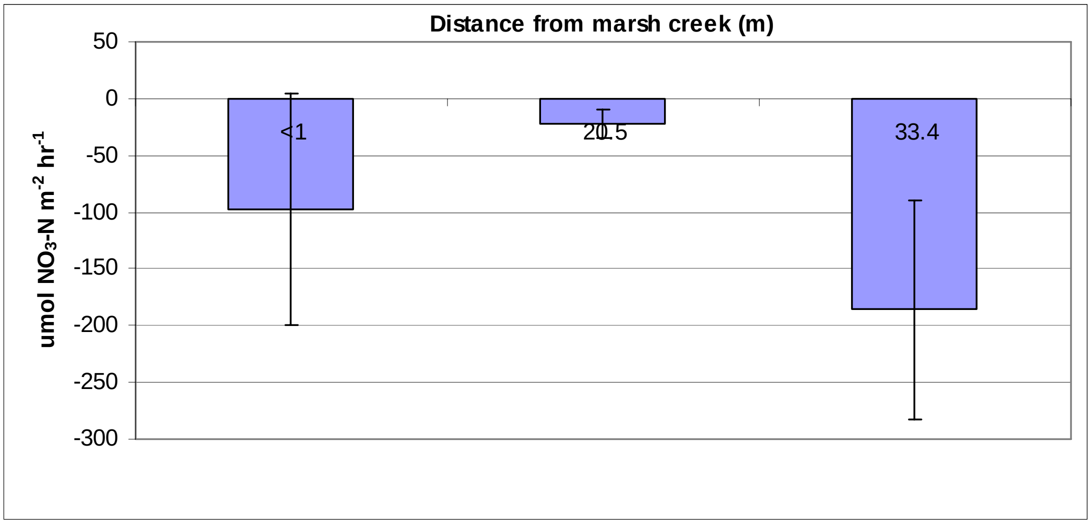


Figure 4.5. Flux of NO_3-N measured during core incubations for samples along a 35 meter transect. Cores sampled 3/19/08.

Net fluxes of nitrite, NO_2-N, were again only reported for March. Fluxes ranged from -118 to – 228 µmol NO_2-N m^{-2} hr^{-1} which indicates that fluxes were largely directed into the sediment (Fig. 4.6). The reduction of NO_2 over time was strongly correlated for the sites sampled greater than 20 meters from the creek bank (r^2 values > 0.93); however, of all samples analyzed, only two had strong regression values, so no error is reported for the sites. The average NO_2-N for the March 2009 measurements was -173 µmol NO_2-N m^{-2} hr^{-1}.

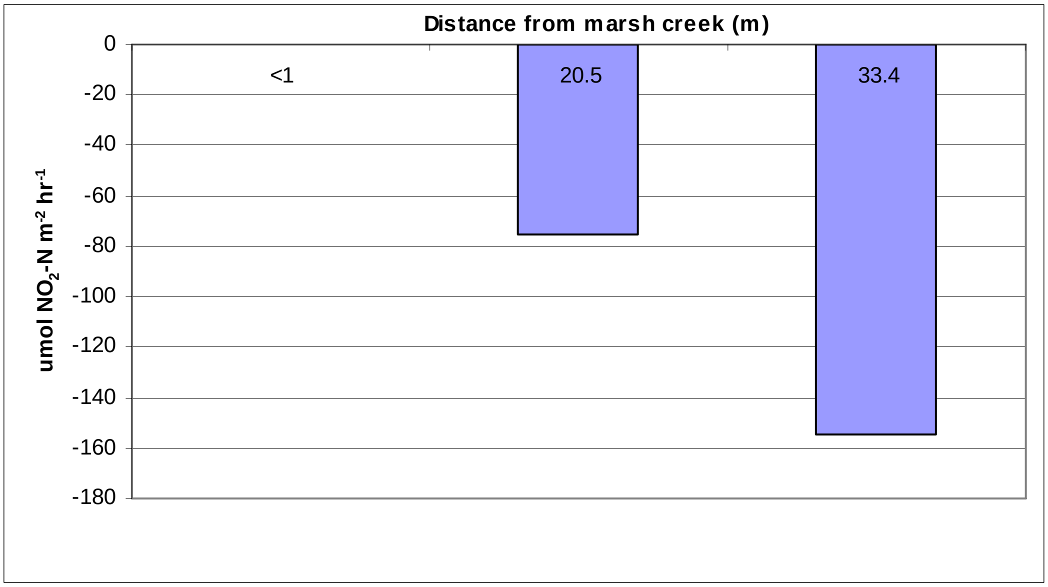


Figure 4.6. Flux of NO_2-N measured during core incubations for samples along a 35 meter transect. Cores sampled 3/19/08.

Net fluxes of ammonium, NH_4-N, ranged from – 77.9 (in March) to 140 (in June) µmol NH_4-N m^{-2} hr^{-1} (Fig. 4.7). For the March measurements, fluxes were largely directed into the sediment, but for the June measurements, fluxes were largely into the water column. The reduction of NH_4 over time was strongly correlated for the sites sampled (r^2 values ranged from 0.77 to 0.92). The regression value for the sample <1 meter from the creek bank was low ($r^2 = 0.77$) for the March measurements; however, the value was still used for analysis because the flux was into the sediment, and the same order of magnitude of the other samples. No error was reported for the samples because not enough samples showed a strong correlation to calculate error. The average NH_4-N flux for the March measurements was -66.6 µmol NH_4-N m^{-2} $hr^{-1}$and for the June measurements was 109.7 µmol NH_4-N m^{-2} hr^{-1}. Previously in Patuxent River wetlands, Greene (2005*b*) measured a range of NH_4–N fluxes from -118 to 934 µmol NH_4-N m^{-2} hr^{-1} with a range of 0 to 200 µmol NH_4-N m^{-2} hr^{-1} most commonly observed.

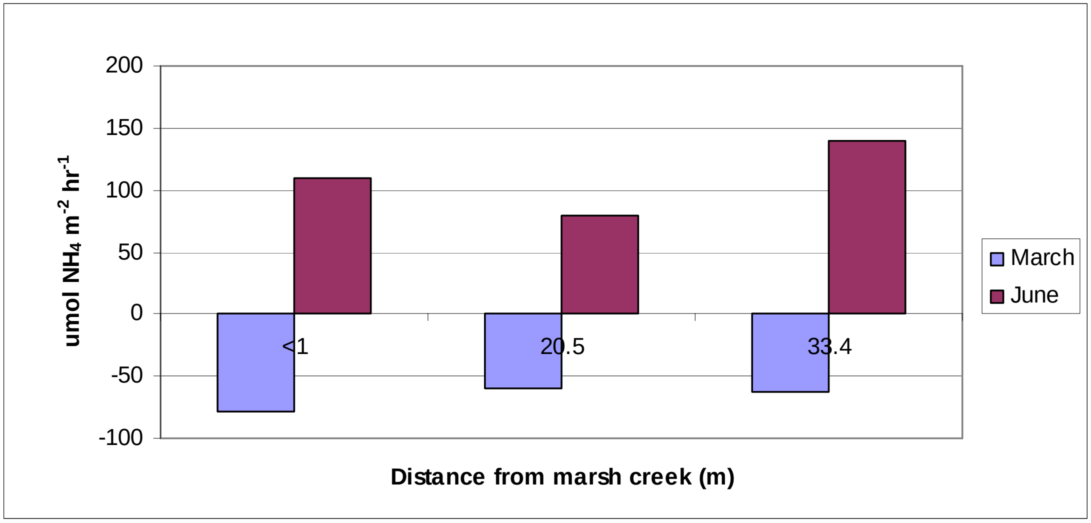


Figure 4.7. Flux of NH_4-N measured during core incubations for samples along a 35 meter transect. Cores sampled 3/19/08 and 6/9/09.

