ABSTRACT

Title of Thesis: NUTRIENT REMOVAL BY TIDAL FRESH AND OLIGOHALINE MARSHES IN A CHESAPEAKE BAY TRIBUTARY

Sarah E. Greene, M.S., 2005

Thesis Directed By: Professor Walter R. Boynton
University of Maryland Center for Environmental Science
Chesapeake Biological Laboratory

Located at the interface between estuaries and surrounding uplands, tidal marshes are in position to receive and transform material from both adjacent systems. Of particular importance in eutrophic estuarine systems, tidal marshes permanently remove nutrients via two mechanisms - denitrification and long-term burial. Denitrification was measured (monthly) in two marshes in a Chesapeake Bay tributary for 7 months, using the MIMS technique. Burial of nitrogen (N) and phosphorus (P) was measured using ^{210}Pb techniques. Strong spatial and temporal patterns emerged, and there was a Michaelis-Menten type response in denitrification rates to experimentally elevated nitrate levels. Denitrification rates measured may account for removal of 22% of N inputs to the upper estuary on an annual basis. Burial rates could account for 30% of N inputs and 60% of P inputs. Based on the cost of nutrient control technologies, Patuxent marsh nutrient removal may be valued at $10 to 30 million yr^{-1}.

NUTRIENT REMOVAL BY TIDAL FRESH AND OLIGOHALINE MARSHES IN A CHESAPEAKE BAY TRIBUTARY

by

Sarah E. Greene

Thesis submitted to the Faculty of the Graduate School of the
University of Maryland, College Park in partial fulfillment
of the requirements for the degree of
Master of Science
2005

Advisory Committee:

Professor Walter R. Boynton, Chair
Research Associate Professor Jeffrey C. Cornwell
Professor Thomas R. Fisher

DEDICATION

This work is dedicated to Gonzo science and all other endeavors undertaken in true Gonzo spirit.

ACKNOWLEDGEMENTS

I would first like to thank my advisor, Dr. Walter Boynton, for guidance at some times, for independence at others, and always for patience, support and inspiration. I also thank my committee members, Dr. Tom Fisher and Dr. Jeff Cornwell, for their contributions of knowledge, support and scientific rigor. In addition, I would like to thank Dr. Todd Kana for use of his mass spectrometer and Dr. Marcelino Suzuki for guidance in exploring molecular approaches to measuring denitrification.

Thanks are also due to the Boynton Lab scientists – Eva Bailey, Eric Buck, Maria Ceballos, Paul Smail, Heather Soulen, Bob Stankelis, Sarah Kolesar, Katie Johnson and Sarah Stein – for help in the field and in the lab, as well as for their friendship. I am still in debt (quite literally) to the Nutrient Analytical Services Lab, especially Carolyn Keefe, Kathy Wood, Maggie Weir and Nancy Kaumeyer. Many thanks to Bud Millsaps for help with filtration and constant temperature rooms. Thanks also to members of the Cornwell Lab – Erica Kiss, Mike Owens, Becky Holyoke, Jen O'Keefe and Jessie Burton – for help with incubation and lead extraction techniques, and to Adrienne Sutton and Michael Williams of the Fisher lab for sharing their knowledge on several occasions. I am also grateful to Chris Swarth and the staff of Jug Bay Wetlands Sanctuary for providing access to a wonderful research site, to Jackie Weimeyer for access to the King's Landing State Park boat ramp, and to Mary-Ellen Boynton for use of the family canoe.

Last and most importantly, I would like to thank my friends and family for their support. Thanks to the Happyhour crew and the Cistas soccer team for the good times, and to my brave fellow Flop House residents - Janet, Danika, Becca and Bosco. I also thank Mom, for encouraging me to go to graduate school and anywhere else I've ever wanted to go, and Dad, for teaching me to explore and to love the Chesapeake. Thanks to Kristen who is example of real perseverance, and to Rob, who has always been a kindred spirit. Finally, thanks to Alex Yasbek for the use of his Biodiesel car in the field, and for being my constant and true companion in every possible way.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION:
NUTRIENTS IN ESTUARINE WATERS AND TIDAL MARSHES

EUTROPHICATION

History, causes and consequences

The terms "oligotrophic" and "eutrophic," first introduced to ecology in 1907 to describe soil conditions in German bogs, appeared in limnology in 1919 as a scheme for the classification of lakes (Hutchinson 1969). In its early application, the concept of eutrophy referred in theory to lake waters with high nutrient content, and in practice to lake waters with large phytoplankton communities, but the concept was soon broadened to encompass the entire watershed-lake-sediment system (Hutchinson 1969). Two important corollaries have emerged since. First, eutrophication is not merely a phenomenon of ecological succession, but is often an anthropogenic trend. Second, anthropogenic eutrophication occurs not only in lakes, but also in coastal marine and estuarine systems (Fisher et al. *in press*) previously believed too well flushed to be impacted (Schindler 1981).

As limnological studies with a trophic orientation progressed, it was quickly recognized that anthropogenic inputs to lakes enhance both the extent and rate of eutrophication. For example, investigations of German lakes in areas of intense farming revealed that eutrophication of these systems was greatly accelerated by domestic sewage and agriculture (Ohle 1955). The effects of anthropogenic inputs on sediment-water interactions were also soon discovered. In noting that the release of iron-bound phosphorus (P) from sediments to the water column during anoxia is a mechanism for

internal fertilization of phytoplankton, Mortimer (1941) mentioned that this process should be readily observable in lakes with substantial "cultural" influences. Anthropogenic eutrophication is often referred to as "cultural eutrophication," but Rodhe (1969) wrote that "it is not culture but progress of civilization that is the villain in the present tragedy of so many waters. Our modern civilization has done more harm to lakes in a few decades than human culture did during preceding millennia." Recently, Castro (2003) reported that nitrogen (N) inputs to the Atlantic and Gulf coasts of the USA are now up to 20 times greater than during pre-industrial times.

Though most eutrophication research in the first half of the 20th century focused on lacustrine systems, anthropogenic eutrophication is now a well-recognized phenomenon in coastal marine and estuarine environments (Nixon 1995). Eutrophication occurs around the globe and has been reported in the Baltic, Adriatic, Black and North Seas, and in the coastal waters of Japan, China and Australia (Vitousek et al. 1997; Bricker et al. 1999). In the US, 44 estuaries have been identified as highly eutrophic, and a high level of human influence is associated with 36 of these (Bricker et al. 1999).

Nixon (1995) suggested that eutrophication be defined as "an increase in the rate of supply of organic matter to an ecosystem." It has been shown that the availability of nutrients (N in particular) is the dominant control on the rate of organic production in marine environments (Ryther and Dunstan 1971; D'Elia et al. 1986; Fisher et al. 1999). A number of responses to eutrophication and its primary cause – nutrient loading - have been observed, with the most direct and obvious impacts being increased phytoplankton biomass and reduced water clarity (Nielsen et al. 2002). Reduced water clarity and consequent decreased light penetration, as well as shading due to vigorous epiphyte

growth, have been cited as primary factors in the decline of seagrass populations (Neckles 1993; Short et al. 1995). As phytoplankton populations senesce and settle, decomposition can result in bottom water hypoxia and anoxia, with subsequent impacts to benthic fauna (Diaz and Rosenburg 1995). For instance, macrobenthic biomass in regions of the Chesapeake Bay affected by low-oxygen conditions is much lower than predicted, given the amount of phytoplankton productivity available for food (Kemp et al. 2005).

Sediment-water biogeochemical processes are also affected by eutrophication, and in particular by low benthic oxygen concentrations, as many biogeochemical reactions are redox-dependent. Large P fluxes from sediments have been observed under low-oxygen conditions due to dissolution of P-containing iron-oxides in surface sediments (Krom and Berner 1981; Cowan and Boynton 1996). Large ammonium fluxes have also been observed under low-oxygen conditions, which may be attributed to "an ironic sequence of interactions" in which nitrification is inhibited, allowing ammonium that would normally be converted to nitrate (which could then be denitrified) to remain in its reduced form and diffuse out of sediments (Kemp et al. 1990). Both of these processes represent positive feedbacks in which eutrophication creates low-oxygen conditions in sediments, causing recycling of N and P to the water column where these nutrients can then fuel more organic matter production.

Less direct and more far-reaching effects of eutrophication are evident in alterations of fish community composition. Fish kills are a common manifestation of hypoxia, generally due to loss of habitat and mortality of egg and larval stage fish that are unable to move from low-oxygen environments (Breitburg 2002). Reduced species abundance

and reduced rates of growth and reproduction are also attributed to hypoxia (Howell and Simpson 1994; Jones and Reynolds 1999). At the ecosystem scale, it has been suggested that the redistribution of fishes according to the impact of increased phytoplankton biomass and hypoxia on respective life strategies can alter the ratio of pelagic to demersal fish in a system (Caddy 1993; de Leiva Moreno et al. 2000).

Despite the litany of "negative" impacts of eutrophication on coastal ecosystems, there may be some correlation between anthropogenic nutrient subsidies and increased secondary production. In the introduction to the proceedings of the International Symposium on Eutrophication (National Academy of Sciences 1969), we are reminded that "our first knowledge of eutrophication was derived from efforts to increase production of fish ponds through fertilization." There is evidence for increased production via fertilization in less highly engineered systems as well. A positive relationship between N loading and fisheries yields was reported for the Baltic Sea, and loch fertilization experiments in Scotland during WWII produced enhanced phytoplankton, zooplankton, infaunal and fish communities (Nixon and Buckley 2002). It has also been proposed that through "controlled eutrophication," it would be possible to develop aquaculture systems that produce valuable food while taking up waste nutrients from coastal waters (Ryther et al. 1972). While high nutrient loads are most often portrayed as pollutants, an alternative view of nutrients as subsidy also exists.

Eutrophication in the Chesapeake Bay

Though the general symptoms of eutrophication are common, the specific response of individual estuaries to eutrophication is influenced by differences in freshwater inputs, stratification, bathymetry, climate, and watershed geology and

demographics. The Chesapeake Bay has been characterized as highly eutrophic, and currently exhibits high levels of phytoplankton and epiphyte biomass, low dissolved oxygen, and severe SAV loss (Bricker et al. 1999). Chlorophyll-a has increased in surface waters of the Bay since the 1950's and concurrent shifts in phytoplankton community composition (including harmful algal blooms) have been reported (Kemp et al. 2005). Physical stratification combines with decomposing algal biomass to create, respectively, a spring oxygen decline and summer hypoxia/anoxia in Chesapeake Bay bottom waters (Hagy et al. 2004). In recent years, more extensive hypoxia has been observed than predicted from past correlations between nitrate (NO_3) inputs and dissolved oxygen concentration, suggesting that the Bay may have become more vulnerable to N loading (Hagy et al. 2004). Sediments exposed to hypoxic/anoxic conditions tend to exhibit enhanced ammonium and phosphate recycling, as previously discussed, and this phenomenon is particularly vigorous in mesohaline regions of the Bay (Cornwell and Sampou 1995; Cowan and Boynton 1996). Low-oxygen conditions in the benthos also limit macrofaunal habitat, and severe degradation of benthic communities has been reported in mesohaline regions of the Chesapeake Bay and its tributaries (Dauer et al. 2000). Finally, loss of oyster habitat (due in part to eutrophication itself) has impeded reestablishment of an important negative control on eutrophication – biofiltration of phytoplankton and suspended particulates by oysters (Baird and Ulanowicz 1989; Porter et al. 2004).

The geomorphology of the Chesapeake Bay and its watershed also influence eutrophication. The land:water ratio in the Chesapeake watershed is large, which results in the funneling of artifacts of human activity over a particularly vast area of land to a

relatively small volume of water. Over 75% of the N load to the Chesapeake Bay estuary is of upland origin (Castro et al. 2001). Terrestrial sources dominate P loading to the Bay as well, and diffuse sources are more than twice as large as point sources for both N and P (Boynton et al. 1995). These non-point source inputs are particularly difficult to manage first because the steps needed to prevent creation of the pollutants are difficult to implement across the many political boundaries within the watershed, and also because of the practical dilemma of trapping diffuse pollutants for removal after their creation and dispersal. There does exist, however, a natural vehicle for removal of nutrient loads to portions of the Chesapeake Bay – tidal marshes.

TIDAL MARSHES

Marshes of the Chesapeake Bay

Tidal marshes cover 826 km^2 adjacent to the Chesapeake Bay and its tributaries (Reshetiloff 1995). Marshes on much of the western shore of the Bay are generally accreting, whereas many eastern shore marshes are undergoing rapid submergence and/or erosion (Khan and Brush 1994; Ward et al. 1998; Merrill 1999). Marshes on both shores compete with sea level rise to maintain elevation, so differential patterns of marsh accretion and erosion can been attributed to differences in sediment inputs, land subsidence and herbivore impact. Sustained sediment inputs to western tributaries due to continued development and deforestation provide ample material for marshes to accrete at the same pace as, if not faster than, sea level rise (D'Elia et al. 2003). On the eastern shore, land subsidence due to groundwater withdrawal, past herbivory by exotic rodent populations, and reduced sediment inputs in lower-estuary marshes have contributed to marsh losses (Stevenson et al. 1986; Kearney et al. 1994; Haramis 1997; Ward et al. 1998). The Patuxent River, a western Chesapeake Bay tributary (Fig. I-1), provides an illustration of the role of terrigenic sediments in forming and maintaining tidal marshes.

Marshes of the Patuxent River

The Patuxent watershed has been inhabited by humans for at least 12,000 years (E. Chaney pers. comm.). Early inhabitants of the watershed numbered in the low 1000's and practiced rotational, slash and burn agriculture with limited impacts to forest area and soils (E. Chaney pers. comm.; R. DeFries 1986). When European settlers arrived in the mid 17th century, the Patuxent River was navigable to ocean-going ships 95 km upstream of its mouth (Gottschalk 1945). As the settlers cleared 70-80% of the land to support

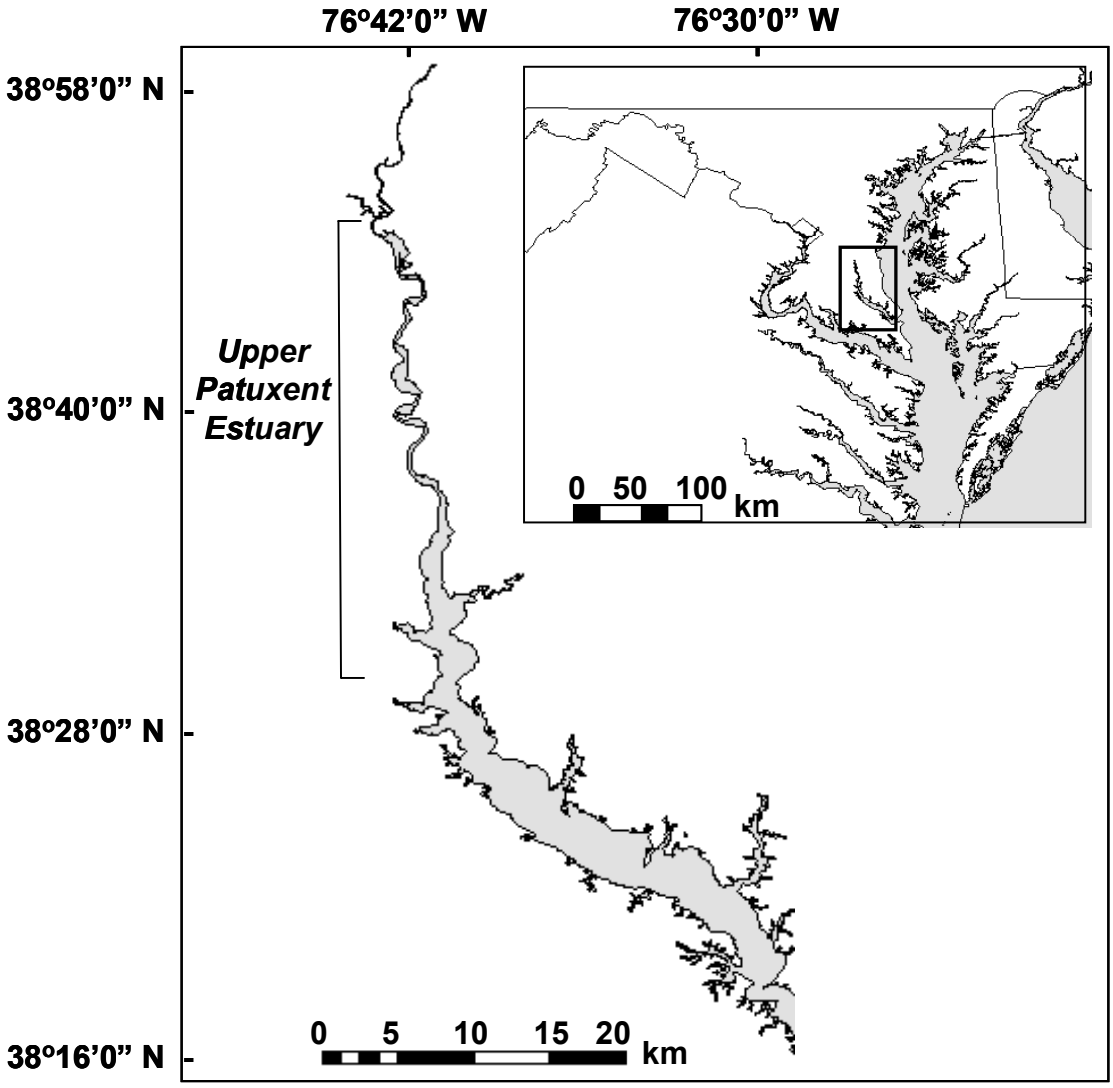


Figure I-1. The Patuxent River (main), a Chesapeake Bay (inset) tributary. The Upper Patuxent Estuary is shown, which includes tidal fresh and oligohaline portions of the river.

grain and tobacco farming, sediment inputs to the river increased by 400%, turning harbors into marshes and mudflats (Gottschalk 1945; Khan and Brush 1994). To a large degree, suspended sediment loads are trapped in upper estuaries (Ward et al. 1998), and the anthropogenic sediment loads generated by colonial farmers led to high sedimentation rates and extensive marsh development in the upper reaches of many Chesapeake Bay tributaries (Fig. I-2). Developments in agricultural technology such as the evolution of

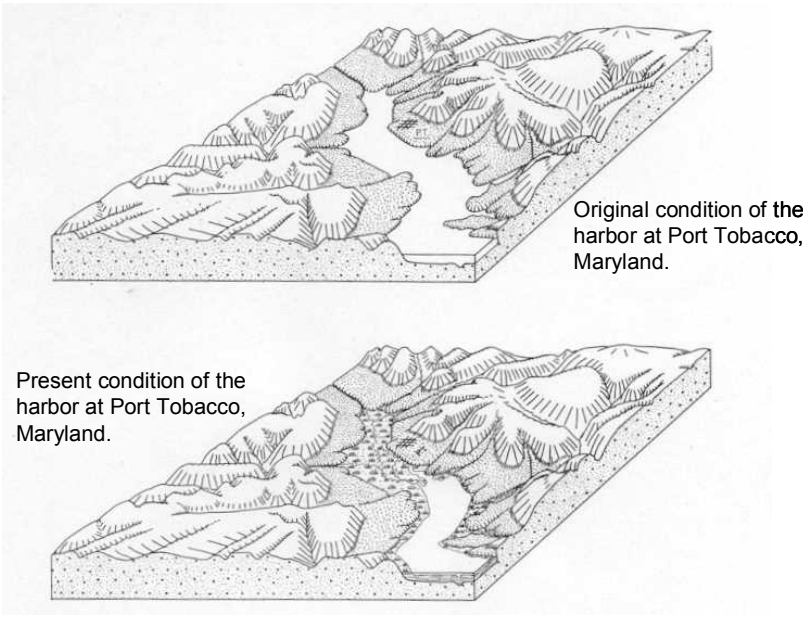


Figure I-2. Tidal marsh formation resulting from anthropogenic sedimentation in the Port Tobacco River, Maryland. Similar patterns of tidal marsh formation occurred in the Patuxent River and other Chesapeake Bay tributaries (modified from Gottschalk 1945).

the plow from a shallow-penetrating wooden device to a deep-penetrating steel implement added to sediment inputs from deforestation (Brush and Hilgartner 2000). Today the portion of the Patuxent River navigable to ships drawing more than 8 feet is less than half of what it was in the 17th century (~45km; Gottschalk 1945).