2. Implications

4.2.1 In-stream nitrogen processing

Denitrification occurs when nitrate is present in low oxygen environments with available electron donors present. On a flooding tide through to an ebb tide, denitrification is expected. Two reaches (50- and 100-m) were tested to encompass reach length into the study, thus eliminating the possibility of sampling over too short of a reach. A smaller reach means that the water has less time to interact with the surrounding banks and stream bed. Again, denitrification rates are greatest where water residence times are the longest (Kjellin et al., 2007). Longer reaches are not good tests for in-stream denitrification due to significant inputs from tributaries that might be significantly larger than the small ones noted in this reach. Previous studies suggest that in-stream denitrification is not significant in higher order streams because the nitrate isn't coming into contact with heterotrophic denitrifiers in the suboxic zones (e.g. Findlay, 1995). Over a period of a few hours, denitrification is most likely to occur in aquatic sediments and soil microsites, and not within the water column (Seitzinger et al., 2006). Conversely, nitrification was another possible process occurring in the water column through the aid of vegetation oxidizing the sediments. If nitrification were occurring, an increase in nitrate concentrations would be measured, but this was not seen in the data either (Fig. 4.1). It is possible; however, that nitrification and denitrification are coupled. In this case, denitrification may mask the effects of nitrification.

Water column, or in-stream denitrification, is a more dominant process in stratified lakes and estuaries. In this system, the water column acts to transport, but not process nitrogen. In-stream denitrification may occur in the smaller stream orders that are significantly shallower and therefore, may provide more contact with marsh surfaces. Due to the rapid increase in channel depth and surface area with stream order (see Chapter 2), most of the channel bed surface area in a tidal marsh is contained in the higher order channels.

4.2.2 Groundwater nitrogen processing

In tidal wetlands, groundwater is recharged by the nitrate-rich channel water during flooding tides, but drainage from the groundwater is limited to areas directly adjacent to the channels. Phemister (2006) determined that groundwater fluxes are larger along higher order channels, where the tidal range is higher and groundwater gradients are steeper. Total groundwater flux, however, is small compared with the water carried in the tidal channels (Phemister, 2006). There is evidence that denitrification occurs in the groundwater because the nitrate concentrations from the seeping groundwater were close to zero. Commonly, denitrification rates are high within the groundwater, but the gas samples in this study were collected in November when the water temperatures were as low as 3.6^{o}C, and as high as 14.4 ^{o}C. Denitrification greatly slows when temperatures near freezing (Holtan-Hartwig et al., 2002). There is evidence of groundwater denitrification, and we can infer that rates will be greater during the growing season. Denitrification is difficult to measure in an open system. Future testing using groundwater taken from piezometers will more accurately determine the magnitude of denitrification within the groundwater.

Finally, the hydraulic conductivity of the sediment can restrict denitrification. Phemister (2006) evaluated hydraulic conductivity in the marsh system as a function of depth, and determined that the highest values of conductivity were restricted to a narrow zone between the marsh surface and the rooting depth of the vegetation (within the first 0.75 m of the marsh). Compacted marsh vegetation in deeper samples had relatively low hydraulic conductivities (Phemister, 2006).

4.2.3 Marsh surface nitrogen processing

Sediment core incubations were used to accurately quantify potential denitrification rates within a closed system. Greene (2005*b*) extensively measured denitrification rates in Jug Bay using MIMS, and determined that the average denitrification rate was 120 μmol N_2 m^{-2} hr^{-1}. The majority of the data ranged from 10 to 200 μmol N_2 m^{-2} hr^{-1}. The greatest variance in rates was among the seasons, and not location within the marsh. Merrill and Cornwell (2000) found similar denitrification rates of 28 μmol N_2 m^{-2} hr^{-1} in the fall and 60 μmol N_2 m^{-2} hr^{-1} in the spring. In this study, the denitrification rates fell within the ranges measured by both Greene (2005*b*) and Merrill and Cornwell (2000). Since freshwater tidal marshes have homogenous substrates, i.e. muddy soils relatively devoid of extensive root systems, (Garofalo, 1980), and the denitrification rates are similar, data from Greene (2005*b*) conducted at the adjacent Jug Bay marshes can be used to estimate seasonal variations in denitrification for this site.

Seasonal variations in denitrification were documented through core incubations. The most apparent change was in denitrification rates with position in the marsh through the seasons. In the early spring, the highest denitrification rates were near the marsh creek, and the other rates were markedly lower 20 meters or more along the transect. These rates were mostly likely controlled by the organic matter available for organic matter mineralization. In the spring, the near creek marsh surface area likely has more labile forms of organic matter compared to the higher marsh areas that are inundated to a lesser degree. These organic matter reserves are utilized in the early spring, and are therefore less available in the early summer. The organic matter ultimately controls the levels of denitrification. More testing of organic matter content with position in the marsh, and seasonal variations of core incubations are necessary to validate the above speculation.

The marsh surface was the location for the greatest net nitrate retention. This was determined because marsh surface area increases with channel order, and in-stream and groundwater denitrification were minimal. Marsh surface processing doesn't account for the entire loss process within the wetland system. The ultimate fate of all nitrates is still largely unknown. Plant assimilation, burial, recycling, etc. are all possible pathways of nitrate loss. A much more complex experimental design is necessary to detail all of these loss pathways. The mass balance approach within this study incorporated all of these processes by measuring the net nitrate retention even though the exact processes weren't enumerated.

CHAPTER 5

This study has documented the amount of nitrate retention in freshwater tidal network marshes of varying scale. Tidal channels within the marsh system bring nitrate-rich water into the marshlands where nitrogen processing can take place. Nitrogen retention within the marsh system increases exponentially with stream order, and reflects the increase in tidal marsh area with stream order. When nitrogen retention is normalized for marsh area, it suggests that larger tidal network marshes may have nitrogen retention amounts that are an order of magnitude less than these of the smaller marsh areas. The disparity in processing suggests that there is either spatial variation in nitrogen processing within the larger tidal networks, or shorter inundation processing times in the marshes at the head of the systems. These spatial differences may include microsites created by changes in marsh surface topography, or density of vegetation and microbial mats. Within the larger systems, the spatial variability is magnified because of the large marsh surface area in comparison to smaller orders with smaller surface area with less opportunity for variability. Alternatively, the time of inundation may be the cause of the difference in processing rates. The smaller order exterior channels closely follow the tidal inundation patterns of the mainstem, but the larger orders follow by a much greater lag. Therefore after factoring water travel time, the larger channels with highly branched channels may be inundated for a smaller range of time compared to exterior smaller orders. Future research is needed to correctly identify the spatial heterogeneity, and duration of inundation between the orders.

In addition, comparison of nitrogen retention determined from the mass balance considerations with those measured from core incubations in this and other studies, suggests that measured nitrogen loss at the upper end of the tidal network is considerably higher than denitrification alone (Table 5.I). This suggests other processes are occurring in addition to denitrification, such as biotic assimilation or burial. Ultimately, the results suggest that the true value of freshwater tidal wetlands for nitrogen retention is largely under-estimated in many studies because ecosystem functioning is determined by denitrification rates alone. The results of this study support the notion that ecosystem nitrogen processing can't be determined by scaling up of denitrification rates alone. Since there are still many unknown factors controlling ecosystem nitrogen processing, the well-studied controls of denitrification are evaluated in the next section.

Table 5.I. Comparison of calculated net nitrate retention rates and measured denitrification rates

Channel order	Net nitrate retention (moles)[a]	Net nitrate retention per unit area (moles m^{-2})[a]	Nitrate retention rate (µmol m^{-2} hr^{-1})[b]	Denitrification rate (µmol m^{-2} hr^{-1})[c]
2	3.4 (± 0.34)	5.07×10^{-3}	500-1200 (10-4 hrs)	17 to 142 (Fall range)
3	13.2 (±1.32)	2.26×10^{-3}	226-565 (10-4 hrs)	
5	240.3 (±24.03)	5.43×10^{-4}	95-271 (6-2 hrs)	

a-From mass balance calculations (see chapter 3) measured in the Fall 2008. A 10% error is included for net nitrate retention. Even with the 10% errors, a difference in processing is seen between channel orders.

b-Range of nitrate retention rates for each channel order per unit area and inundation time. The rates given are for a range of probably inundation times. The inundation times were calculated based on measured field velocities.

c- Range of denitrification rates from Greene (2005*b*) measured on the marsh surface of Jug Bay in September and October 2004.

1. Controls on denitrification

Denitrification rates are controlled by temperature, the availability of organic matter, amount of oxygen, and nitrogen availability (Seitzinger, 1988; Cornwell et al., 1999). The greatest denitrification rates observed in the Patuxent River marshes occurred during the spring (Merill, 1999; Greene, 2005*b*). Denitrification activity is dependent on temperature. Potential denitrification rates at 4°C can be as much as 77% lower than rates at 22°C (Pfenning and McMahon, 1996). Although the work presented above was completed at different points throughout the seasons, the trends of denitrification are the same, only the magnitude of processing differs.

The rates of denitrification are highest in spring not only because of temperature, but also because of organic matter content. In the spring, accumulated pools of organic matter are likely present from the previous year, and therefore are a source of carbon that is readily decomposed after the winter thaw (Bastviken et al., 2007). The quality, but also the availability of organic matter can control denitrification. The greatest denitrification rates will occur in areas with the greatest availability of labile carbon. In freshwater tidal wetlands, organic matter content is fairly high compared to other wetland types. Measured organic matter concentrations ranged from 8.4 (+/- 0.03)% to 15.1 (+/-0.08)% with an overall average of 10.6 (+/-2.1)% for Patuxent River wetlands with no trend in composition in relation to distance from main tidal channel or depth (Phemister, 2006). Hopfensperger et al. (2009) also found that organic matter content and plant community composition are correlated with elevation, but denitrification enzyme activity didn't differ across elevation. Oxidation of organic matter is an important pathway for denitrification, but the magnitude of oxidation didn't change much with respect to vegetation type or location within the marsh in their study; however, this isn't a widespread trend.

Regardless of the dominant type of vegetation, denitrification rates are correlated with sediment oxygen consumption (Setizinger 1990; Seitzinger 1994). As seen by the core incubations, denitrification rates increase as the oxygen consumption increases. In other words, the oxygen concentration decreases because the autotrophic microbes consume the oxygen in the sediment to complete the denitrification process. Denitrification rates also increase when the concentration of nitrate increases in the overlying water (Koerselman et al., 1989; Merrill and Zak, 1992; Seitzinger, 1994), but water column nitrate concentrations aren't the best predictors of denitrification because nitrate is also produced through the coupled nitrification-denitrification process. In some cases, nitrate from the overlying water provides only ~20-50% of the nitrate needed to support denitrification, and the rest of the nitrate comes from the groundwater or nitrification of ammonium released during mineralization of organic nitrogen (Seitzinger, 1994).

Generally, in tidal freshwater wetlands of the Chesapeake, nitrification and denitrification are coupled within the sediment (Setizinger et al., 2006). Plants can introduce oxygen into the root zone which facilitates nitrification and produces nitrate. That nitrate then diffuses into the nearby anaerobic zone and the nitrate is transformed into N_2 gas through denitrification. Nitrate also diffuses into the tributary sediments from the nitrate-rich tidally introduced waters. Nitrification occurs in the water column and at the oxidized sediment-water interface, and denitrification occurs in the anaerobic sediments (Reddy et al., 1989). As expected, the greatest nitrogen processing occurred on the marsh surface, and the channel network influenced the magnitude of processing. As the marsh surface area increased exponentially, the magnitude of nitrogen processing also increased exponentially.

Based on previous research, denitrification is an important loss pathway for nitrate (Bowden, 1986; Seitzinger, 1988; Joye and Paerl, 1994; Mitsch and Gosselink, 2000). The experimental design of this study is such that overall nitrogen loss is measured, which is mainly via denitrification. It is important to remember that denitrification isn't the only pathway for nitrogen removal from a system. Another major source of nitrogen loss within freshwater tidal wetlands is plant or biotic assimilation of nitrogen. This is an important factor for nitrogen loss along with burial, but ammonium is used more readily than nitrate, which leaves an excess of nitrate in the system. Assimilation is a seasonally dominant process. In the beginning of the growing season/early spring, assimilation is a much more dominant process, but once the vegetation is established, the process is no longer dominant (Boyd, 1969). Additionally, nitrate is produced by the nitrification of mineralized ammonium (Reddy et al., 1989), which again can attribute to the elevated nitrate concentrations. These ideas are supported by the above results; ammonium concentrations were much lower than nitrate concentrations (e.g. Fig. 3.3). Therefore, although greatly important to ammonium loss, assimilation has less of an effect on net nitrogen loss, but can be a controlling factor seasonally. Additional pathways such as dissimilatory nitrate reduction to ammonium and anaerobic ammonium oxidation (annamox) exist, but are more common in freshwater lakes or deeper aquatic systems (Burgin and Hamilton, 2007), and therefore play a small role in nitrogen removal in this study.

Although there are numerous controls on denitrification, freshwater tidal wetlands are conclusively excellent sites for denitrification. Although sites for nitrogen processing are spatially variable, the created framework to investigate the importance of the tidal channel network encompassed this variability by exploring the relationship between geomorphology and hydrology with biogeochemistry.

2. Synthesis and future research

Previous research has identified the importance of tidal wetlands for denitrification (e.g. Bowden, 1987; Seitzinger, 1988), but there has not been much attention paid to the geomorphic and hydrological organization of the tidal marshes and their effect on nitrogen processing and retention. Although this study points to the importance of the tidal network for nitrogen processing, the ultimate relief from eutrophication still lies in the reduction of nutrients coming into the Bay ecosystem. Long-term research is needed to explore the relationship among increased nutrient loading, sea-level rise, marsh growth, and the potential of tidal networks as long-term sinks for these nutrients.

As is true for most research projects, there are many unanswered questions generated from this study. In particular, I think that the following research topics are worthy of future research attention:

1. What is the difference in nitrogen processing between interior and exterior channel networks?
    a. What is the distribution of hydrological fluxes within interior tidal marsh networks? What is the influence of elevation gradient, marsh

surface ponding depth and duration, and the timing of incoming and outgoing discharges within the tidal network system?

    b. What is the influence of vegetation roughness heights on flow velocities and nitrate fluxes? Does it vary seasonally and is it different for interior and exterior channels?

2. Do seasonal differences in vegetation and flow resistance affect inundation duration and nitrogen processing within the tidal network?
3. How does position within the marsh (e.g. distance from the channel boundary or distance upstream from the main channel) affect nitrogen processing?