Approximately 30 km^2 of tidal marshes exist on the Patuxent today, and in all likelihood the formation of these marshes was a direct result of increased sedimentation due to human activity. The vast majority of Patuxent marshes are located in oligohaline and tidal fresh reaches (Fig. I-1), where marsh area exceeds the area of the tidal river (Fig. I-3; Fisher et al. 2005). Coincident with sediment loading, modern agricultural activities and development have increased N and P loads to the Patuxent nearly 5- and 20-fold, respectively, with marked ecological effects (Boynton et al. 1995). Located at

the interface between land and water, tidal marshes in the Patuxent and other systems are believed to play a mitigating role in the movement of nutrients from terrestrial sources to estuarine systems (Williams et al. 2005).

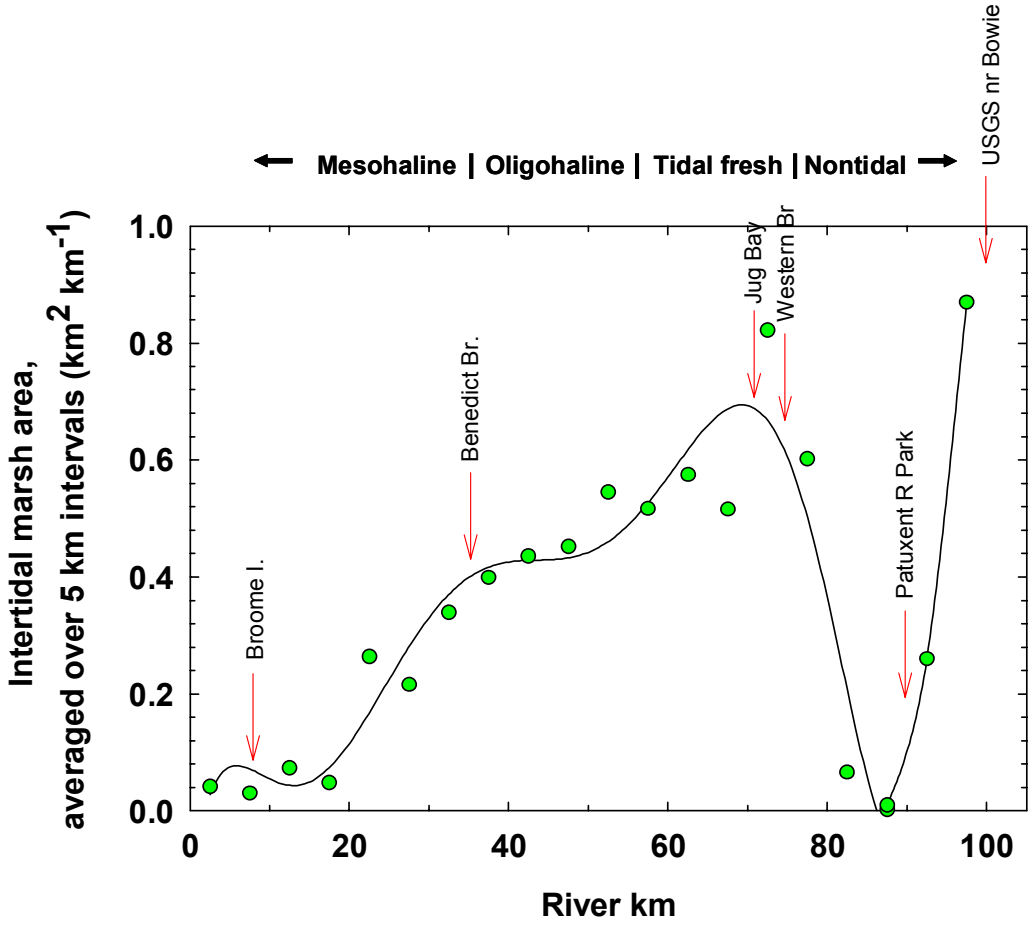


Figure I-3. Intertidal marsh area in the Patuxent River, averaged over 5 km intervals (Fisher et al. 2005). The majority of tidal marsh area is in tidal fresh and oligohaline reaches of the river.

Tidal marshes and nutrient ecology

Because tidal wetlands are located between a terrestrial landscape on one side and estuarine waters on the other, there are two unique interfaces across which these marshes can interact with adjacent ecosystems. The idea that marshes intercept and remove nutrients from terrigenous runoff is well accepted (e.g. Gosselink et al. 1973; Simpson et al. 1983a). Additionally, marshes have been employed for decades in engineered

systems for wastewater treatment, with excellent results (e.g. Todd and Josephson 1996; Bachand and Horne 1998; Mitsch and Jorgensen 2004). Engineered or natural, marshes remove nutrients in at least two ways. First, inundated marsh sediments foster a complex redox environment in which bacteria employ alternate electron acceptors to oxidize organic matter in the absence of dissolved oxygen. In denitrification, NO_3 is reduced to dinitrogen (N_2) gas, which diffuses to the atmosphere and is effectively lost from the system. Though there is no analogous process for the removal of P, it can be sorbed to the surface of oxidized metal compounds (Sundby et al. 1992), and both N and P are also removed by plant and microbial uptake for growth. If N and P-containing organic matter remains in an accreting marsh after the growing season, it will eventually be buried beneath accumulating sediments. Nutrients in sediments within the plant root zone may be remineralized, but below the root zone burial results in long-term removal from the system, barring large erosional events. If, instead of being buried, organic litter is swept off the marsh by tidal waters, then N and P losses due to plant uptake are only temporary. This seasonal aspect of the uptake and burial process forms the basis for interactions across the second marsh interface – that with the estuary.

Perhaps the most classic and controversial topic in tidal marsh ecology (and central to the discussion of marshes as nutrient sinks) is whether tidal marshes act as net sources or net sinks for materials and nutrients in adjacent estuaries and coastal waters. In an early synthesis on marsh ecology, John Teal (1962) concluded that nearly half of the salt marsh production off Sapelo Island, Georgia was removed by tides, making this production unavailable to marsh consumers and providing material to consumers in the surrounding waters. Several years later, Odum (1968) put forth the "outwelling

hypothesis" in which *outwelling* of nutrients and organic matter from tidal marshes subsidizes production in adjacent waters, much as the *upwelling* of materials from the deep ocean subsidizes surface communities. It is interesting to note, however, that the outwelling hypothesis was actually first presented as a conclusion, and was only later referred to as a hypothesis, long after it had become dogma in marsh ecology (Nixon 1980). Impetus for questioning the outwelling hypothesis has sprung largely from observations of nutrient removal mechanisms in tidal wetlands (e.g. Kaplan et al. 1979; Delaune et al. 1981; Simpson et al. 1983a). Arguments for nutrient removal by tidal marshes seem at least as strong as those for subsidy, and simultaneous acceptance of the conflicting models by the ecological community led Nixon (1980) to describe current thought on tidal marshes as "Orwellian." The sink vs. source controversy thrives even today, though it could be argued that at the watershed scale, any accreting tidal marsh that fosters denitrification and burial of terrigenous nutrients can be designated as a sink, regardless of the direction of net flux of other material between the marsh and adjacent estuary.

Role of tidal marshes in Patuxent River nutrient economy

Recent nutrient modeling and budget construction efforts suggest an important role for tidal marshes in Patuxent nutrient dynamics (Merrill 1999; Fisher et al. 2005; W. Boynton, unpublished data). In general, when tidal marsh processes are not explicitly included in nutrient models and budgets, model predictions tend to overestimate nutrient concentrations in the water column compared to observed values due to underestimates of nutrient sinks (Williams et al. 2005; W. Boynton, unpublished data). There is evidence

to suggest that tidal marsh processes can account for some, if not all, of these discrepancies (Merrill 1999).

In a water quality model for the Patuxent River that did not include tidal marshes, Fisher et al. (2005) found consistent overpredictions of water column N concentrations (Fig. I-4a). The magnitude of the model error (predicted minus observed values) was positively correlated with marsh area (Fig. I-4b). In another effort, a nitrogen budget for the Patuxent River included river bottom N burial and denitrification, but tidal marshes were again treated as neutral. Estimated N outputs from the middle estuary were ~1300 kg N d^{-1} less than what was required to balance the estimated inputs (Fig. I-5). Given that tidal marshes are a dominant feature of the landscape in this portion of the river, it is likely that marsh processes (e.g. denitrification and long-term N and P burial) impact the budgets in a quantitatively important manner.

Though coastal wetlands have received attention in the nutrient literature, the focus has largely been on salt marsh systems like the Great Sippewissett Marsh and Louisiana salt marshes (e.g. Kaplan et al. 1979; DeLaune et al. 1981). Data from these studies suggest that tidal salt marshes denitrify and bury nutrients at substantial rates. However there is also evidence for significant export of materials from these marshes to surrounding ecosystems (Kaplan et al. 1979; DeLaune et al. 1981; Valiela et al. 2000). Far fewer data exist for tidal fresh and oligohaline marshes such as those found in the Patuxent (Merrill 1999; Kahn & Brush 1994). These authors suggest that tidal fresh marshes, like salt marshes, denitrify and bury nutrients at substantial rates.

Additionally, though denitrification has been known to scientists for over a century (Zumft 1997), very few rate measurements are present in the literature prior to the

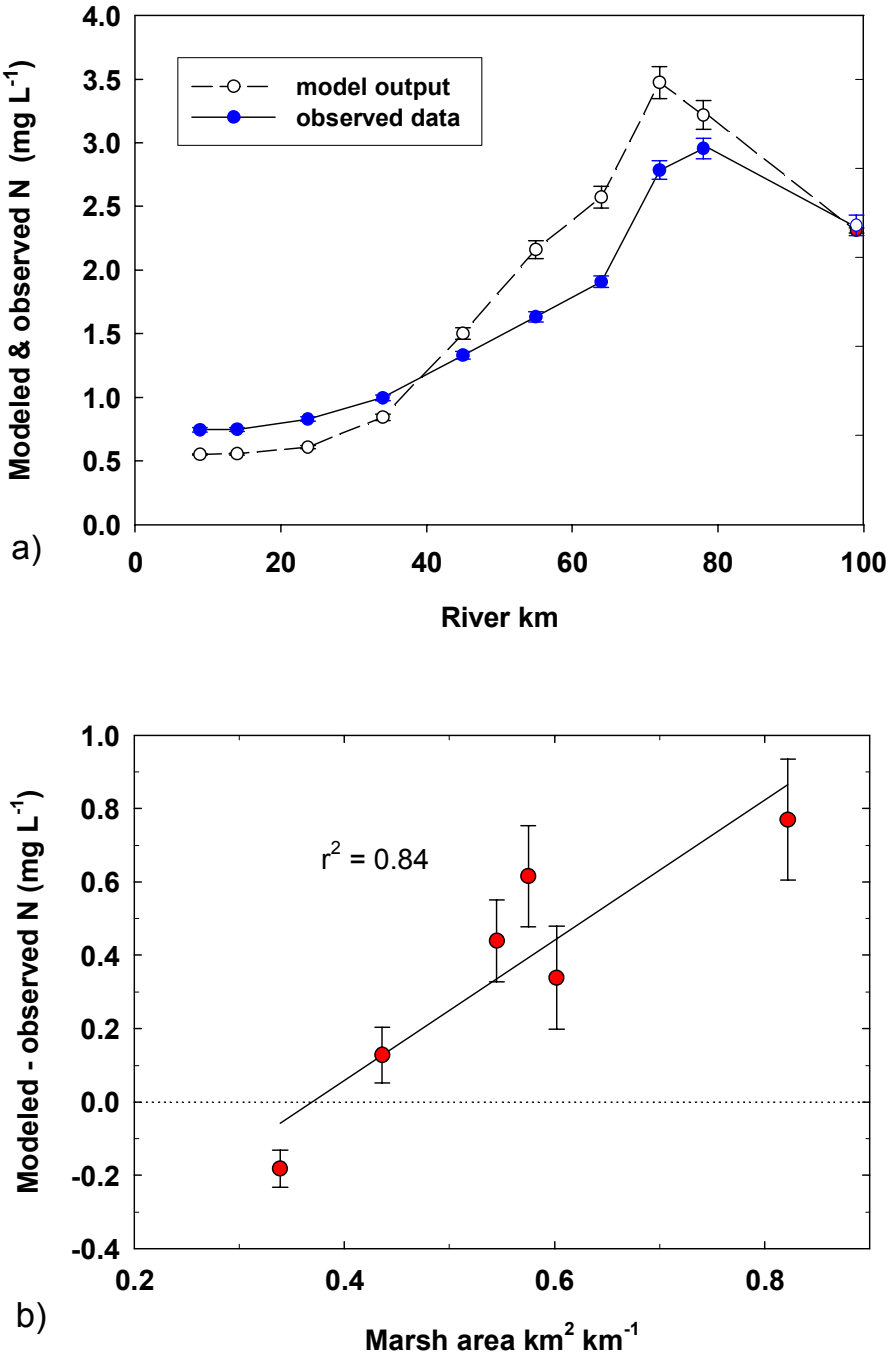


Figure I-4. Comparison of model output and observed data for TN at monitoring stations in the Patuxent estuary (a); Relationship between marsh area and model output error (b). Marsh area is expressed as the summed marsh area over 5 km intervals, divided by 5 km. Adapted from Fisher et al. 2005.

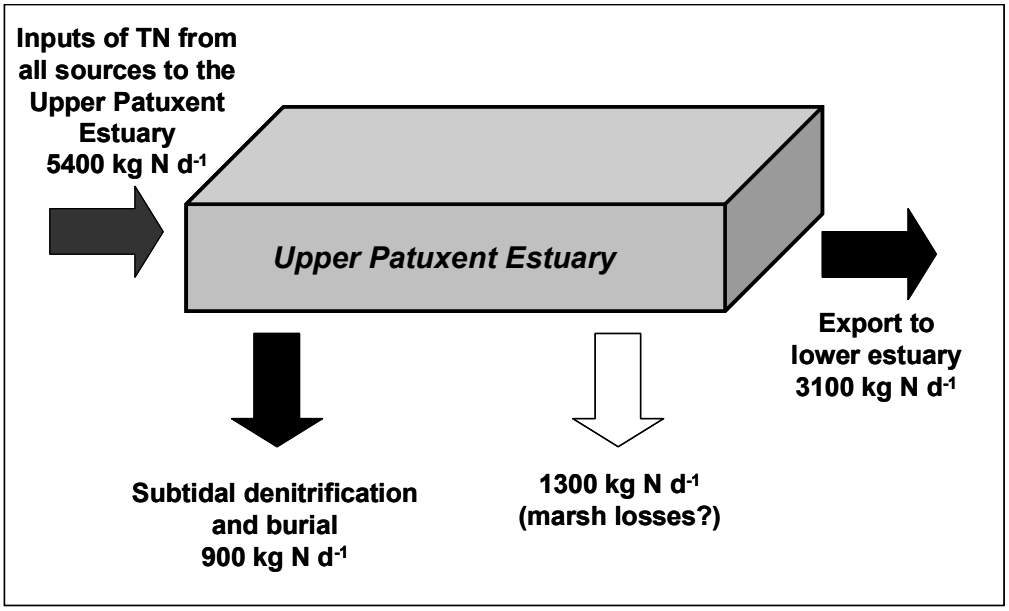


Figure I-5. A simple nitrogen input/output budget for the upper Patuxent estuary, illustrating a large N sink not attributable to subtidal losses or export to the lower estuary (W. Boynton, unpublished data). Inputs include all atmospheric, terrestrial and upstream riverine sources.

1980's (Fig. I-6). New techniques have been developed since then and many more measurements made, but there is a rather spirited discussion concerning the relative merits and shortcomings of each (e.g. Seitzinger et al. 1993; Eyre et al. 2002). A literature review of denitrification measurements made over the past 5 decades in various environments (Chapter 1) illustrated that efforts to measure denitrification are growing, especially using new techniques (Greene 2005). The review also revealed that the highest natural denitrification rates measured to date have been measured in estuaries, and that coastal wetlands appear to denitrify at higher median rates than other environments (Greene 2005; Chapter 1).

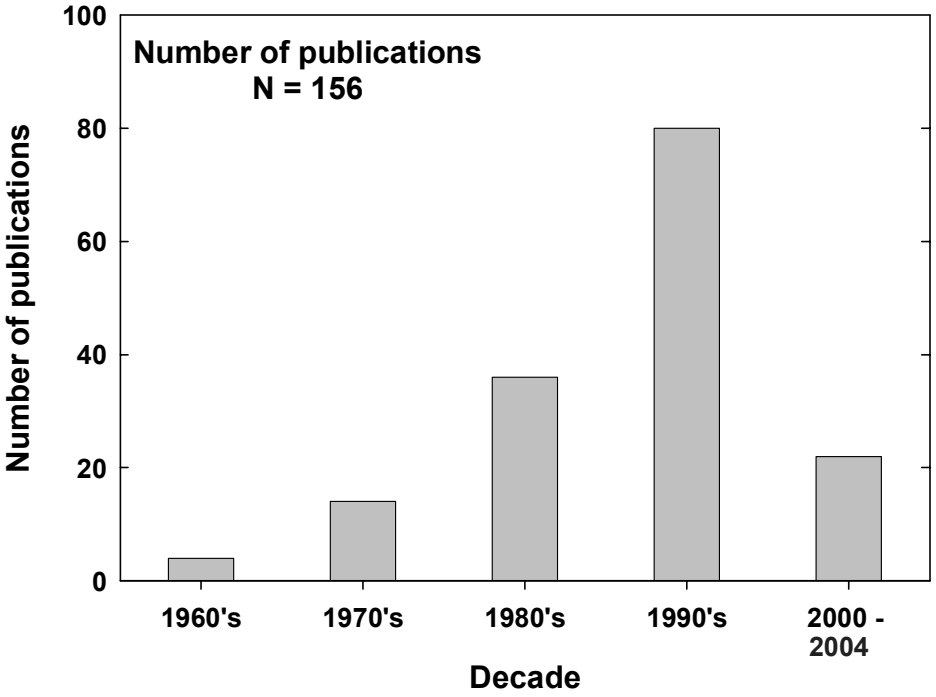


Figure I-6. Number of publications reporting denitrification measurements, identified in a literature review (Greene 2005).

GOALS OF THIS STUDY

Given the questions raised by nutrient models, and given the uncertainties in existing knowledge, there is a need for studies of nutrient removal processes in tidal fresh and oligohaline marshes, using the most direct measurement techniques that current technology permits. A large investigation of nutrient biogeochemistry in the mainstem Patuxent is currently underway. Impetus for the project (Sediment Nitrogen And Phosphorus Interactions, or SNAPI) stems from the need for information to aid in nutrient management in the Patuxent, and specifically from observations that fresh and saltwater primary production are limited differently by P and N (Smith 1984). Since estuaries are transition environments between fresh and saltwater, there may be shifts in nutrient limitation within the estuary, and the SNAPI project is an examination of changes in N and P biogeochemistry along the estuarine salinity gradient (Cornwell et al. 2002). To a large extent, the biogeochemical processes that take place in subtidal sediments also occur in marshes. The goal of this thesis is to investigate nutrient biogeochemistry (and in particular, removal processes) in Patuxent tidal marshes along a portion of the salinity gradient, with attention to factors affecting extrapolation from individual study sites to the full Patuxent marsh community for modeling and budget applications.

Chapter 1 of this thesis deals with denitrification as a removal process for N in Patuxent River tidal marshes. Data from a literature review provided insight into the range of denitrification rates that have been measured in diverse environments. Flux experiments were performed with sediment cores from two marshes to determine whether or not differences exist between tidal fresh and oligohaline marsh denitrification rates.

Measurements were made during a period of 7 months so that seasonal patterns in denitrification could be examined, and samples were taken from different areas of the marsh surfaces and marsh creeks to investigate spatial heterogeneity. In addition, NO_3 loading experiments were performed to investigate the response of marsh denitrification rates to increased NO_3 availability. Inorganic nutrient and oxygen fluxes were measured in concert with N_2 fluxes to elucidate patterns in sediment remineralization and their relationship to denitrification.

The focus of Chapter 2 is an investigation of long-term N and P burial in Patuxent tidal marshes. Since two burial studies have been conducted in Patuxent marshes (Khan and Brush 1994; Merrill 1999), measurements for this thesis were made with the goals of a) expanding earlier results and b) more closely examining spatial heterogeneity of burial within a marsh, which was not resolved by earlier studies. Toward those ends, sediment accretion rates were estimated using ^{210}Pb-dating of cores from the marsh surface in an oligohaline Patuxent marsh. Dated sediments were analyzed for particulate nutrient concentrations, and the nutrient data were used in concert with accretion rates to estimate burial.

In Chapter 3, the results of the denitrification and burial studies were synthesized and placed in the larger context of a Patuxent River budget focused on the tidal fresh and oligohaline portion of the estuary. Extrapolation of measurements from the two study sites to the full Patuxent marsh community was examined, and the size of the potential marsh sink relative to other components of the Patuxent nutrient budget is discussed. Past and present management efforts, as well as future management implications, were also considered.

CHAPTER 1:
NITROGEN DYNAMICS IN TIDAL FRESH AND OLIGOHALINE MARSH SEDIMENTS – DENITRIFICATION AND NET SEDIMENT-WATER NUTRIENT FLUXES

INTRODUCTION

Nitrogen is the principal nutrient limiting primary production in most coastal marine environments, though P can be limiting on a seasonal or local basis (Ryther and Dunstan 1971; Fisher et al. 1999). Since the industrial revolution, fixation of biologically inaccessible N in the atmospheric pool to bioavailable forms in the terrestrial pool has doubled (Vitousek et al. 1997). As a result, N inputs to the coastal ocean have increased. On a global scale, riverine fluxes of N to estuaries sum to around 40 Mt yr^{-1} (Tappin 2002), and in the US these fluxes represent a 2 to 20-fold increase over pre-industrial inputs (Castro et al. 2003). Elevated N concentrations in coastal waters support increased primary productivity, and the direct and indirect effects of enhanced production bring about readily observable, ecosystem-scale changes in coastal environments (e.g. Nixon 1995; Cloern 2001; Kemp et al. 2005). Recognition of the large impact of enhanced N inputs on coastal systems has fostered interest in removal mechanisms for N. Denitrification, the microbially-mediated conversion of dissolved to gaseous N_2, is an important sink in the global N budget (Seitzinger 1988). This process is of special interest in eutrophic coastal ecosystems because of its role in the removal of anthropogenic nitrogen.

Microbial & ecological significance of denitrification

Nitrate can be used by heterotrophic bacteria as an alternative terminal electron acceptor (TEA) in the absence of oxygen (O_2). Whether NO_3 or a different TEA is used depends on the specific redox regime of the environment, as well as the relative abundance of the various TEA's (Santschi et al. 1990). Bacterial use of NO_3 as a TEA involves a stepwise reduction to N_2, with each step catalyzed by a different enzyme. Of particular interest, and perhaps of greatest ecological significance, is the step in which nitrite (NO_2) is reduced to nitric oxide (NO). At this point, N that was in a bioavailable, dissolved form becomes a biologically inert gas. Upon further reduction of NO to N_2, the N reaches a more chemically stable state and diffuses to the atmosphere. This closes a major loop in the anthropogenic N cycle, as N_2 is often removed from the atmosphere by humans to make fertilizer. Nitrogen fixed from the atmospheric N pool for fertilizer is moved around the terrestrial landscape and applied to agricultural fields. Residual, biologically active forms of N may then be nitrified to NO_3 and move from the terrestrial N pool into inland and coastal waters (aquatic/oceanic N pool). Denitrifiers in aquatic and marine sediments return this N to the atmospheric pool as N_2. In addition to returning N to the atmospheric pool, the ecological significance of denitrification is that it permanently removes from a system N that would otherwise be available for primary production. This sort of loss is of special interest in eutrophic, N-limited systems like the Chesapeake Bay where substantial anthropogenic N inputs fuel high primary productivity with a host of ecological and economic implications (Kemp et al. 2005). Denitrification is also of interest because it is the only mechanism (short of physical export) by which N

is truly removed from the system; when N is taken up by biota or buried in sediments it can be made available again via decomposition or erosion processes.

Denitrification in aquatic environments

An important, initial component of this work was a literature review of denitrification measurements, which enabled assessment of the range of denitrification rates commonly observed in different environments (Greene 2005). Since the 1960's, denitrification has been measured in a large variety of terrestrial and aquatic environments, both natural and engineered. Denitrification rates between 10 and 100 μmoles N m^{-2} h^{-1} are most frequently reported, though rates well over 1000 μmoles N m^{-2} h^{-1} have been observed in certain systems (Fig. 1-1; Table 1-1). Rates near 20,000 μmoles N m^{-2} h^{-1} have been measured in human engineered systems and estuaries, though median rates for these environments are not so high as to be outside the range of normally measured rates (Table 1-1).

Median rates appear highest in lakes (37 μmoles N m^{-2} h^{-1}), estuaries (40 μmoles N m^{-2} h^{-1}) and coastal wetlands (54 μmol N m^{-2} h^{-1}; Table 1-1). In estuaries, where more measurements of denitrification appear to have been made than in any other environment (Table 1-1), the most commonly reported rates were between 1 and 100 μmoles N m^{-2} h^{-1} (Fig. 1-2), and more specifically between 1 and 50 μmoles N m^{-2} h^{-1}. The range of rates measured in estuaries and was higher than that of any other natural system by an order of magnitude (Table 1-1).

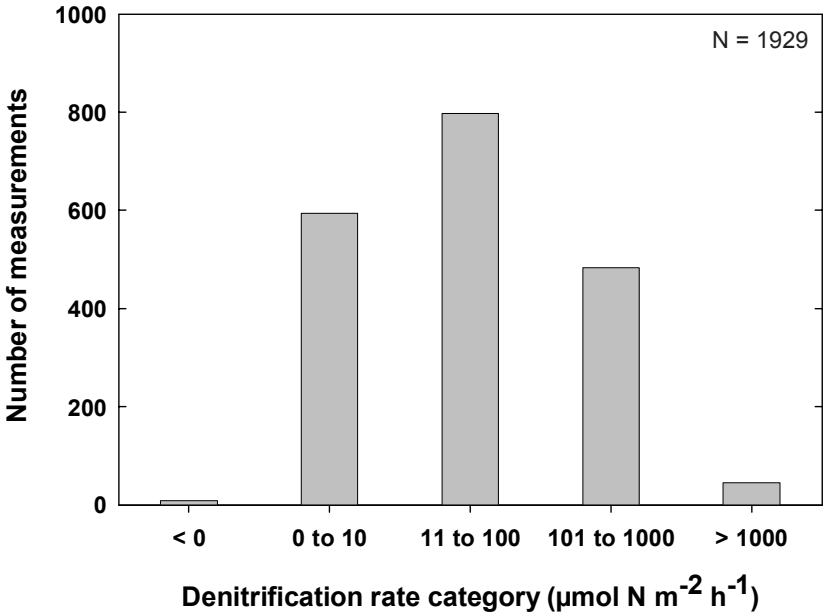


Figure 1-1. Number of denitrification measurements reported for various ranges of rates. Data represent a range of environments, including estuaries, mudflats, seagrass beds, lagoons, reefs, continental shelf, lakes, creeks, wetlands (coastal and inland) and human engineered systems (data from Greene 2005).

Table 1-1. Characteristics of denitrification rate measurements made in various environments. Rates are in µmoles N m^{-2} h^{-1} (data from Greene 2005).

	Min	Max	Mean	Median	Range	n
Human engineered	0	24143	695	1	24143	68
Wetlands (fresh)	0	330	39	4	330	52
Creeks (fresh)	0	1200	195	32	1200	20
Lake	0	490	89	37	490	90
Coastal wetland	-200	1865	94	54	2065	167
Mudflat	2	213	71	31	211	61
Seagrass Bed	2	167	29	8	165	13
Lagoon	-20	290	21	9	310	116
Estuary	-93	19616	197	40	19709	1188
Reef	0	533	58	4	533	40
Continental Shelf	0	1658	104	15	1658	113

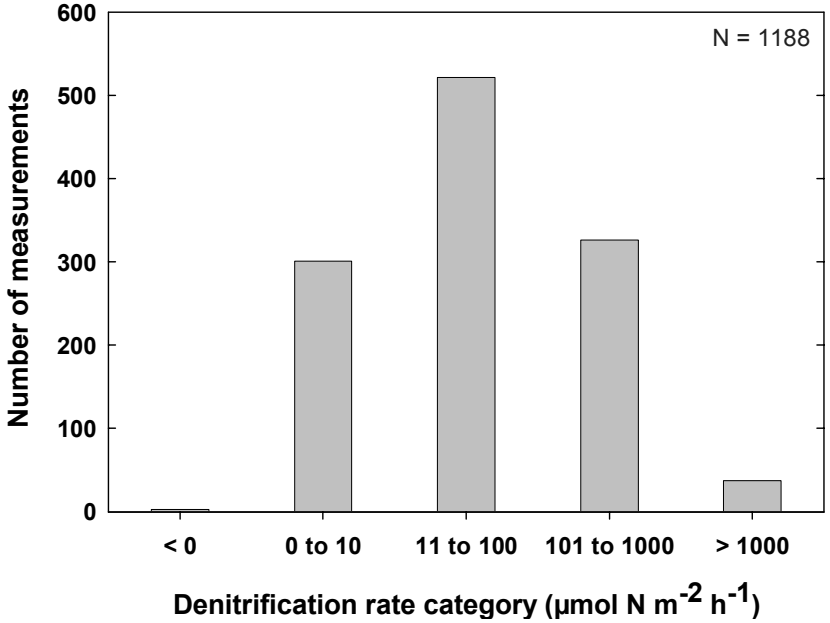


Figure 1-2. Frequency distribution of denitrification measurements made in estuaries for given rates (data from Greene 2005). Typical Chesapeake Bay rates are slightly higher than the global distribution (J. Cornwell, unpublished data).

Denitrification in Chesapeake Bay tributaries and tidal marshes

Denitrification in the Chesapeake Bay and in tributaries like the Patuxent River is of special interest due to the high degree of N-related eutrophication (D'Elia et al. 2003). The incorporation of denitrification ("biological nitrate reduction," or BNR) into wastewater treatment in the Patuxent watershed has led to marked reductions in point source N loads to the river and estuary (D'Elia et al. 2003). However, N loading in the Patuxent watershed is primarily non-point (Boynton et al. 1995), so mechanisms by which non-point N may be reduced or removed are also of interest. Tidal fresh and oligohaline marshes are located between estuarine waters and the surrounding uplands, in a position to receive and transform non-point N runoff before it reaches the estuary. Nitrogen from all sources can be removed in tidal marshes via two mechanisms –

long-term burial (Khan and Brush 1994; Merrill 1999; Chapter 2, this study) and denitrification (Merrill 1999).

Though data on N removal by Patuxent marshes are limited, the role of Patuxent River *subtidal* sediments as a sink for N via denitrification is well established (Jenkins and Kemp 1984; J. Cornwell, unpublished data). Despite a few unusually high rates measured in estuaries, denitrification rates of 1-100 μmoles N m^{-2} h^{-1} are by far the most common rates observed (Fig. 1-2), and Chesapeake sediments appear to denitrify at rates favoring the higher portion of this range (J. Cornwell, unpublished data). On occasions, rates in excess of 100 μmoles m^{-2} h^{-1} have been observed (J. Cornwell, pers. comm.). Boynton et al. (1995) estimated that 380 kg N d^{-1} were denitrified in subtidal sediments of the upper Patuxent River. Given this estimate, subtidal denitrification may remove 7% of N inputs to the upper Patuxent (Fig. 1-3). Since marsh area exceeds the area of tidal river bottom in portions of the upper Patuxent, wetlands may play a similar, or perhaps more important, role in N removal (Williams et al. 2005).

Despite the fact that Patuxent River marshes are intuitively promising environments for denitrification, only one attempt to measure the process in Patuxent marshes has been made to date. In that study, a limited number of denitrification measurements were made at Jug Bay on a seasonal basis (spring, summer and fall; Merrill 1999). Though a growing number of denitrification measurements have been made in salt marshes (e.g. Kaplan et al. 1979; Koch et al. 1992; Joye & Paerl 1993; Anderson et al. 1997), rates from the previous Patuxent marsh denitrification study were the first direct measurements of denitrification in a tidal fresh marsh (Merrill 1999).

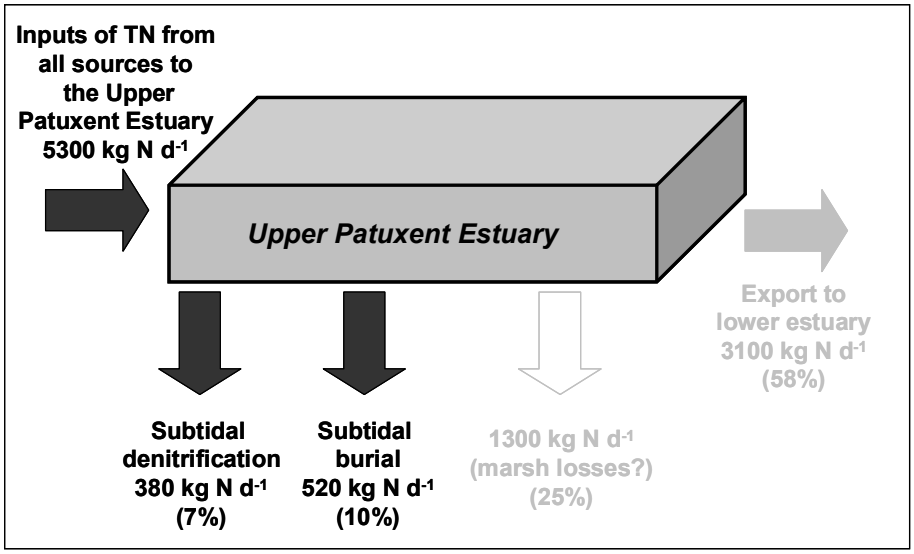


Figure 1-3. A nitrogen budget for the upper Patuxent estuary, attributing the loss of ~7% of N inputs to subtidal denitrification (data from Boynton 1995 and W. Boynton, unpublished data). Nitrogen inputs include atmospheric, terrestrial and upstream riverine sources. Loss terms as "percent of inputs" are included in parentheses.

One reason low salinity marshes may foster denitrification is that they are high NO_3 environments. Kemp and Boynton (1984) documented a strong pattern in dissolved inorganic nitrogen (DIN) along a salinity gradient in the Patuxent, finding rapid removal of DIN by primary producers and other loss mechanisms in tidal fresh and oligohaline reaches, with resultant lower DIN concentrations downstream. Given this pattern, low-salinity tidal marshes are in a geographic position to receive the highest concentrations of DIN, which has positive implications for both denitrification and productivity.