Also, there is a need for continued research of this nature to determine the overall effect of sea level rise on the importance of the tidal network. As mentioned previously, the network may become even more important for processing since a greater volume of water will be flooding the marsh surface with an increase in sea level and tidal range. Tidal network marshes are effective sites for denitrification; therefore, the increased volume of nitrate-rich water might result in increased levels of denitrification. This scenario is only plausible if the wetlands are able to accrete quickly enough to keep up with sea level rise. A converse scenario is that the marshes will quickly become submerged, and the tidal network will become less important for processing once it is no longer intact. In subsiding freshwater wetlands of the Chesapeake Bay, the interior tidal networks appear to be the first areas affected by sea level rise, where channels appear to respond by widening and marsh loss results in the development of interior ponds (Kearny et al., 1988). Additionally, in the Chesapeake Bay system, eutrophication compounds the effects of sea level rise because the excess nutrients can reduce carbon storage in the sediment resulting in marsh subsidence (Turner et al., 2009). The effect of sea level rise largely depends on sediment availability and transport, which calls for an additional study.

This research project has helped to outline future research directions. The culmination of this work will hopefully facilitate scientists and practitioners to view and calculate ecosystem processing on differing scales to ultimately understand the importance of tidal freshwater wetlands with increased eutrophication and sea level rise.

Appendix A: Tides at Hill's Bridge (Rt. 4)

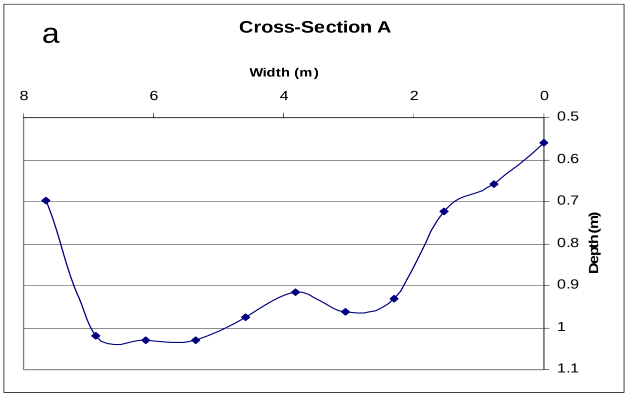
Table I. Tides at Hills Bridge (Rt. 4), Patuxent River, MD for 2008 sampling (provided by Maryland Department of Natural Resources Fisheries Service)

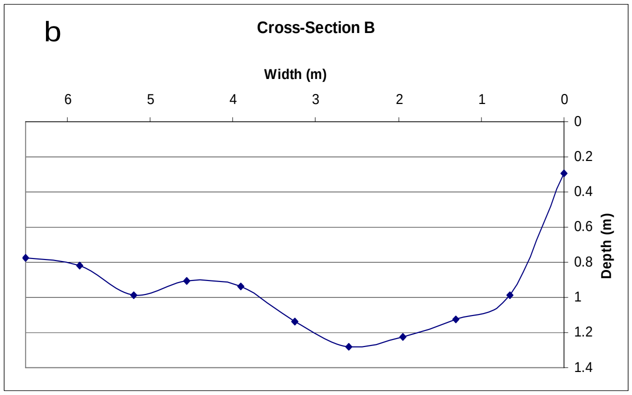
Day	High/Low	Tide Time	Height Feet	Sunrise/ sunset	Moon	Time	% Moon Visible
5/4/08	High Low High Low	5:04 AM 12:49 PM 5:17 PM 11:36 PM	4.3 0.7 2.6 0.2	6:05 AM 8:02 PM	Rise Set	5:05 AM 7:29 PM	3
6/25/08	Low High Low High	5:23 AM 10:41 AM 5:58 PM 11:46 PM	1.5 3.5 0.9 3.5	5:43 AM 8:36 PM	Set Rise	12:11 AM 12:25 PM	66
7/7/08	Low High Low High	3:59 AM 9:36 AM 4:59 PM 10:15 PM	1.1 3.9 0.9 3.5	5:49 AM 8:34 PM	Set Rise	10:57 AM 11:30 PM	18
7/17/08	High Low High	5:51 AM 1:39 PM 5:59 PM	4.1 1.3 2.6	5:56 AM 8:30 PM	Set Rise	4:57 AM 8:24 PM	98
7/18/08	Low High Low High	12:03 AM 6:26 AM 2:10 PM 6:43 PM	1.1 4.1 1.3 2.6	5:57 AM 8:29 PM	Set Rise	5:59 AM 8:58 PM	99
7/19/08	Low High Low High	12:49 AM 7:01 AM 2:41 PM 7:24 PM	1.1 4.1 1.1 2.8	5:58 AM 8:29 PM	Set Rise	7:04 AM 9:27 PM	99
9/20/08	Low High Low High	5:30 AM 9:31 AM 3:57 PM 10:32 PM	1.5 2.8 0.7 4.6	6:53 AM 7:07 PM	Set Rise	1:02 PM 10:16 PM	75
9/24/08	High Low High Low	1:49 AM 9:41 AM 1:53 PM 8:40 PM	4.1 1.5 2.8 0.9	6:57 AM 7:00 PM	Rise Set	1:38 AM 4:33 PM	31
10/1/08	Low High Low High	2:35 AM 7:12 AM 1:50 PM 8:01 PM	1.3 3.0 0.7 4.1	7:03 AM 6:49 PM	Rise Set	9:27 AM 7:39 PM	2
10/15/08	Low High Low High	12:30 AM 5:10 AM 11:49 AM 5:58 PM		Data	Not	Available	

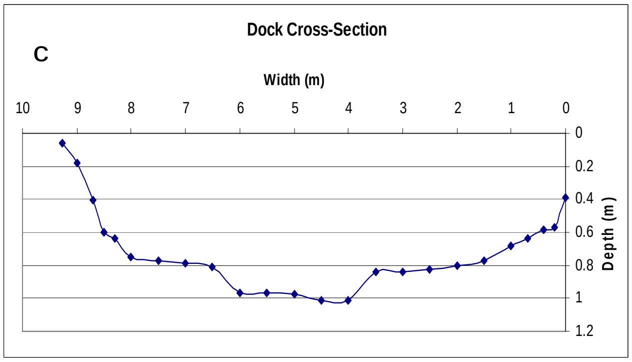
Table II. Tides at Hills Bridge (Rt. 4), Patuxent River, MD for 2009 sampling (provided by Maryland Department of Natural Resources Fisheries Service)

Day	**High/Low**	**Tide Time**	**Height Feet**	**Sunrise/ sunset**	**Moon**	**Time**	**% Moon Visible**
3/19/09	High Low High Low	12:10 AM 6:39 AM 1:06 PM 8:47 PM	1.7 0.2 2.4 0.9	7:11 AM 7:18 PM	Rise Set	3:14 AM 12:28 PM	48
5/29/09	Low High Low High	4:27 AM 10:18 AM 5:59 PM 10:58 PM	0.9 3.9 0.9 3.3	5:45 AM 8:24 PM	Set Rise	12:32 AM 11:17 AM	25
6/9/09	Low High Low High	12:53 AM 7:24 AM 3:18 PM 7:42 PM	0.9 4.1 1.1 2.4	5:41 AM 8:31 PM	Set Rise	6:58 AM 10:23 PM	98

Appendix B: Sampling site cross-sections







Figures 1 a-c. Cross-sections of sampling sites for in-stream denitrification: a) cross-section A within a 5th order channel b) cross-section B located 50 meters away downstream of A c) cross-section near the dock (boat launch) located 100 meters downstream of A. The right bank is the 0 point of the width measurement.