Productivity, in turn, may exert a positive effect on denitrification. Primary production delivers organic matter to the sediments, which is a direct source of C and an indirect source of NO_3 (via ammonification and nitrification) for denitrification. Decomposition of organic matter also creates the low-O_2 conditions necessary for denitrification. Tidal fresh marsh plants appear to decompose even more rapidly than

those of higher salinity marshes (Odum and Heywood 1977), and tidal freshwater sediments may also not be subject to the same limitations on nitrification (and hence on denitrification) as their saltwater counterparts (Joye and Hollibaugh 1995). These differences between tidal fresh and salt marshes suggest that rates of denitrification in tidal fresh marshes may be higher than in those exposed to more saline waters. However, not enough measurements of denitrification have been made in tidal marshes to support conclusions one way or the other.

In all tidal marshes, the cyclical exposure of sediments to air may enhance coupled nitrification-denitrification. The coupling of nitrification and denitrification, facilitated by spatial redox gradients, has been suggested for Patuxent River subtidal sediments (Jenkins and Kemp 1984). In particular, infaunal burrowing and plant rhizospheres create oxidized zones for nitrification in otherwise anoxic sediments (Reddy et al. 1989; Webb and Eyre 2004). Furthermore, there is evidence for facilitation of coupled nitrification-denitrification via *temporal* redox gradients. An and Joye (2001) reported increased denitrification rates (due to enhanced nitrification) during periods of benthic photosynthesis by microalgae. The pulsed O_2 subsidy to marsh surface sediments with the tidal cycle may be analogous to the diel pulsing of benthic autotrophs described by An and Joye (2001).

A better understanding of the mechanisms driving denitrification in tidal marshes will facilitate efforts to quantify denitrification, which is a primary objective of this study. The central hypothesis to be tested is that denitrification is an important loss term in the N economy of the Patuxent River, though spatial and temporal patterns in

denitrification and the relative importance of coupled versus direct denitrification pathways are also of interest.

Objectives

The following questions will be addressed in this work:

1. At what rate is denitrification occurring in tidal fresh and oligohaline Patuxent marshes, and are these rates comparable to those previously measured?
2. What seasonal patterns exist in denitrification rates in different marsh environments? What factors appear to cause these patterns?
3. Is there evidence regarding the importance of the coupled nitrification-denitrification pathway in Patuxent marshes?
4. To what extent do marsh denitrification rates respond to elevated water column NO_3 concentrations?

SITE DESCRIPTIONS

Two study sites were chosen to reflect the gradient of conditions in upper Patuxent estuary marshes. Jug Bay Wetlands Sanctuary (38° 46' 45" N, 76° 42' 30" W; Fig. 1-4) is a tidal fresh environment that typically experiences salinities less than 0.2.

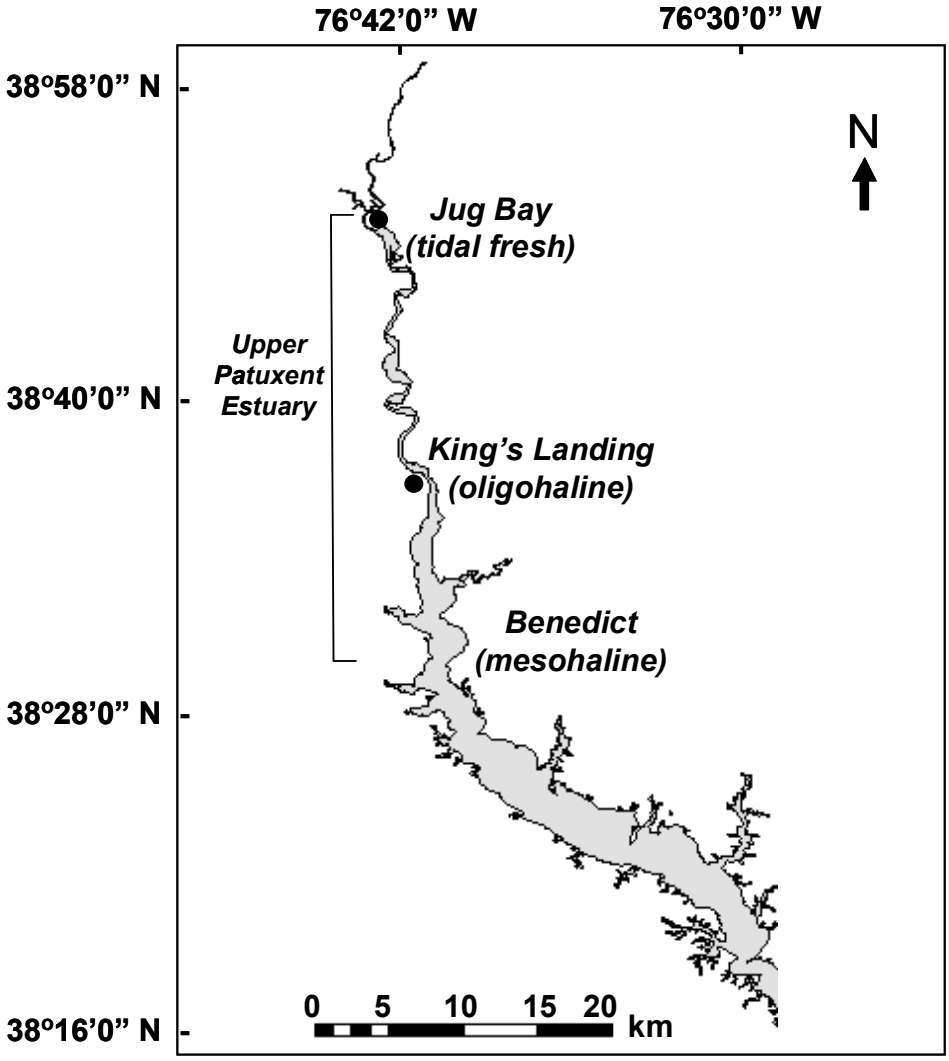


Figure 1-4. Location of study sites, Jug Bay and King's Landing, on the Patuxent River, Maryland. Tidal fresh, oligohaline and mesohaline regions of the river are indicated. Geographical context for the Patuxent River is provided in Figure I-1.

Tides at Jug Bay are semi-diurnal with a range of 0.6 m (National Estuarine Research Reserve System 2004). The study area is composed of three local environments – low marsh, mid marsh and high marsh. The low marsh zone, directly adjacent to a tidal creek, is inundated the longest of the three marsh environments (8-9 hours during a tidal cycle; Khan and Brush 1994). Low marsh environments at Jug Bay are dominated by broadleaved *Nuphar advena*, while the mid marsh plant community is a mixture of *Nuphar advena* and *Sagittaria spp*., as well as some *Typha spp.* The high marsh zone is more diverse, with *Typha spp*., *Phragmites australis, Sagittaria spp*. and several ericaceous species. The high marsh sediment contains large pieces of organic matter, and this environment is inundated for the shorter periods of time than low and mid marsh environments (2-4 hours each tidal cycle; Khan and Brush 1994).

The marsh creek is unbranched and is characterized by rather compact sediments at its head and looser sediments at its mouth. Large SAV communities (likely composed of *Hydrilla spp., Ceratophyllum demersum and Najas guadalupensis*) form at the mouth during the summer growing season. The marsh plant community changes considerably on a seasonal basis, with die-back of vegetation in the fall, flushing of plant litter throughout the winter, initial development of broadleaved communities (e.g. *Nuphar*) in the spring, and growth of reeds, rose mallow and other plants throughout the summer.

King's Landing Marsh (38° 37' 29" N, 76° 40' 54" W; Fig. 1-4) is an oligohaline environment that typically experiences salinities of 0.2 to 5. Broadleaved plants are much less dominant than at Jug Bay, and the vast majority of the marsh could be described as mid marsh, as opposed to Jug Bay where the three marsh zones are approximately equal in area. A visual survey of the Patuxent marsh community revealed

that the King's Landing Marsh is more representative of "typical" Patuxent marshes than Jug Bay. Tides at King's Landing are semi-diurnal, and low marsh environments experience longer periods of inundation than the high marsh. The low marsh zone is small in area and dominated by *Peltandra virginica*. Low marsh areas fringe the main marsh immediately adjacent to the mainstem creek and also exist in frequently flooded, low lying areas of the marsh. The mid marsh is dominated by *Spartina cynosuroides* with (sometimes large) pockets of *Phragmites australis*. The high marsh zone is more diverse, but still dominated by *Spartina* and *Phragmites*. Located closer to land and receiving more freshwater inputs, the high marsh also includes stands of *Typha spp.*

The marsh creek system at King's Landing is branched, or hierarchical, with a main creek that feeds the Patuxent River at its mouth and is itself fed by a fresh stream which is embedded in the terrestrial landscape at its head. Fresher water near the head of the main creek may be the cause of higher plant diversity in the high marsh. As in Jug Bay, there is a seasonal succession of plants at King's Landing, with die-back in the fall, flushing in winter (though to a far lesser extent than at Jug Bay), and development of broadleaved plants and then reeds, grasses and flowering plants throughout the spring and summer.

METHODS

Field techniques

Marsh surface sediments at each site were sampled in low, mid and high marsh zones. At Jug Bay, marsh creek sediments were sampled at the head, middle and mouth regions of the creek. At King's Landing, samples were taken from first, second and third order (mainstem) creeks. All marsh surface samples were taken by hand using 30 cm long (10 cm inner diameter) PVC cores, to a depth of approximately 15 cm. Marsh creek cores were taken with a pole corer, using the same 30 cm PVC cores. Samples were transported to the Chesapeake Biological Laboratory on ice and placed in a temperature control room, which was maintained at the temperature of marsh creek water measured in the field that day (Table 1-2). During transport, marsh creek cores had ~5cm of water overlying the sediment, whereas marsh surface cores were transported without overlying water (and were generally collected without water covering the surface). The cores were placed under water that was collected from the marsh creek and filtered to 0.5 microns. Cores were left in the dark with bubblers to equilibrate overnight.

Table 1-2. Temperature and salinity of water at Jug Bay (marsh creek) and King's Landing (Patuxent River) at the time of core collection. Asterisks indicate field trips from which cores were used for both routine incubations and NO_3 loading experiments.

Month of	Jug Bay		King's Landing		Incubation
2004	Temperature	Salinity	Temperature	Salinity	Temperature
April	9	0.13	11	1.40	9
May	23	0.15	25	0.20	25
June	26	0.10	25	0.32	25
July	28	0.20	26	1.60	27
August	24	0.12	26	0.45	25
September	23	0.17	26*	3.76*	26*
October	15	0.16	15*	2*	14*

Incubation techniques

After ~16 hours of equilibration, core tubes were sealed with polycarbonate lids equipped with o-rings, magnetic stirbars and valved sampling ports, with only water (no air) in the headspace (Fig. 1-5a). The cores were arranged around a central magnetic "fan" which turned the stirbars at low rpm (Fig. 1-5b,c). Cores were incubated in the dark in this manner for 6 hours (8 hours in April, when water temperature was <12^{o}C). Initial aliquots were drawn from the headspace of each core (30 mL for nutrient analyses and duplicate 5 mL aliquots for N_2 and O_2 analyses), and then every 1.5 hours thereafter (30 mL for nutrients and single 5 mL aliquots for N_2 and O_2) for the duration of the incubation. Volumes of water drawn for samples were replaced with water from the bath that had been placed in a cubitainer at the beginning of the incubation. Control core tubes without sediment were treated along with the experimental cores.

Bubbles formed under the lids of the cores on several occasions. In most cases, the source of bubbles appeared to be air pockets in the sediment or from anaerobic sediment metabolism over the course of the incubation, as opposed to a faulty seal in the lid. Cores with bubbles were not discarded from the experiment, but time of appearance and size was noted for all bubbles that developed.

N_2, O_2 and nutrient analyses

Water samples for nutrient analysis (NH_4, NO_3, NO_2 and PO_4) were collected in plastic syringes, filtered to 0.2 microns and immediately frozen. Samples for N_2 analysis were collected in gas-tight, ground glass stoppered vials, killed with mercuric chloride ($HgCl_2$) and stored underwater at ambient temperature or lower to prevent degassing.

Nutrient samples were analyzed by the Chesapeake Biological Laboratory's Nutrient Analytical Services Lab using standard methods (Keefe et al. 2004).

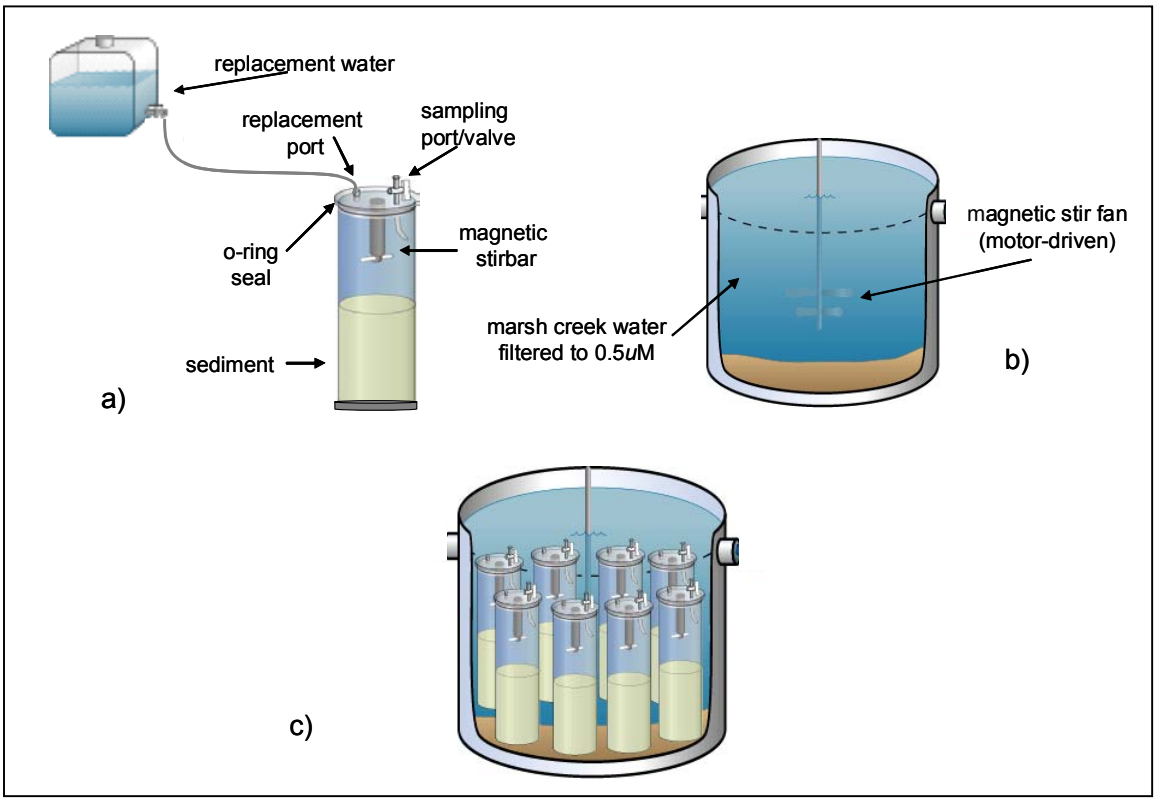


Figure 1-5. Equipment for flux experiments. Core with sediment and flux lid (a); Incubation tank with filtered water and magnetic stirfan (b); Cores arranged around stir fan in tank (c). Images from IAN Symbol Library.

Sediment-water fluxes for dissolved nutrients were determined according to the following formula (Fig. 1-6):

$$F = S * h * k,$$

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

S = slope of the best fit line from linear regression of concentration change on time in µmoles L^{-1} h^{-1},

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

and k = constant (10) derived from the conversion of 1 L to 1000 cm^3 and 10,000 cm^2 to 1 m^2.

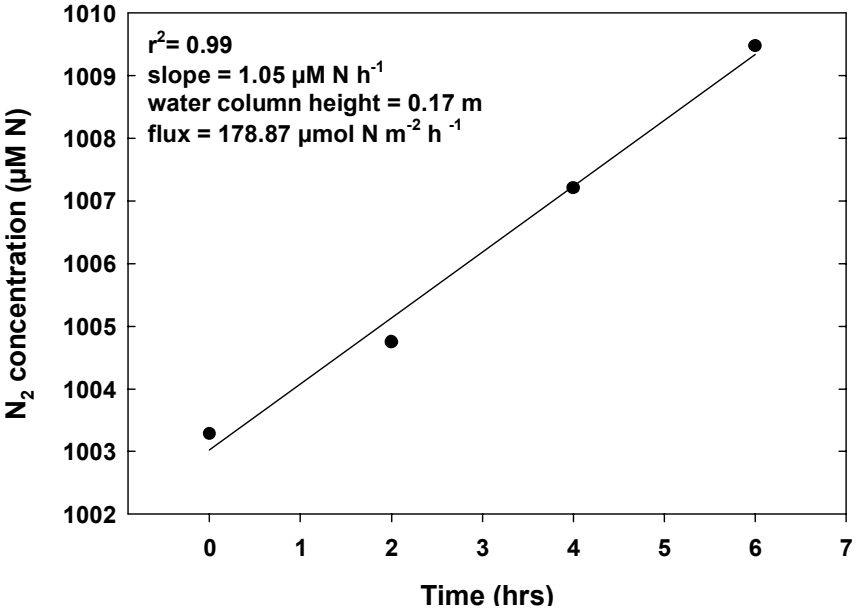


Figure 1-6. Example of concentration changes with time used to calculate fluxes. Data shown are N_2 concentrations generated during incubation of mid marsh sediments taken from Jug Bay in 2004.

Regressions of analytes versus time yielding an r^2 of <0.87 (4 observations) or <0.90 (3 observations) were designated as "not interpretable," and regressions in which the total concentration change was less than twice the limit of detection for that nutrient were designated as having a flux of zero. Single outliers were removed prior to regression analysis if a strong pattern was evident in 3 of 4 observations.

Samples designated for quantification of dissolved gases were analyzed within 2 weeks of collection using Membrane Inlet Mass Spectrometry (Kana et al. 1994). Water samples were pumped through a gas permeable silicon membrane under high vacuum so that dissolved gas molecules from the samples passed into the attached mass spectrometer. Dissolved gas concentrations (N_2, O_2 and Ar) were determined from the

intensities of mass spectrometer signals at m/e 28, 32 and 40, respectively. Measuring N_2 and O_2 concentrations relative to the concentration of Ar, a conservative gas, allowed an order of magnitude increase in measurement precision over measurement of N_2 and O_2 alone (Kana et al. 1994). Data were corrected for instrument background and drift, and for differences in gas solubility due to temperature and salinity differences between incubations and mass spectrometer standards. Changes in dissolved gas concentration ratios with time were used to calculate sediment-water N_2 and O_2 fluxes as described above for nutrients. Control core fluxes were noted for each incubation, but received separate treatment during data analysis.

Nitrate loading experiments

Two experiments were performed in which cores were incubated with elevated NO_3 concentrations in overlying water. For practical reasons, both experiments were performed using cores collected for routine incubations. Cores for the first experiment were collected from King's Landing in September and included 5 mid marsh cores, 1 low marsh core and 1 core from the marsh creek. Cores for the second experiment were collected from King's Landing in October and included 4 high marsh cores, 1 mid marsh core, 1 low marsh core and 1 marsh creek core. In each experiment, KNO_3 was added to overlying water immediately after cores had undergone routine incubation, in order to raise the headspace NO_3 concentration to 50 μM (2 cores), 150 μM (2 cores), and 600 μM (1 core) above ambient concentrations, which were later confirmed to be low. One core with ambient NO_3 and 2 control cores were also incubated in each experiment. After NO_3 addition, cores were left uncapped with bubblers to equilibrate for ~16 hours, and then incubated as previously described.

RESULTS

Ambient dissolved oxygen and nutrient fluxes

Oxygen

Oxygen (O_2) fluxes were directed, without exception, into the sediment. Fluxes of 1000 to 3000 μmoles O_2 m^{-2} h^{-1} were most commonly observed, with a total range of rates from 470 to 5293 μmoles O_2 m^{-2} h^{-1} (Fig. 1-7). Control core (water but no sediments) fluxes were small (<500 μmoles O_2 m^{-2} h^{-1}, with 2 exceptions) (Table 1-3). The majority of fluxes were in the range reported by Boynton and Kemp (1985) for oligohaline and mesohaline Chesapeake Bay sediments, but some unusually high rates (>4500 μmoles O_2 m^{-2} h^{-1}) were observed. More recently, Boynton and Kemp (2005) have reported that rates of sediment oxygen consumption (SOC) around 975 μmoles O_2 m^{-2} h^{-1} are most common in shallow tidal fresh and oligohaline sediments. In this study, slightly higher SOC fluxes were observed in the high and mid marsh areas than in the low marsh and marsh creeks (Fig. 1-8a). Average monthly SOC increased from April through August, then decreased through October (Fig. 1-8b); there was a strong positive correlation between SOC and temperature ($r^2 = 0.84$; Fig. 1-9).

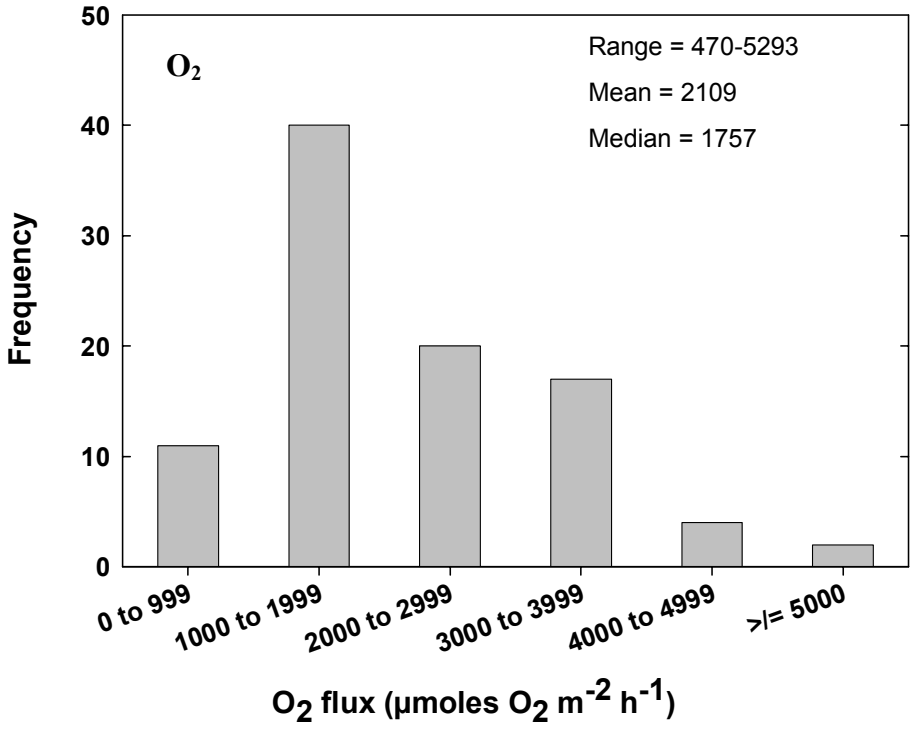


Figure 1-7. Frequency distribution of dissolved O_2 fluxes measured in Patuxent River marshes, April through October, 2004. All fluxes were directed into the sediment.

Table 1-3. Fluxes of NO_3, NH_4, PO_4, N_2 and O_2 measured in control incubations (core tubes without sediments). Negative numbers indicate net flux *into* sediments. All values are given in µmol X m^{-2} h^{-1}, where X is either N or P; oxygen fluxes are given as µmol O_2 m^{-2} h^{-1}. A value of "ND" indicates that no data were collected and values of "NI" indicate that data were not interpretable. Data from most non-interpretable blank fluxes suggested near-zero activity.

	NO_3		NH_4		PO_4		N_2		O_2	
	Control A	**Control B**	**Control A**	**Control B**	**Control A**	**Control B**	**Control A**	**Control B**	**Control A**	**Control B**
Jug Bay										
April	NI	ND	NI	ND	NI	ND	121	ND	-84	ND
May	-8	ND	62	ND	NI	ND	16	ND	-858	ND
June	NI	-5	15	0	0	0	56	NI	-600	-521
July	-28	NI	0	0	8	0	0	0	-448	-451
August	16	-12	-13	0	-16	-24	0	-82	-335	-488
September	NI	NI	107	0	10	1	176	203	-336	-409
October	NI	NI	-13	-11	NI	-4	51	28	-242	-265
King's Landing										
April	0	ND	-107	ND	-7	ND	92	ND	-390	ND
May	NI	ND	0	ND	-7	ND	NI	ND	-286	ND
June	4	11	29	0	-3	0	15	-16	-269	-310
July	NI	ND	0	ND	0	ND	NI	ND	-263	ND
August	-51	ND	0	ND	-9	ND	0	ND	-230	ND
September	NI	-7	0	0	-7	-3	NI	-206	-411	-408
October	0	NI	-22	0	-4	-2	0	0	-116	NI

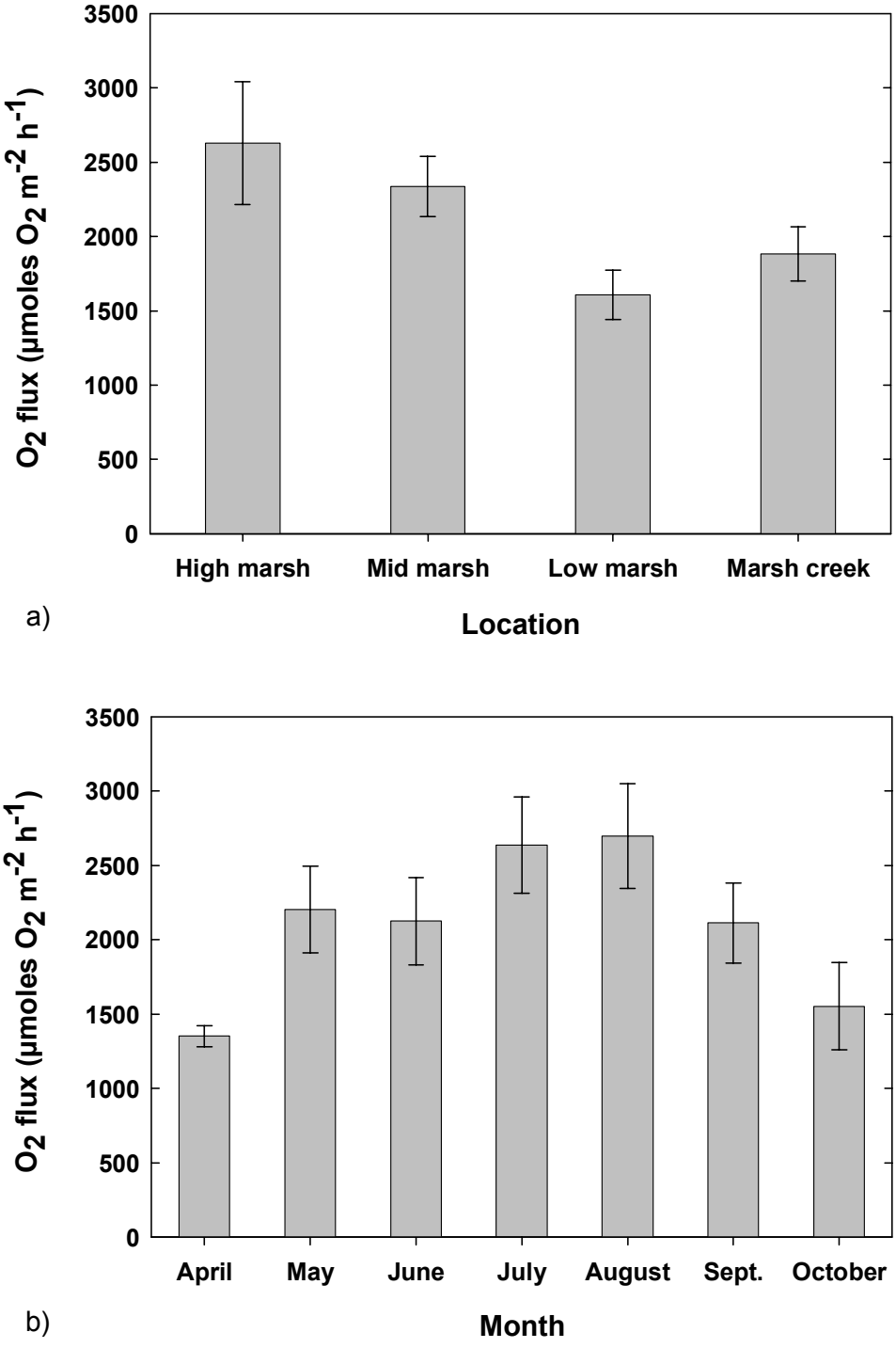


Fig. 1-8. Average spatial (a) and temporal (b) patterns in sediment oxygen consumption for Patuxent marshes, April through October 2004.

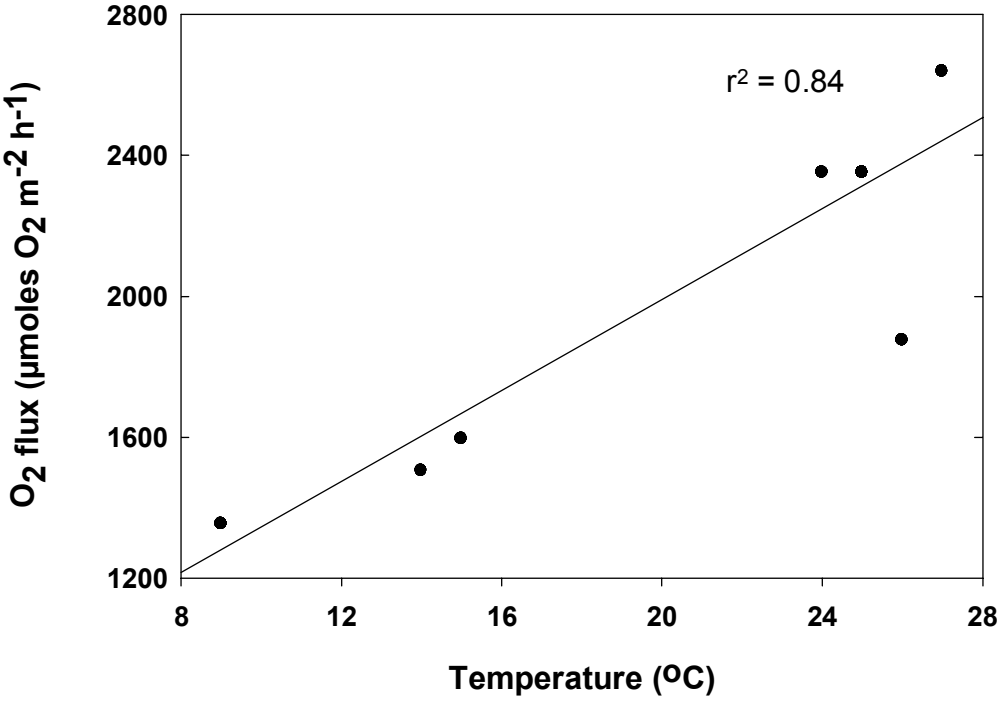


Figure 1-9. Relationship between average monthly SOC and temperature observed during routine incubations of cores from Jug Bay and King's Landing. O_2 fluxes are directed into sediments.

Ammonium

Fluxes of dissolved inorganic nutrients also exhibited some strong patterns. Ammonium fluxes were directed predominantly out of the sediment (positive). Fluxes of 0 to +200 µmoles NH_4-N m^{-2} h^{-1} were most frequently observed, with a total range of -118 to +934 µmoles NH_4-N m^{-2} h^{-1} (Fig. 1-10). Control core NH_4 fluxes were generally small, but a large negative flux of 107 µmoles NH_4-N m^{-2} h^{-1} was observed at King's Landing in April (Table 1-3). The most frequently observed NH_4 fluxes were within the range previously reported for oligohaline and mesohaline Chesapeake Bay sediments, but the substantial number of observations above 200 µmoles NH_4-N m^{-2} h^{-1} is somewhat unusual (Boynton & Kemp 1985; Bailey 2005). There was a strong spatial pattern

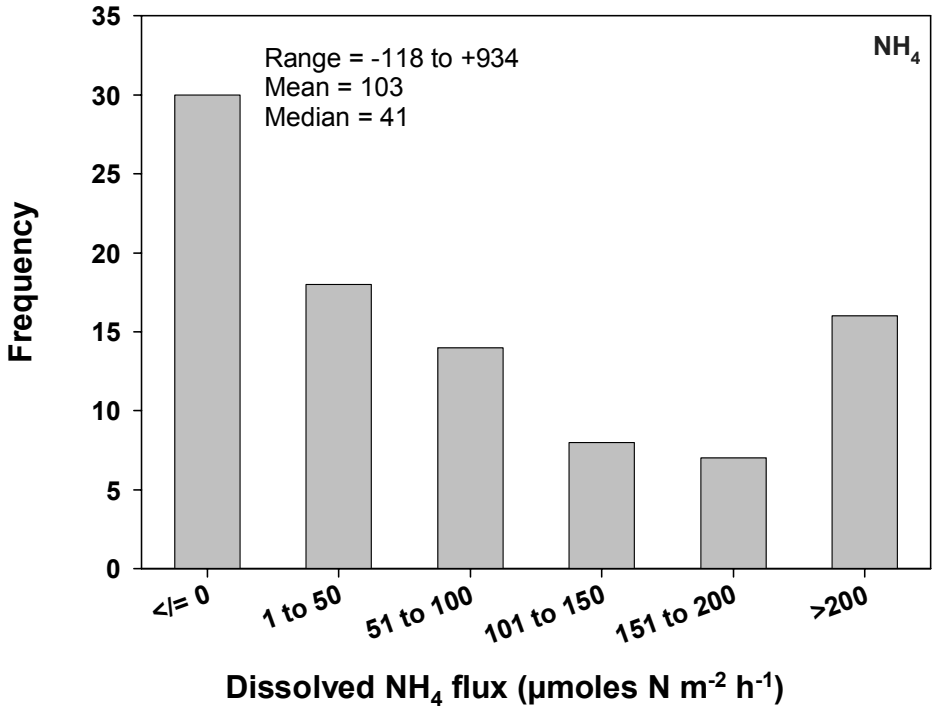


Figure 1-10. Frequency distribution of dissolved NH_4 fluxes measured in Patuxent River marshes, April through October, 2004.

in NH_4 fluxes, where marsh creek sediments released the most NH_4 and high and mid marsh sediments released less by a factor of 4 or more (Fig. 1-11). At King's Landing, average NH_4 fluxes were similar in all months except September, when average flux was high due to an observation of 495 µmoles NH_4-N m^{-2} h^{-1} (Fig. 1-12). At Jug Bay, average fluxes increased from April to May, then decreased through October.