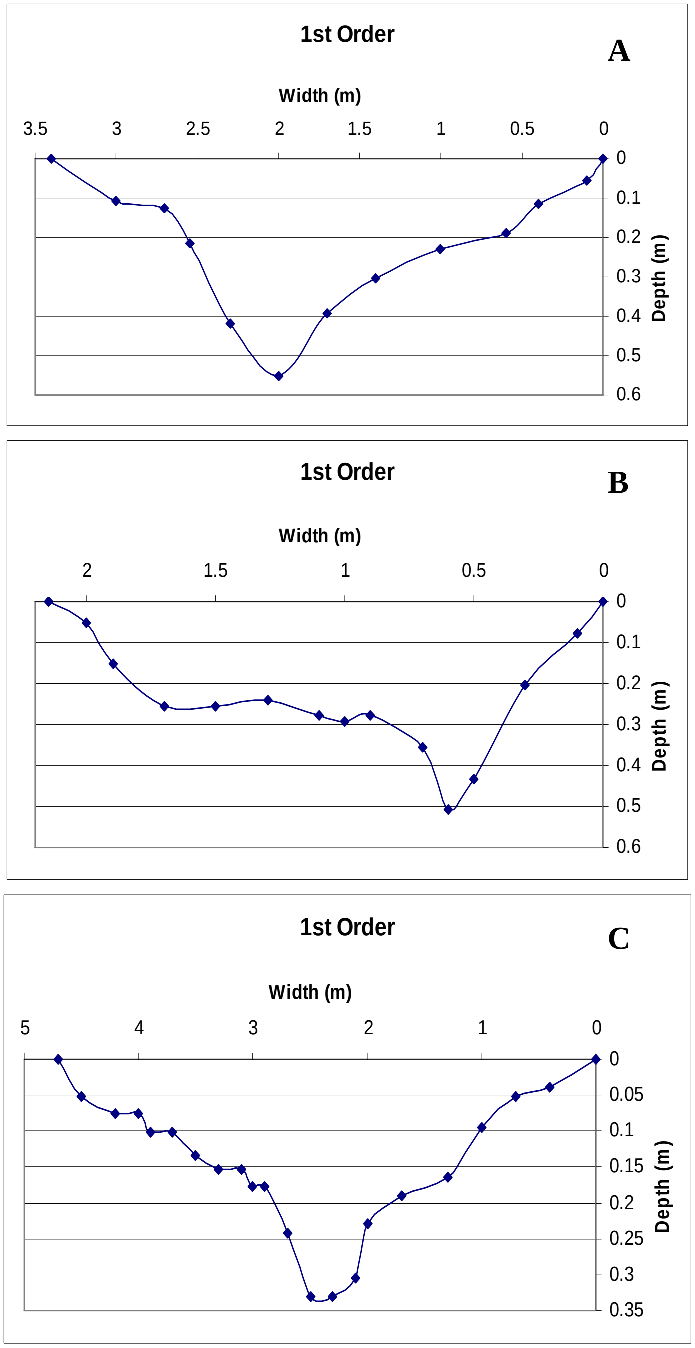


Figure 2. a-c. Cross-section measured at the mouth of each 1st order site. The right bank is the 0 point of the width measurement. The referenced 1st order within the study is figure 2c.

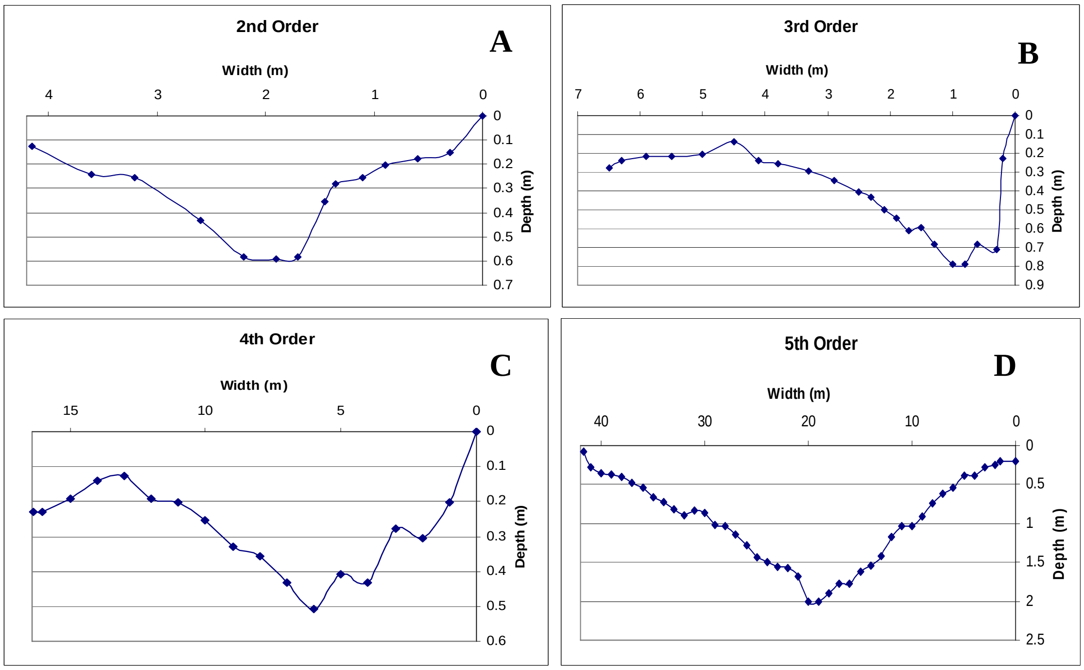


Figure 3. a-d. Cross-section measured at the mouth of each site for a 2nd, 3rd, 4th, 5th channel (a-d respectively). The right bank is the 0 point of the width measurement.

Table I. Characteristics of cross-sections for all sampling locations

Channel Order	Width (m)	Depth (m)	Width:Depth
1	3.4	0.551	6.17
1	2.15	0.508	4.23
2	4.15	0.591	7.02
2	4.7	0.33	14.2
3	6.5	0.787	8.26
4	16.35	0.508	32.2
5	41.7	2.01	20.7

Appendix C: Geomorphologic relationships

Table I. Geomorphologic data for interior and exterior channels from Smith-Hall (2002)

Exterior Channels		
Order	**Length (m)**	**Basin Area (m^2)**
1	23.8	135
2	38.2	461
3	23.4	159
Interior Channels		
Order	**Length (m)**	**Basin Area (m^2)**
1	13.05	63.0
2	28.5	734.1
3	129.2	7082

Table II. Geomorphologic data for interior channels from Phemister (2006)

Width (m)	**Cross-sectional Area (m^2)**
8.6	3.4
14.2	8.2
8.2	3.3
3.7	1.2
12.1	6.7
12.2	6.2
12.8	7.7
15.2	11.0
6.1	2.1

Table III. Geomorphologic data for exterior channels

Order	**Width (m)**	**Cross-sectional Area (m^2)**
1	2.1	0.52
1	3.4	0.82
1	4.7	0.71
2	4.1	1.2
3	6.5	2.4
4	6.5	6.4
4	7.6	6.8
4	16.3	4.8
5	41.7	41.1

Appendix D: At-a-station hydraulic geometry

Table I. Hydraulic geometry measured for in-stream denitrification experiment

Date Sampled: 7/7/08 (50 m reach)			
Time	**Gauge height (m)**	**Average velocity (m/s)**	**Discharge (L/s)**
11:30 AM	0.92	0.12	832.8
11:45 AM	0.90		
12:00 PM	0.82	0.19	1172.7
12:15 PM	0.72		
12:30 PM	0.71	0.26	1392.2
12:45 PM	0.68		
1:00 PM	0.65	0.30	1431.4
1:15 PM	0.64		
1:30 PM	0.61	0.28	1234.3
1:45 PM	0.57		
2:00 PM	0.56	0.28	1155.1
2:15 PM	0.52		
2:30 PM	0.49	0.25	888.7
2:45 PM	0.47	0.32	1085.7
Date Sampled: 7/18/08 (100 m reach)			
Time	**Gauge height (m)**	**Average velocity (m/s)**	**Discharge (L/s)**
9:10 AM	0.57	0.23	1673.9
9:30 AM	0.50		
9:45 AM	0.49	0.23	1508.5
10:00 AM	0.47		
10:15 AM	0.44	0.23	1432.9
10:30 AM	0.43		
10:45 AM	0.42	0.20	1187.4
11:00 AM	0.39	0.20	1139.5
11:15 AM	0.38	0.19	1079.5
11:30 AM	0.35		
11:45 AM	0.34	0.17	910.5
12:00 PM	0.33		
12:15 PM	0.30	0.16	823.2
12:30 PM	0.27		