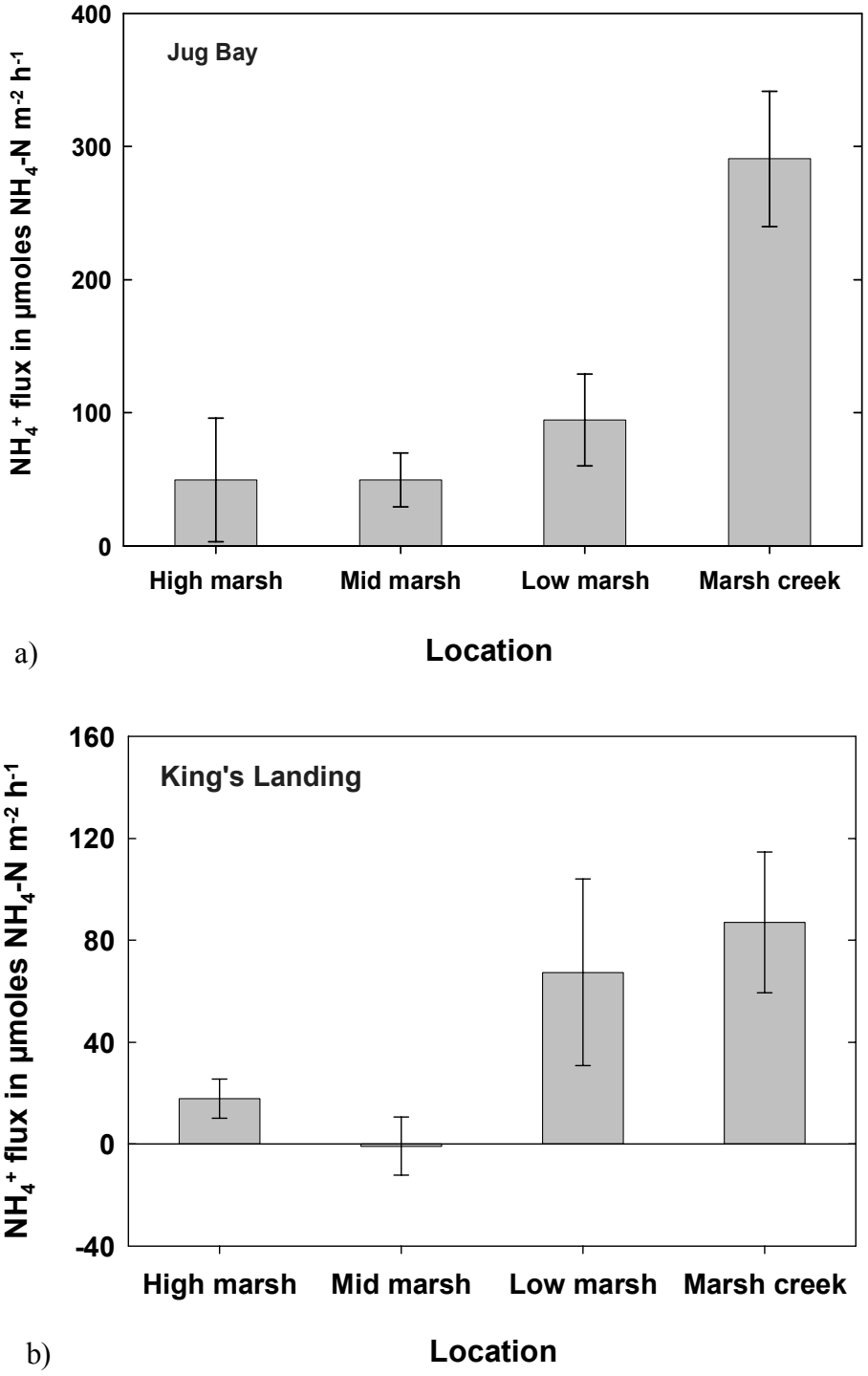
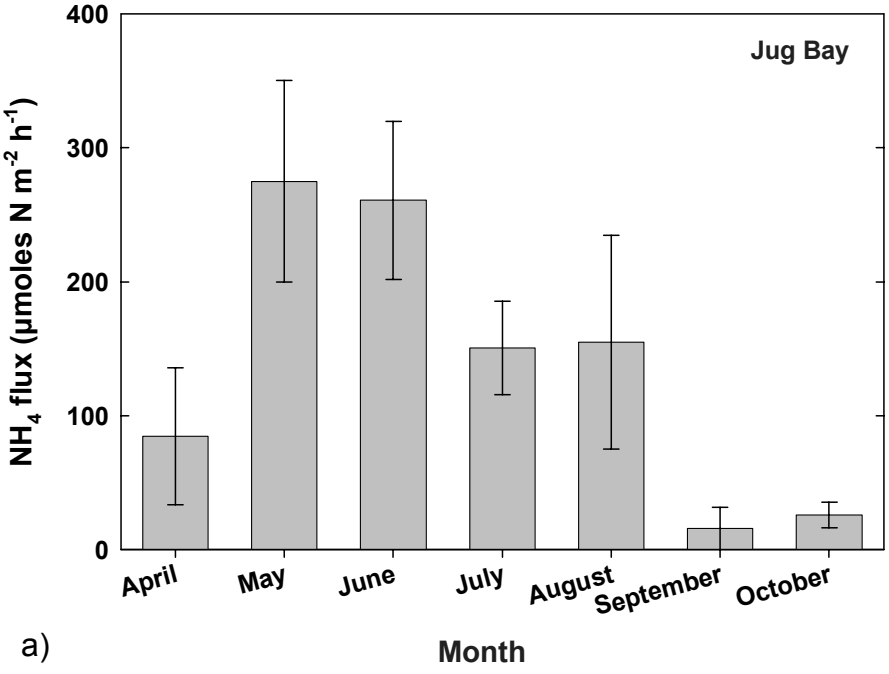


Figure 1-11. Spatial patterns in NH_4 flux rates measured in Jug Bay (a) and King's Landing (b) marshes, April through October, 2004.



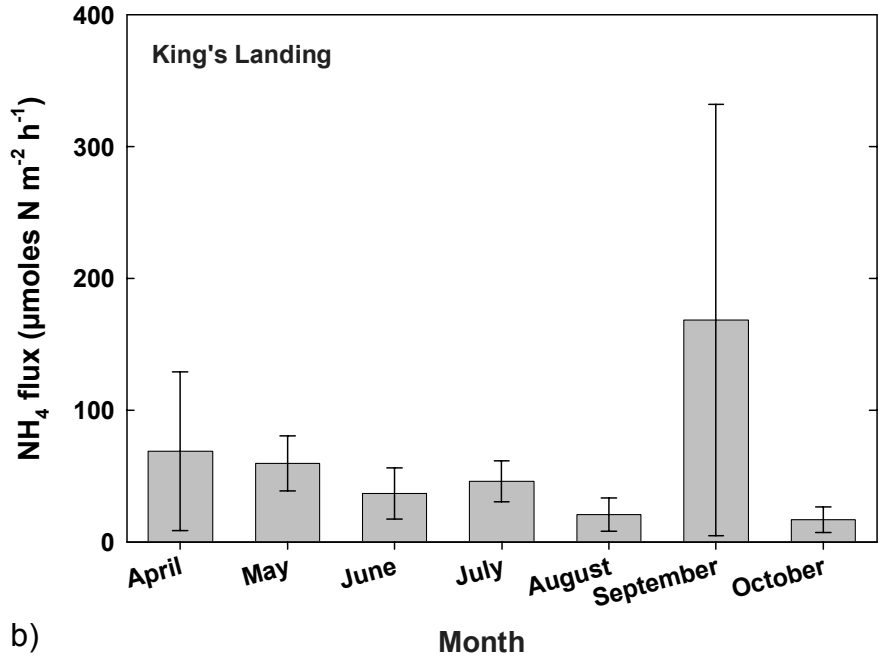


Figure 1-12. Temporal patterns in NH_4 flux rates measured in Jug Bay (a) and King's Landing (b) marsh surface and creek sediments.

Nitrate

Nitrate fluxes were largely into the sediment (negative). Fluxes of -1 to -100 µmoles NO_3-N m^{-2} h^{-1} were most commonly observed, but the total range was from -276 to +84 µmoles NO_3-N m^{-2} h^{-1} (Fig. 1-13). Control core fluxes were small for the

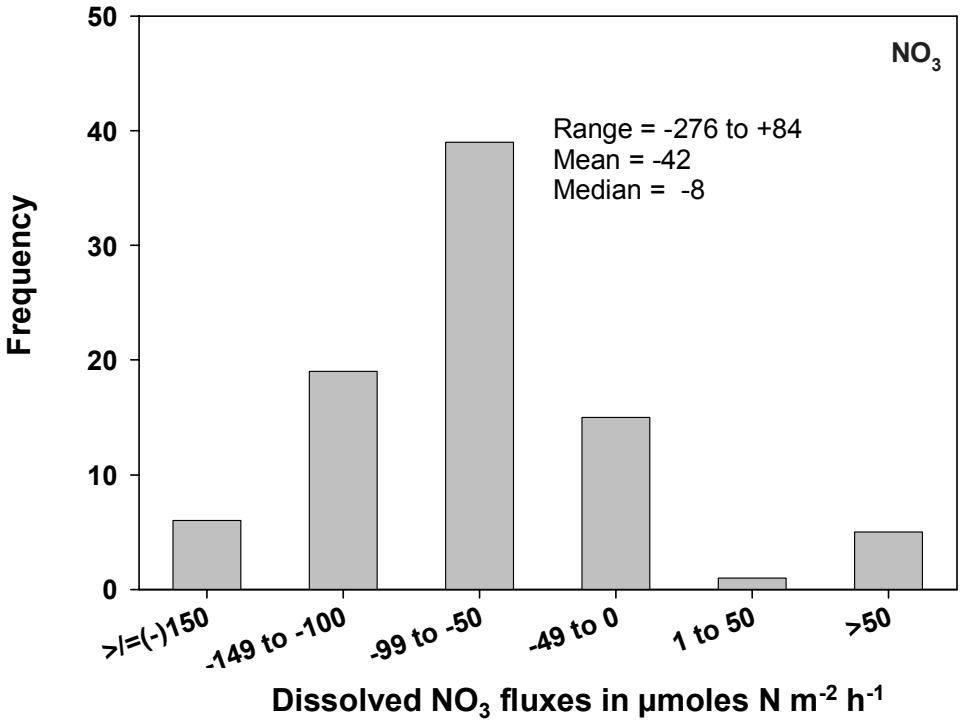


Figure 1-13. Frequency distribution of NO_3 fluxes measured in Patuxent River marshes, April through October, 2004.

most part (Table 1-3). The majority of fluxes were in the range previously reported for oligohaline Chesapeake Bay sediments, but the few positive fluxes that were observed in this study did not follow a temporal pattern, contrary to results from other studies in which NO_3 was released from sediments in late summer (Boynton & Kemp 1985). Spatial patterns in NO_3 fluxes were different between sites (Fig. 1-14). At Jug Bay fluxes were similar in the high marsh, mid marsh and marsh creeks, and directed predominantly into the sediments. Conversely, fluxes in the low marsh were often positive. At King's

Landing, fluxes were also negative and of similar magnitude in the high and mid marsh, but increased in the low marsh and were highest in the marsh creeks. A weak temporal pattern developed in the combined dataset that followed the temporal pattern observed for N_2 fluxes (Fig. 1-15).

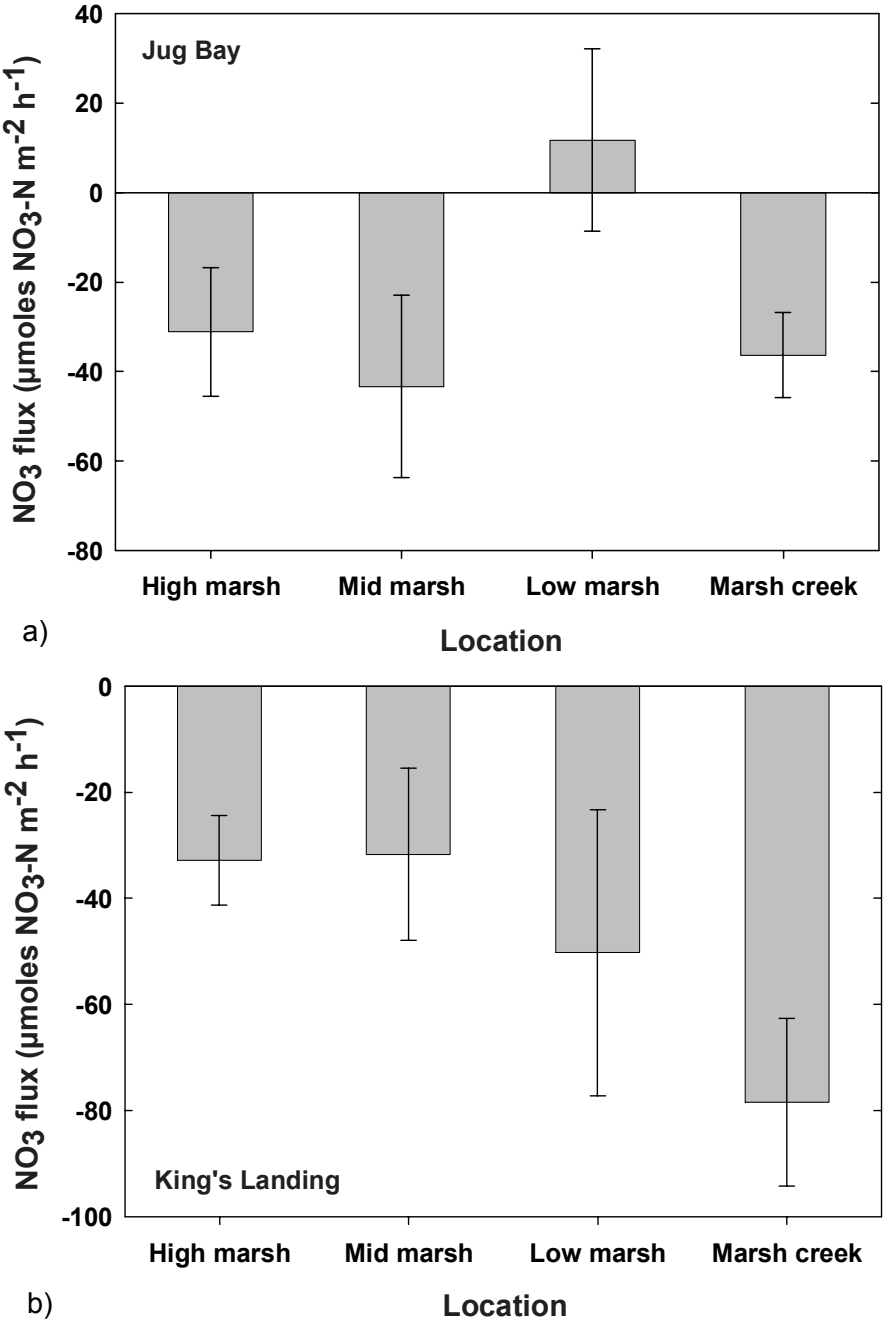


Figure 1-14. Spatial patterns in NO_3 fluxes measured in Jug Bay (a) and King's Landing (b) marshes, April through October, 2004.

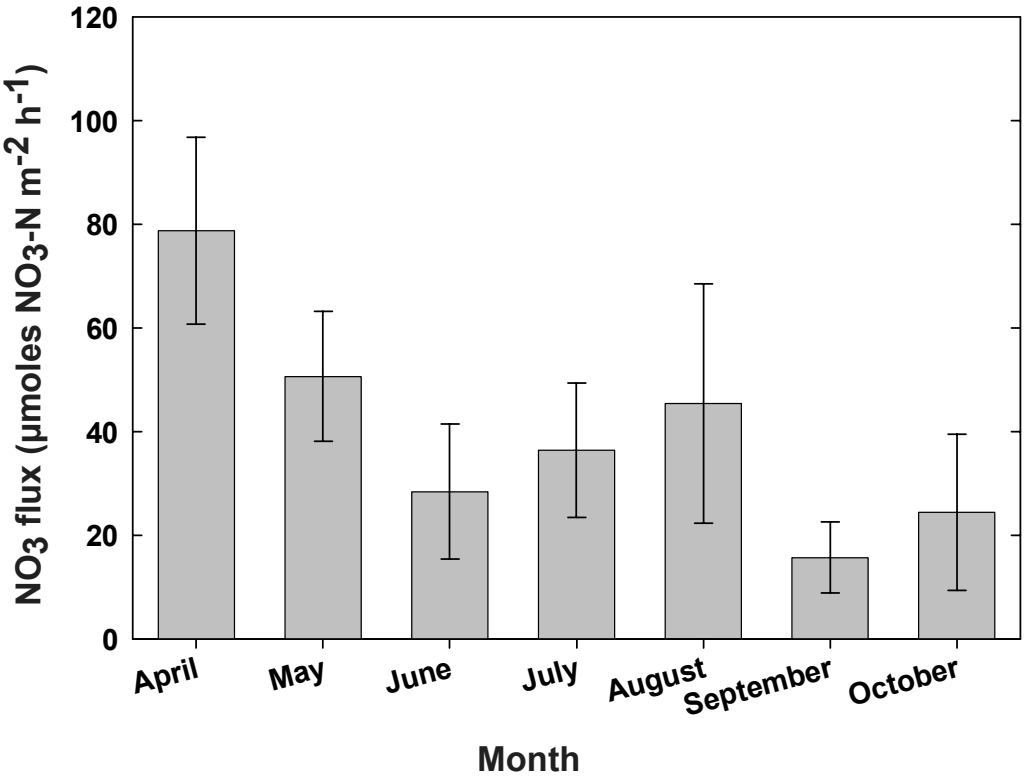


Figure 1-15. Temporal pattern in NO_3 fluxes (from water column to sediments), averaged for both King's Landing and Jug Bay, all marsh environments. Temporal pattern was the same at both sites. Nitrate fluxes exhibit the same bimodal temporal pattern as N_2 fluxes (see Fig. 1-20 for comparison).

Phosphate

Phosphate (PO_4) fluxes were very small to negligible, with a few exceptions. Fluxes ranged from -26 to +38 µmoles PO_4-P m^{-2} h^{-1} (Fig. 1-16), but fluxes of 10 µmoles PO_4-P m^{-2} h^{-1} or greater were observed only in Jug Bay marsh surface and King's Landing marsh creek sediments in May through July. Interpretable, non-zero fluxes were predominantly positive (i.e. out of the sediments). Control core fluxes were negligible (Table 1-3).

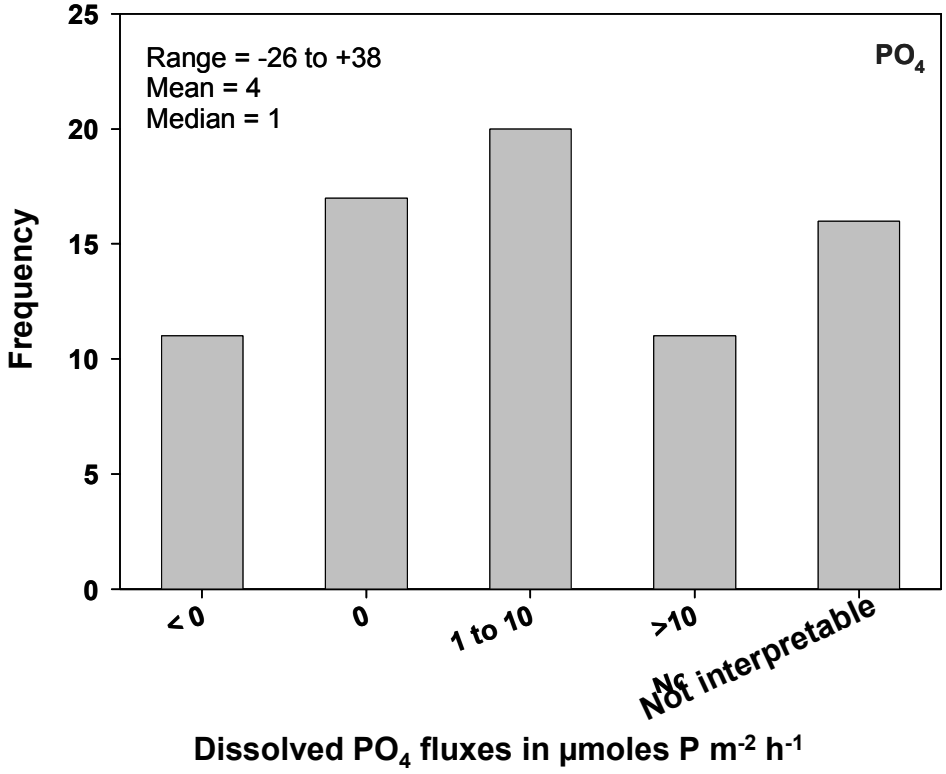


Figure 1-16. Frequency distribution of PO_4 fluxes measured in Patuxent River marshes, April through October, 2004.