Table I. Continued

Date Sampled: 10/15/08 (50 and 100 m reach)			
Time	**Gauge height (m)**	**Average velocity (m/s)**	**Discharge (L/s)**
7:30 AM	0.69	0.10	740.1
8:00 AM	0.66	0.20	1386.5
8:30 AM	0.61	0.27	1745.9
9:00 AM	0.53	0.30	1732.3
9:30 AM	0.45	0.32	1639
10:00 AM	0.37	0.30	1287.7
10:30 AM	0.30	0.27	1019.4
11:00 AM	0.20	0.26	745.4

Table II. Hydraulic geometry measured for denitrification per channel order: 1st order channel

Date Sampled: 9/24/08			
Time	**Gauge height (m)**	**Average velocity (m/s)**	**Discharge (L/s)**
9:15 AM	0.15	0.005	0.18
9:45 AM	0.20	0.005	0.18
10:15 AM	0.28	0.02	0.74
10:45 AM	0.34	0.04	3.3
11:15 AM	0.41	0.03	7.1
11:45 AM	0.44	0.03	9.3
12:15 PM	0.48	0.03	11.1
12:45 PM	0.51	0.02	10.1
1:15 PM	0.52	0.005	2.8
1:30 PM	0.53	0.007	4.8

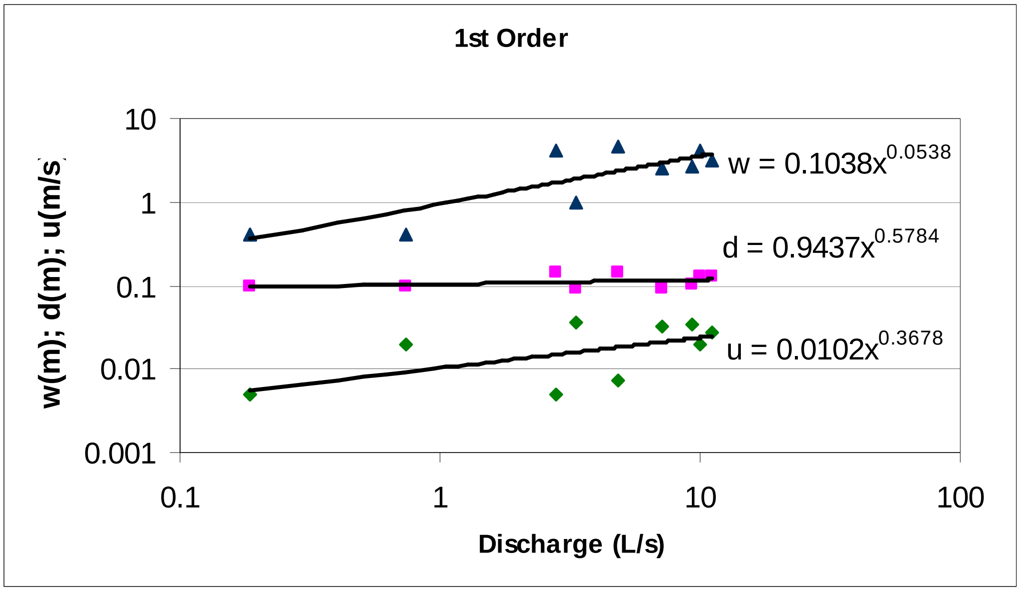


Figure 1. Graphical representation of at-a-station hydraulic geometry for the 1st order channel. Data collected on 9/24/2008; data was collected during the rising limb of the hydrograph. Relationships are valid because b + f + m = 1.

Table III. Hydraulic geometry measured for denitrification per channel order: 3rd order channel

Date Sampled: 10/1/08			
Time	**Gauge height (m)**	**Average velocity (m/s)**	**Discharge (L/s)**
8:30 AM	0.07	0	0
9:00 AM	0.67	0.07	155
9:30 AM	0.63	0.07	152
10:00 AM	0.56	0.11	176.6
10:30 AM	0.51	0.12	151
11:00 AM	0.45	0.11	108.9
11:30 AM	0.39	0.07	51.7
12:00 PM	0.28	0.04	17.4
12:30 PM	0.22	0.04	12.7
1:00 PM	0.13	0.02	4.7
1:30 PM	0.07	0.03	2.9
2:00 PM	0.0	0.02	0.9

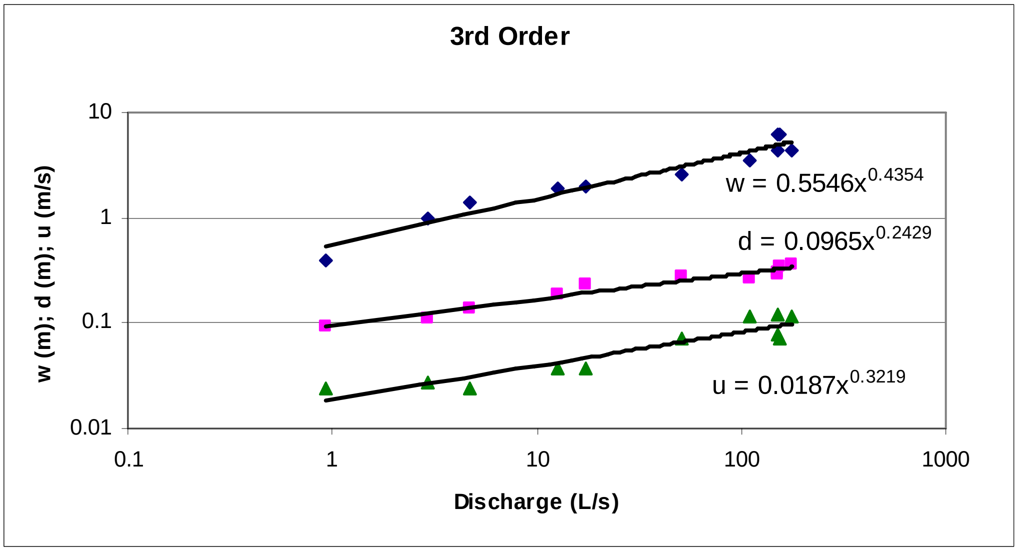


Figure 3. Graphical representation of at-a-station hydraulic geometry for the 3rd order channel. Data collected on 10/1/2008. Relationships are valid because b + f + m = 1.002.

Table IV. Hydraulic geometry measured for denitrification per channel order: 5th order channel

Date Sampled: 10/1/08			
Time	**Gauge height (m)**	**Average velocity (m/s)**	**Discharge (L/s)**
8:45 AM	0.79	0	0
9:15 AM	0.74	0.04	1521.2
9:45 AM	0.70	0.06	2280.4
10:15 AM	0.65	0.07	2582.8
10:45 AM	0.57	0.07	2353.9
11:15 AM	0.50	0.06	1939.4
11:45 AM	0.43	0.05	1376.1
12:15 PM	0.34	0.04	991.8
12:45 PM	0.27	0.04	900.5
1:15 PM	0.19	0.04	799.2
1:45 PM	0.11	0.03	459.9
2:15 PM	0.06	0.01	190.3
Date Sampled: 7/7/09			
Time	**Gauge height (m)**	**Average velocity (m/s)**	**Discharge (L/s)**
9:23 AM	0.46	0.08	3398.6
9:43 AM	0.41	0.07	2824.5
10:21 AM	0.32	0.07	2392.5
10:36 AM	0.28	0.07	2381.3
10:50 AM	0.24	0.07	2222.3
11:10 AM	0.20	0.07	2175.1
11:28 AM	0.16	0.07	2000.8
11: 46AM	0.12	0.06	1664.8

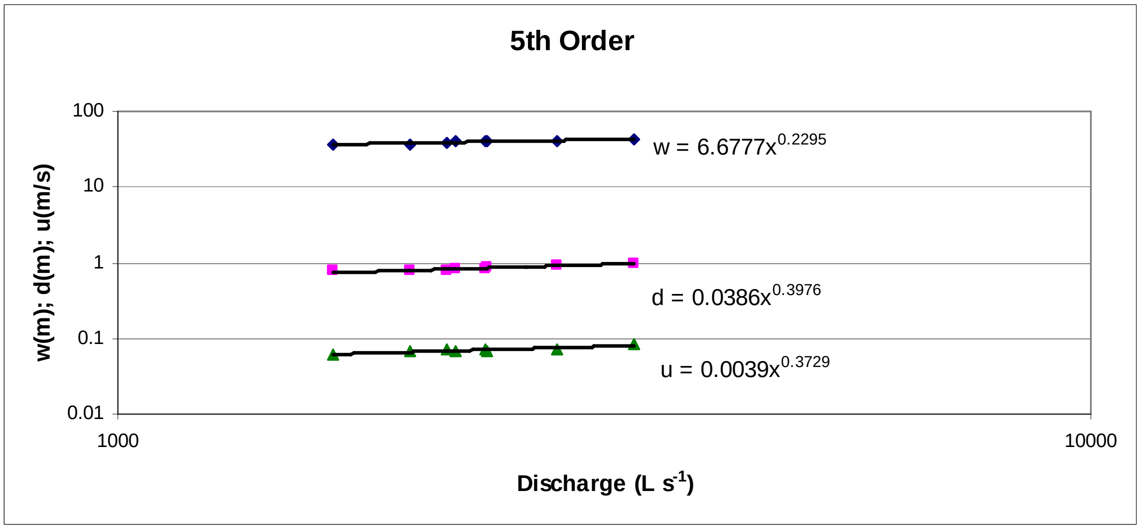


Figure 5. Graphical representation of at-a-station hydraulic geometry for the 5th order channel. Data collected on 5/29/2009. Relationships are valid because b + f + m = 1.

Appendix E: *In situ* nitrogen concentrations per channel order

Table I. Nitrogen concentrations for 1st order channel

9/24/08			
Time	**NH_4-N (µM)**	**NO_2-N (µM)**	**NO_3-N (µM)**
9:15 AM	0.8	16.7	45.4
9:45 AM	2.1	15.4	67.8
10:15 AM	0.0	16.0	59.7
10:45 AM	0.2	17.1	58.5
11:15 AM	0.1	13.8	62.5
11:45 AM	0.0	12.6	61.4
12:15 PM	0.05	14.4	58.7
12:45 PM	0.3	14.6	62.5
1:15 PM	0.1	12.8	56.5
1:45 PM	0.0	14.7	39.0

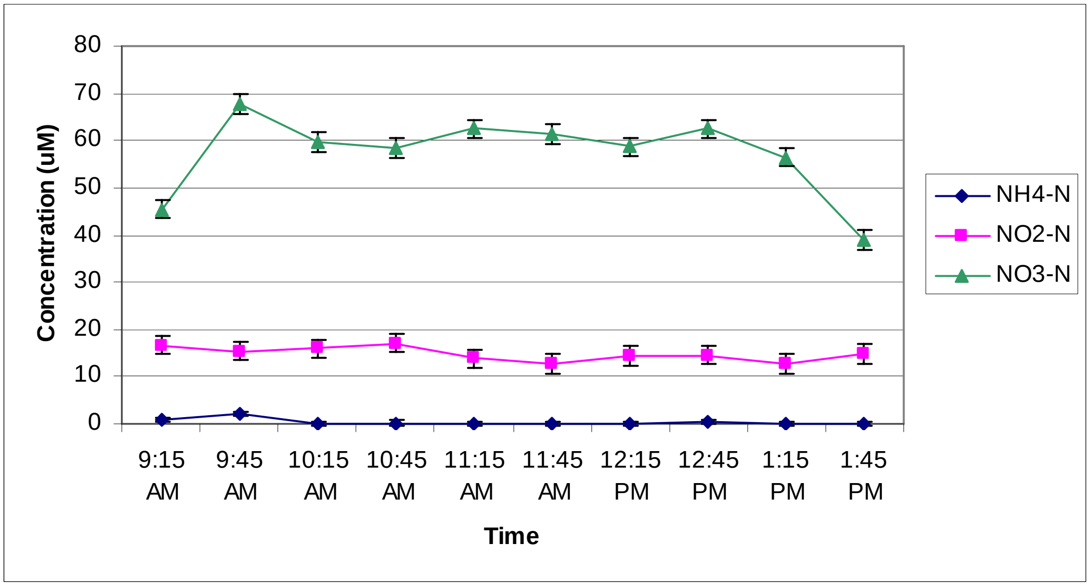


Figure 1. Graphical representation of nitrogen concentrations over time for a 1st order channel. Data collected on 9/24/08 on a flooding tide.

Table II. Nitrogen concentrations for a 3rd order

10/1/08			
Time	**NH$_4$-N (μM)**	**NO$_2$-N (μM)**	**NO$_3$-N (μM)**
8:30 AM	2.3	14.6	26.6
9:00 AM	2.5	14.1	26.7
9:30 AM	1.1	15.1	29.0
10:00 AM	0.5	14.7	24.3
10:30 AM	0.2	15.8	18.3
11:00 AM	0.2	15.1	9.2
11:30 AM	0.3	16.6	4.7
12:00 PM	0.6	16.8	1.3
12:30 PM	0.8	15.9	0.0
1:00 PM	1.4	17.4	0.5
1:30 PM	2.1	17.7	0.0
2:00 PM	3.3	18.3	0.0

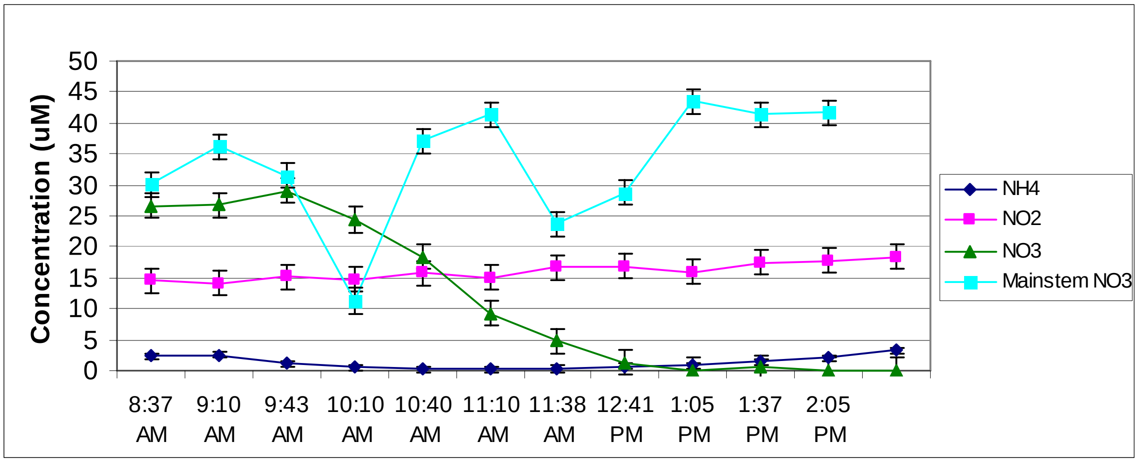


Figure 3. Graphical representation of nitrogen concentrations over time for a 3rd order channel, using data collected on 10/1/2008.