Ambient N_2 fluxes

A broad range of N_2 fluxes (-159 to +846 µmoles N m^{-2} h^{-1}) were measured, with negative fluxes indicating net N_2 movement into the sediment and positive fluxes indicating a net flux to the water column. Despite the large range of rates measured, rates between 10 and 200 µmoles N m^{-2} h^{-1} were most commonly observed (Fig. 1-17). The grand mean of all rates measured was 120 µmoles N m^{-2} h^{-1}. A literature review of tidal wetland denitrification studies (Greene 2005) indicated that rates measured in this study were slightly larger than the population of measurements in the literature (t-test, unequal variances, P = 0.04; Fig. 1-18). However, if the single highest rate measured in this study

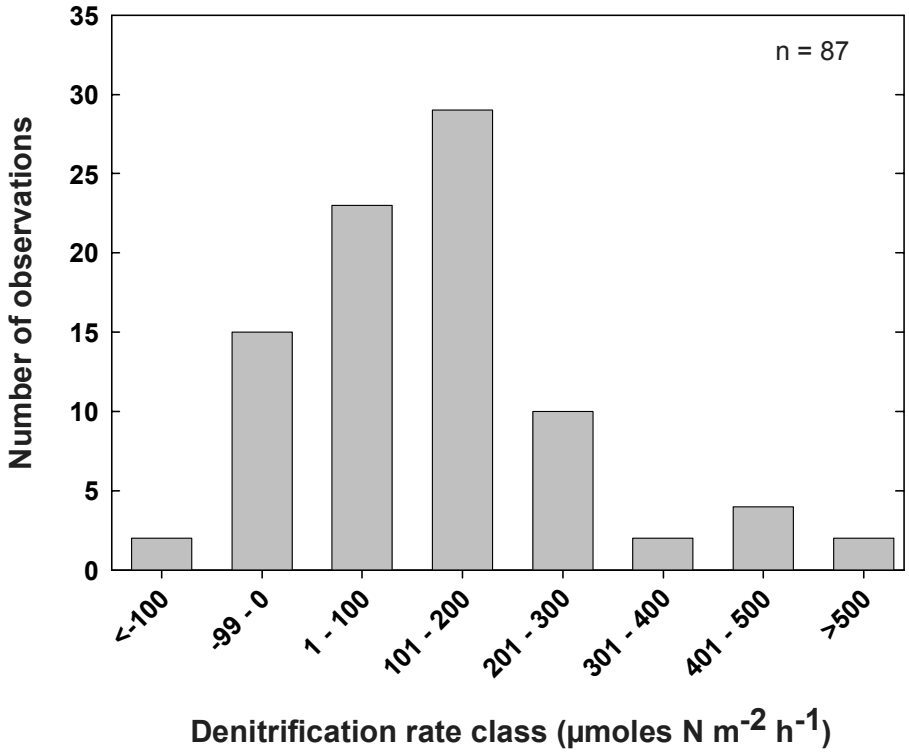


Figure 1-17. Frequency distribution of denitrification rates measured in King's Landing and Jug Bay marshes, April through October,

(846 µmoles N m^{-2} h^{-1}) is removed from calculations, there is no significant difference between rates from this study and those in the literature (t-test, unequal variances, P = 0.07). No significant differences were found between rates measured in tidal fresh (Jug Bay) versus oligohaline (King's Landing) sediments (t-test, P >> 0.05; Fig. 1-18). Dinitrogen fluxes measured in control cores ranged from -206 to +203 µmoles N m^{-2} h^{-1}; however, most fluxes had an absolute magnitude less than 60 µmoles N m^{-2} h^{-1} (Table 1-3).

Since cores were bubbled with air prior to incubation, all cores began incubation with roughly the same amount of O_2, so relationships between water column O_2 concentration and N_2 fluxes could not be explored. However, there was a positive

correlation between N_2 fluxes from the sediment and O_2 fluxes into the sediment for the combined marsh surface and marsh creek datasets ($r^2 = 0.27$; Fig. 1-19a). The correlation between N_2 and O_2 fluxes measured only in marsh surface sediments (both sites combined) was stronger ($r^2 = 0.41$; Fig. 1-19b).

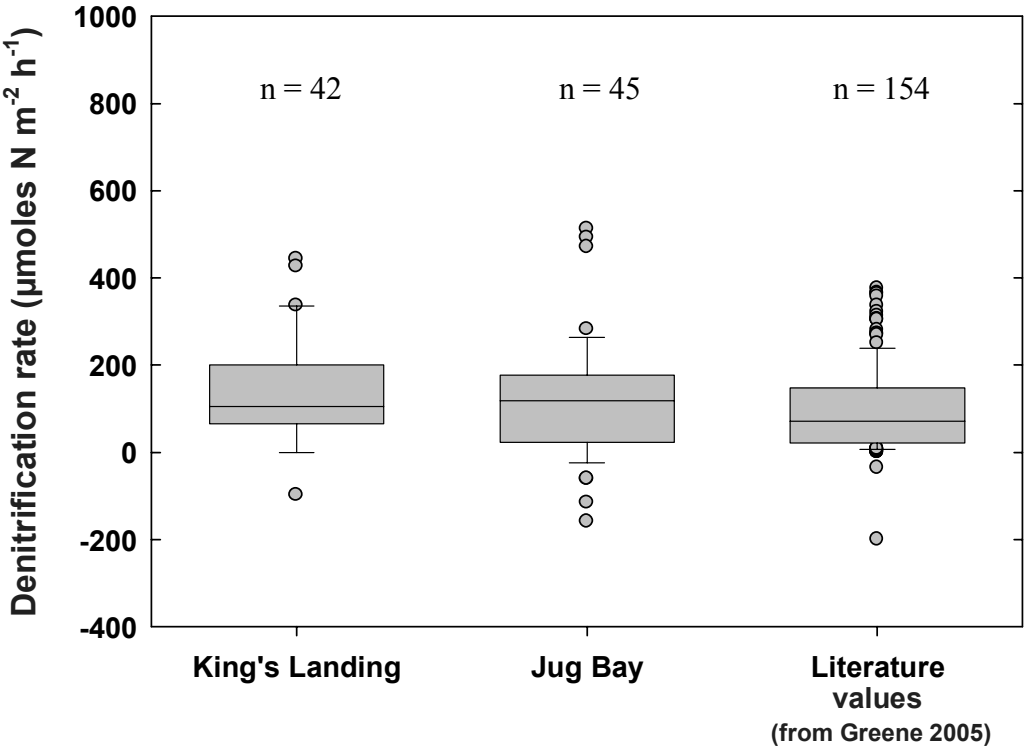
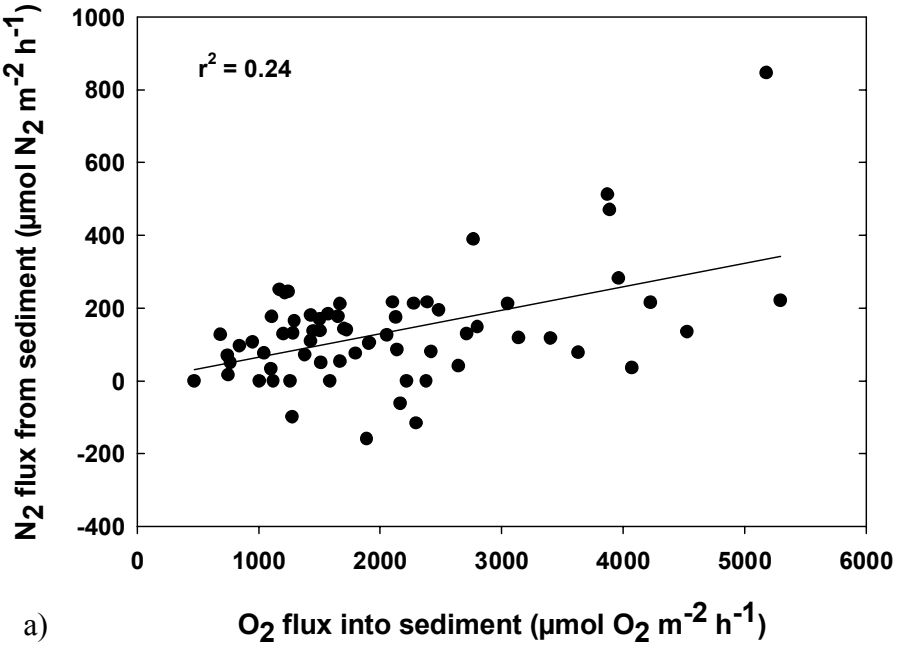
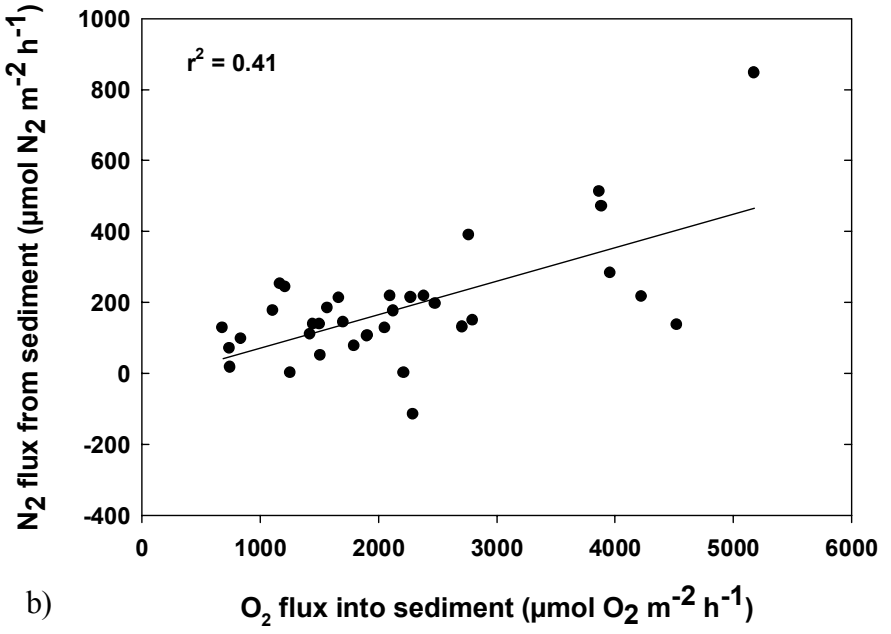


Figure 1-18. Comparison of denitrification rates measured in this study versus rates identified in the literature. Boxes represent 25th, 50th and 75th percentiles, bars represent 5th/95th percentiles and points represent outliers.



a)



b)

Figure 1-19. Relationship between N_2 and O_2 fluxes in all cores (a) and marsh surface cores (b).

Spatial patterns – marsh habitat

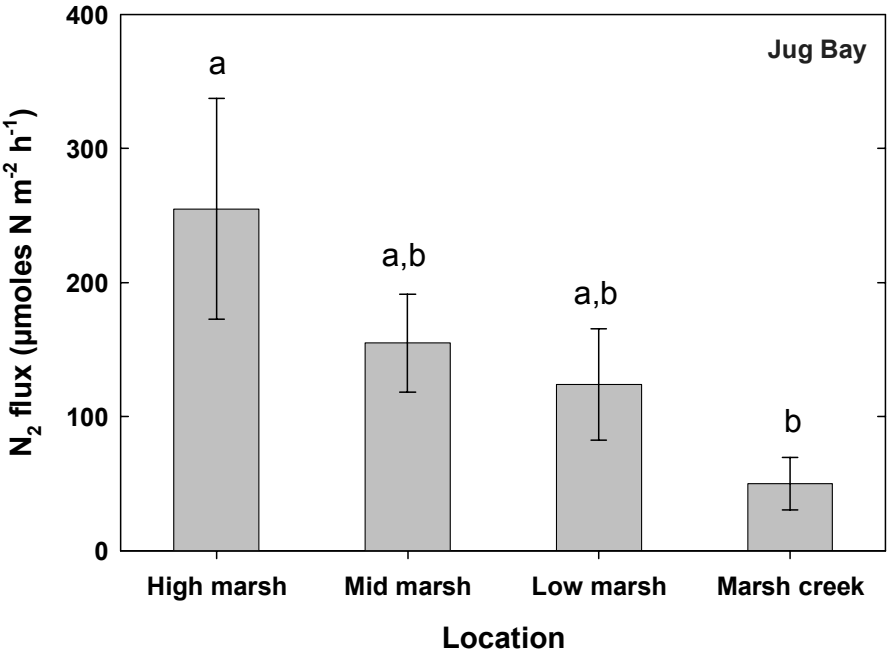
There was a consistent pattern of decreasing denitrification rate with distance from land at both study sites (Fig. 1-20). Rates were highest in the high marsh, decreasing through the mid and low marsh, and lowest in the marsh creeks. Despite the consistent pattern, the only statistically significant difference in rates was between the high marsh areas and marsh creeks in the Jug Bay and combined datasets (Bonferroni t-test P=0.007 and 0.004, respectively).

Fine scale spatial heterogeneity – marsh environment

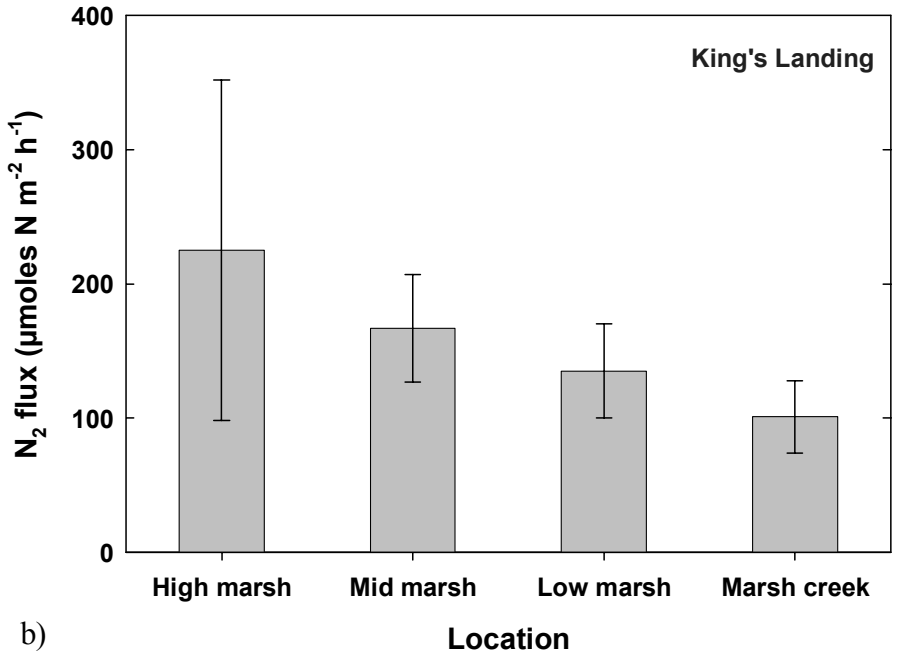
Spatial heterogeneity at fine scales (<5 m) was high (Table 1-4). In September, replicated N_2 flux measurements in the mid marsh areas of Jug Bay and King's Landing exhibited coefficients of variation of 48% and 40%, respectively. Replicated high marsh measurements at King's Landing in October had a coefficient of variation of 38%. Due to equipment limitations, a more extensive investigation of fine scale heterogeneity was not feasible, but these data suggest substantial variation.

Temporal patterns – marsh environment

Temporal patterns in denitrification rates were also observed, though there were no statistically significant differences in denitrification rates between months. At both Jug Bay and King's Landing, denitrification rates declined from April through June, increased in July and then declined through September/October (Fig. 1-21). Rates were higher in April than in September/October, even though temperatures were slightly lower in April (Table 1-2).



a)



b)

Figure 1-20. Spatial patterns in denitrification rates measured in Jug Bay (a) and King's Landing (b) marsh sediments. Rates are 7 month averages. Grouping of environments according to statistically significant differences in mean rates is indicated by letters above columns ("a" and "b") for Jug Bay; no significant differences were found at King's Landing.

Table 1-4. Fine scale heterogeneity in denitrification rates. Values are fluxes (in µmoles N m^{-2} h^{-1}) for replicate cores taken <5 m apart. Range (maximum – minimum rate) and coefficient of variation ("C.V.," as %) are also given.