Table III. Nitrogen concentrations for a 5th order channel

10/1/08			
Time	**NH_4-N (μM)**	**NO_2-N (μM)**	**NO_3-N (μM)**
8:45 AM	3.6	14.3	30.3
9:15 AM	3.1	12.9	33.3
9:45 AM	3.3	13.5	33.4
10:15 AM	2.0	15.5	22.3
10:45 AM	5.8	11.7	20.1
11:15 AM	1.9	14.8	27.7
11:45 AM	2.5	13.4	28.3
12:15 PM	1.0	14.4	21.7
12:45 PM	4.7	15.7	20.1
1:15 PM	0.7	14.8	8.2
1:45 PM	1.0	14.8	14.7
2:15 PM	0.9	15.7	4.8

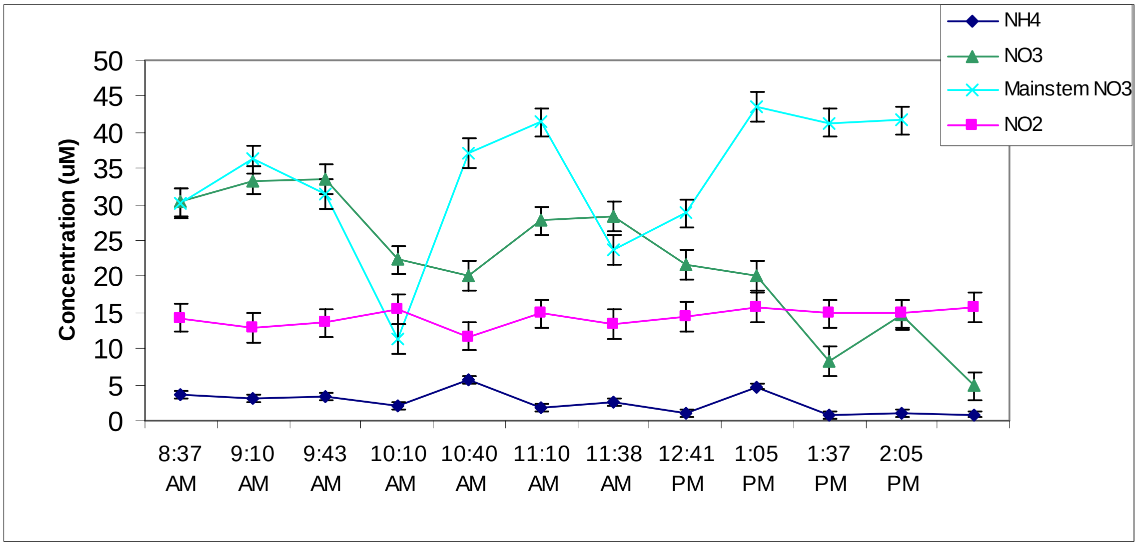


Figure 5. Graphical representation of nitrogen concentrations for a 5th order channel, using data collected on 10/1/2008.

Appendix F: In-Stream nitrogen concentrations

Table Ia. In-stream denitrification 7/7/08 (50 m reach)

Site A			
Time	**NH_4-N (µM)**	**NO_2-N (µM)**	**NO_3-N (µM)**
11:45 AM	3.2	ND	41.8
12:15 PM	2.6	ND	25.4
12:45 PM	1.8	ND	25.5
1:15 PM	1.9	ND	26.5
1:45 PM	1.8	ND	30.2
2:15 PM	2.1	ND	19.7
2:45 PM	4.5	ND	13.2
Site B			
11:45 AM	2.7	ND	42.8
12:15 PM	1.9	ND	42.1
12:45 PM	1.2	ND	9.1
1:15 PM	0.6	ND	30.9
1:45 PM	1.3	ND	23.7
2:15 PM	1.4	ND	22.4
2:45 PM	1.5	ND	45

Table Ib. In-stream denitrification 7/18/08 (100 m reach)

Site A			
Time	**NH_4-N (µM)**	**NO_2-N (µM)**	**NO_3-N (µM)**
9:30 AM	2.1	ND	38.5
10:00 AM	2.5	ND	32.2
10:30 AM	1.4	ND	28.2
11:00 AM	1.1	ND	18.7
11:30 AM	1.3	ND	24.9
12:00 PM	0.8	ND	45.3
12:30 PM	1.2	ND	16.5
Dock Site			
9:30 AM	0.9	ND	35.2
10:00 AM	0.7	ND	30.0
10:30 AM	1.2	ND	31.8
11:00 AM	0.9	ND	25.4
11:30 AM	0.8	ND	20.8
12:00 PM	0.2	ND	17.9
12:30 PM	0.7	ND	13.9

Table Ic. In-stream denitrification 10/18/08 (50- and 100 m reach)

Site A			
Time	**NH_4-N (µM)**	**NO_2-N (µM)**	**NO_3-N (µM)**
7:30 AM	2.8	20.0	99.1
8:00 AM	0.7	21.3	59.4
8:30 AM	0.9	15.7	77.9
9:00 AM	0.1	14.4	88.6
9:30 AM	0.9	16.9	82.0
10:00 AM	0.9	16.7	81.3
10:30 AM	0.05	16.0	88.6
11:00 AM	0.5	16.0	68.3
Site B (50 m)			
7:30 AM	0.8	16.8	71.9
8:00 AM	0.7	22.2	37.7
8:30 AM	0.1	15.9	88.8
9:00 AM	8.4	17.9	86.7
9:30 AM	0.0	15.3	71.4
10:00 AM	0.0	17.2	82.1
10:30 AM	0.1	21.3	52.7
11:00 AM	0.8	16.9	65.7
Dock (100 m)			
7:30 AM	0.7	20.0	58.0
8:00 AM	0.7	13.7	94.1
8:30 AM	1.1	15.4	94.2
9:00 AM	0.0	17.1	98.1
9:30 AM	0.0	16.7	88.1
10:00 AM	6.5	14.7	81.7
10:30 AM	0.4	17.1	67.3
11:00 AM	0.2	13.5	57.2

Appendix G: Core incubations: nutrient fluxes and dissolved gas concentrations

Table I. Nutrient fluxes measured on 3/24/09 along a transect of a 5th order channel. "NI" indicates non-interpretable fluxes. All reported values are in µmol m^{-2} h^{-1}.

Site	NH_4	NO_2	NO_3	O_2	N_2
Low marsh (<1 m)	-78	NI	-97.4	-1463	157
Mid marsh (~20 m)	-59.9	-75.2	-21.6	NI	7.3
High marsh (~30 m)	-62	-154.6	-185.7	-1409.6	27.7
Blank	-43.4	126.6	478.1	-308	69

Table II. Nutrient fluxes measured on 6/9/09 along a transect of a 5th order channel. "NI" indicates non-interpretable fluxes. All reported values are in µmol m^{-2} h^{-1}.

Site	NH_4	NO_2	NO_3	O_2	N_2
Low marsh (<1 m)	109.3	Data	Data	-1337.6	114
Mid marsh (~20 m)	79.6	Not	Not	-1336.7	122.5
High marsh (~30 m)	140	Available	Available	-1601.6	227.5
Blank	-32.4				

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