	Site	Values	Range	C.V.
September, Mid marsh				
	King's Landing	NI*		
		76		
		135		
		NI		
		NI		
			60	40
	Jug Bay	43		
		120		
		168		
		179		
		231		
			188	48
October, High marsh				
	King's Landing	70		
		106		
		151		
		178		
			108	38

*Data suggested near-zero fluxes for non-interpretable results

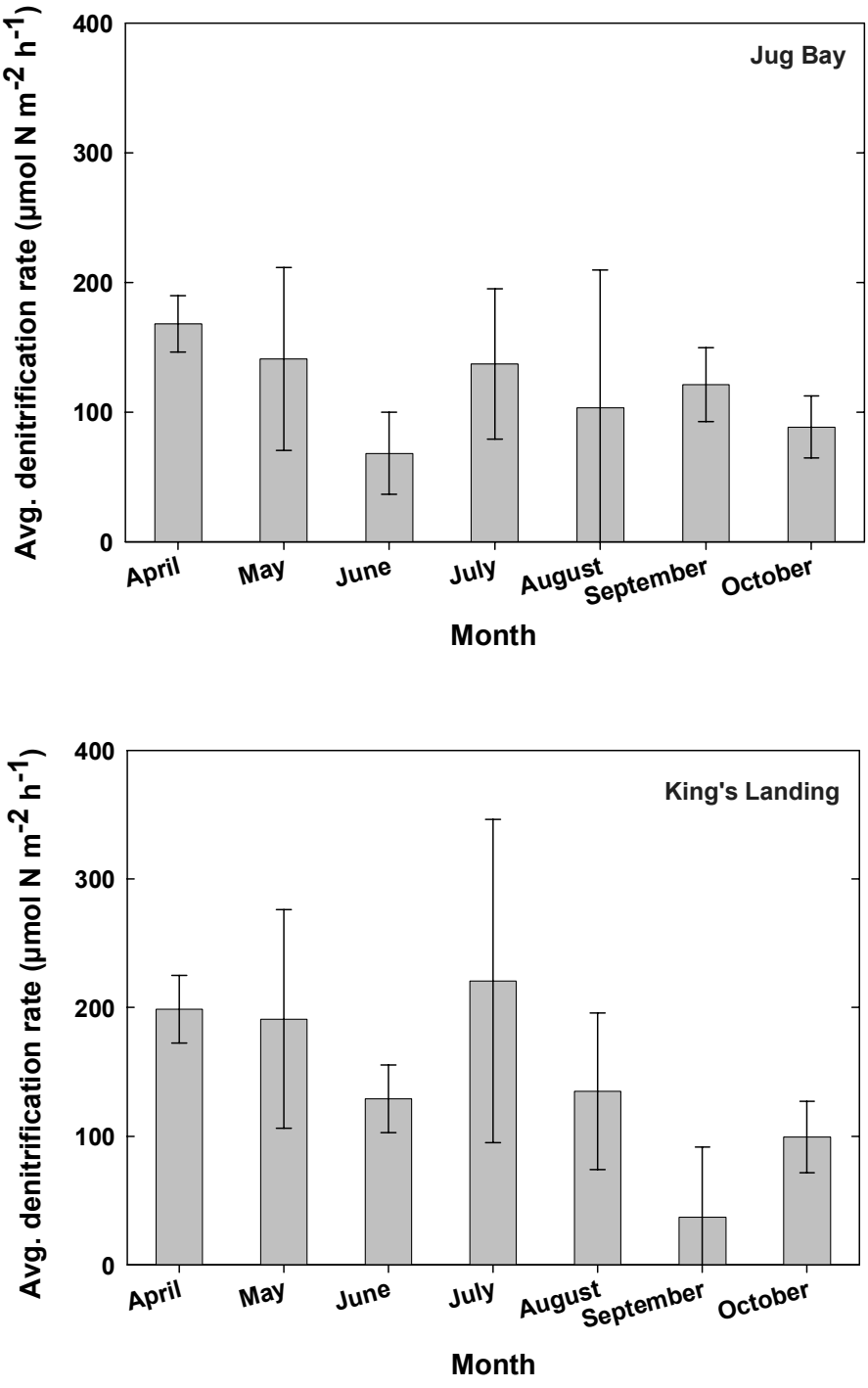


Figure 1-21. Temporal patterns in denitrification rates measured in Jug Bay (a) and King's Landing (b) marsh surface and creek sediments. Rates are averages across all marsh environments and marsh creeks for the site and month indicated.

Marsh creeks

Marsh creek N_2 fluxes ranged from -159 to +181 and -99 to +336 µmoles N m^{-2} h^{-1} at Jug Bay and King's Landing, respectively. No strong spatial or temporal patterns were evident at either site. However, negative fluxes (net N-fixation) were observed only from July onward, and only in the main creek at King's Landing and in the creek mouth at Jug Bay (i.e. portions of the creeks closest to the mainstem Patuxent) (Fig. 1-22).

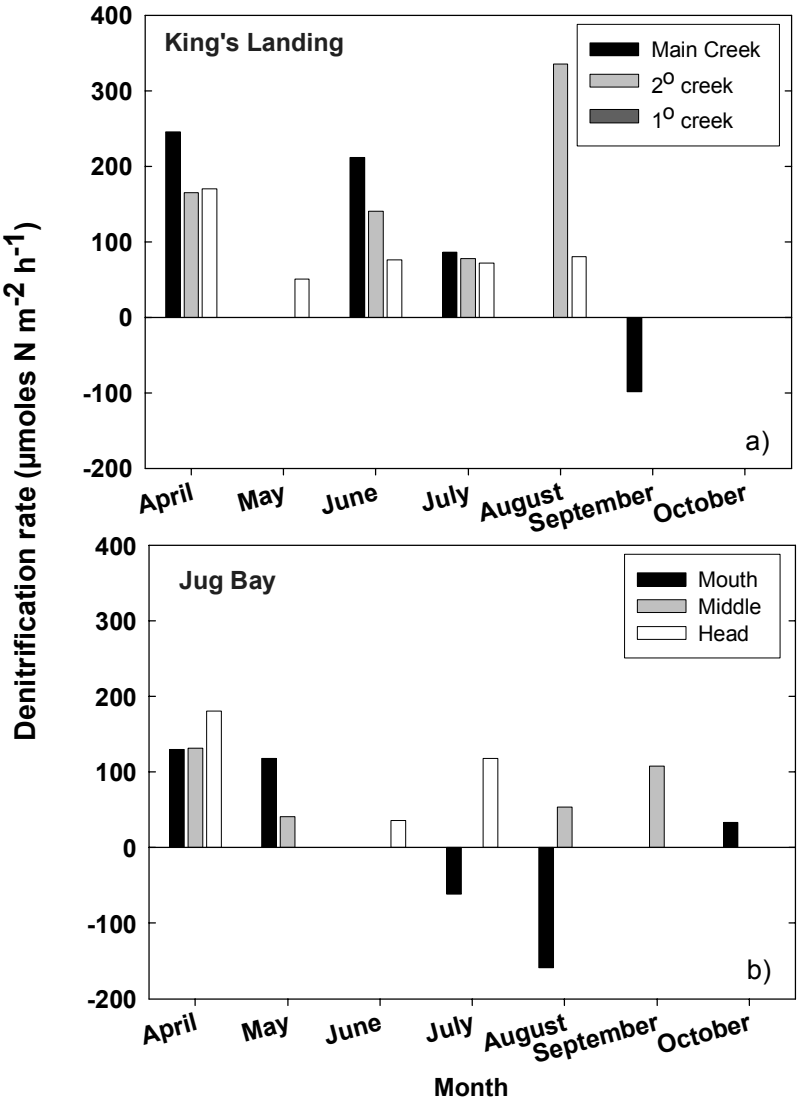


Figure 1-22. Denitrification rates measured in Jug Bay (a) and King's Landing (b) marsh creeks, April through October 2004.

Relationships between water column NO_3 and N_2 flux under ambient conditions

Interestingly, there was not a strong correlation between NO_3 fluxes and N_2 fluxes on a core by core basis; nor was there a strong correlation between water column NO_3 concentrations and N_2 fluxes on a core by core basis in routine incubations, except that negative N_2 fluxes were observed only at low NO_3 concentrations (Fig. 1-23). There was, however, a strong relationship between monthly *average* N_2 fluxes and water column NO_3 concentrations at King's Landing (r^2=0.91; Fig. 1-24). The relationship was not as strong at Jug Bay (r^2 = 0.30; Fig. 1-24) due to the frequently low NO_3 concentrations in water collected for incubations at this site. Water collected at Jug Bay was drawn from marsh creeks, often during ebb tides, whereas water collected at King's Landing was taken directly from the river.

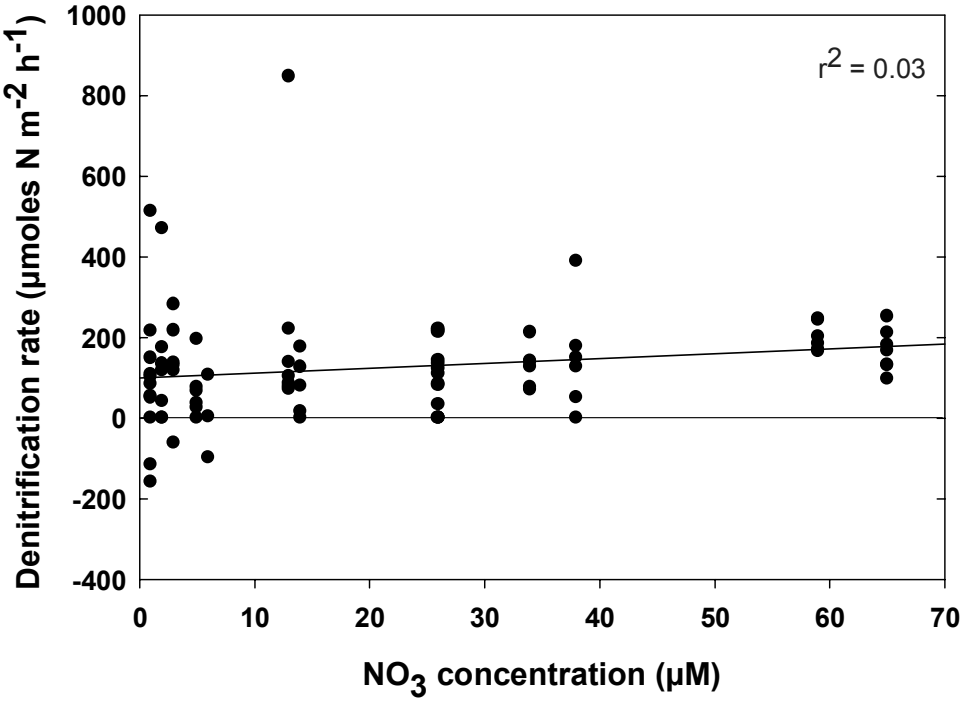


Figure 1-23. Scatter plot of denitrification rates versus initial NO_3 concentrations in overlying waters, observed during routine incubations of cores from Jug Bay and King's Landing.

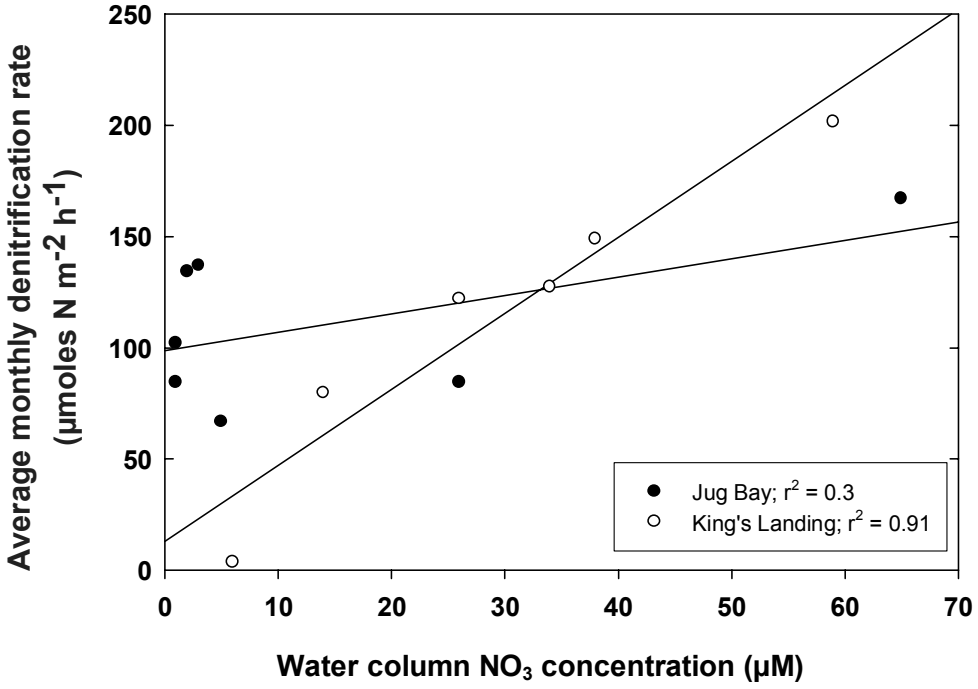


Figure 1-24. Relationship between average monthly denitrification rates and NO_3 concentrations observed during routine incubations of cores from Jug Bay and King's Landing.

Nitrate loading experiments

In general, there was a strong saturation-type response by denitrification rates to increased water column NO_3 concentrations during loading experiments (Fig. 1-25). Dinitrogen fluxes in the first loading experiment increased with NO_3 concentrations to 150 µM in a steep, nearly linear fashion, then increased less sharply at higher substrate concentration. The second loading experiment generated similar results, except that the denitrification rate at 600 µM NO_3 was similar to the rate at 50 µM. Denitrification rates at 0 and 50 µM added NO_3 were almost identical between experiments. Despite the very strong response to elevated water column NO_3, and despite the fact that N_2 fluxes

measured during loading experiments were higher than fluxes generated by the same cores during routine incubations, the highest N_2 fluxes measured in this study were measured during routine incubations, rather than in loading experiments.

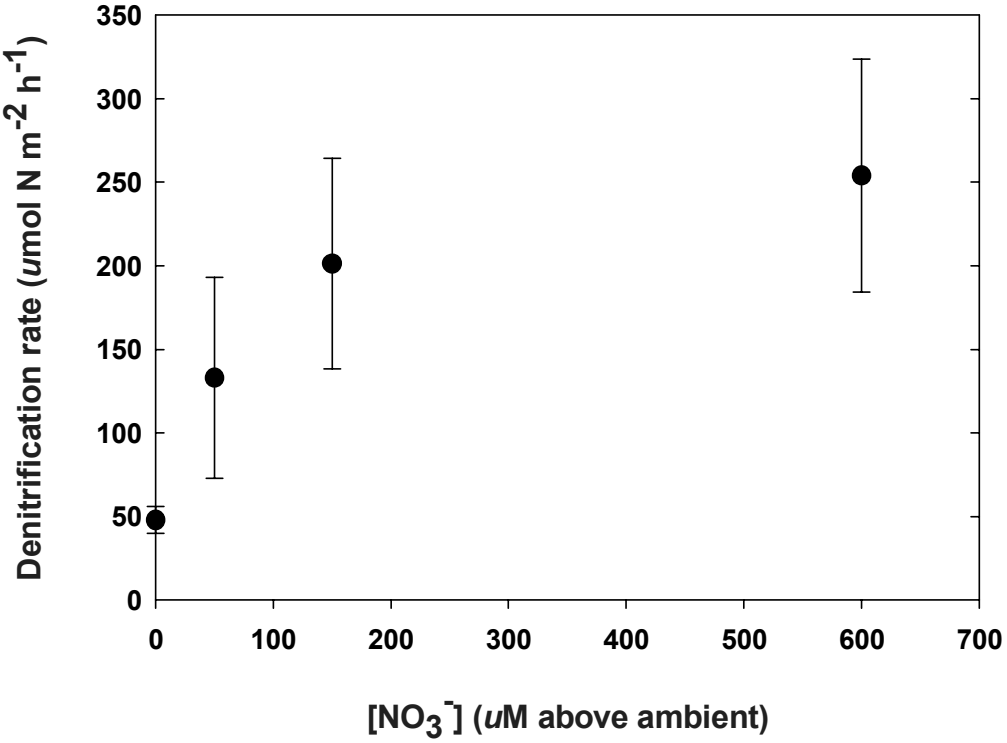


Figure 1-25. Response of denitrification rate to elevated water column NO_3 concentration. Each point represents the averaged denitrification rates observed in two loading experiments for given NO_3 concentrations. In each experiment, there were two cores each with 0, 50 and 150 µM added NO_3, and one core with 600 µM added NO_3.

DISCUSSION

Denitrification occurred in both tidal fresh and oligohaline marsh environments during each of the 7 months in which it was measured. The rates measured were substantial in the context of an ecosystem-scale N budget for the Patuxent River. For example, typical marsh denitrification rates of 40 mg N m^{-2} d^{-1} appear to nearly balance external N inputs per unit estuarine surface area (on a daily basis) at rates of 43 mg N m^{-2} d^{-1} (W. Boynton, unpublished data; Cronin and Pritchard 1975). Denitrification rates were not uniform in space or time, however, and recognizing spatial and temporal patterns is an aid to understanding factors controlling denitrification. These spatial and temporal patterns are also vital to extrapolating rate measurements from study sites to the larger marsh community at seasonal to annual timescales.

Spatial patterns in denitrification

Factors controlling denitrification include O_2 availability (and thus frequency of tidal inundation, physical characteristics of sediments, metabolic rates of aerobic heterotrophs and dominant plant community), NO_3 availability (and thus water column NO_3 and NH_4 concentrations, nitrification rates and competition due to plant and algal uptake), temperature, and the availability of labile organic matter (Seitzinger 1988). With respect to factors that may control spatial patterns in marsh denitrification, two of the most striking differences between marsh environments (i.e. high, mid and low marsh and marsh creeks) are dominant plant community and frequency of tidal inundation. These two properties can create differences in the availability of O_2, NO_3 and C.

Impact of plant community

Labile C and NO_3 availability are important controls on denitrification (Seitzinger 1988; Brettar and Rheinheimer 1992), and both are influenced to a large degree by dominant plant community (Simpson et al. 1983b). Though some chemoautotrophic denitrifiers have been identified, known denitrifiers are largely heterotrophs, and as such denitrify in order to oxidize organic matter (Zehr and Ward 2002). Therefore, plant litter is important to denitrification as a source of carbon. Additionally, though NO_3 from overlying water is important to denitrification (Kana et al. 1998), ammonification and subsequent nitrification of N in plant litter is also a potential source (Caffrey and Kemp 1992). Low marsh plants are typically broad-leaved with small stems, and thus have a relatively low C:N ratio (Heywood 1977; Traband 2003). High marsh plants, however, are largely reeds, grasses or even ericaceous species with prominent stems, large amounts of structural carbon and high C:N ratios (Heywood 1977; Traband 2003). Plants with lower C:N ratios tend to be more labile, and low marsh plants have been shown to decompose at significantly higher rates than high marsh vegetation (Odum and Heywood 1977; Simpson et al. 1983b).

The greater lability of plant litter in low marsh environments should, in theory, enhance denitrification rates due to greater availability of C and N (NO_3). However, C:N ratio does not appear to be a dominant control on denitrification in Patuxent marshes, as high marsh environments exhibited higher denitrification rates than low marsh areas in this study (Fig. 1-20). At Jug Bay, sediment C:N ratios do appear slightly lower in low marsh than in high marsh environments (Chapter 2), but more striking is the fact that there is simply much more organic matter in the high marsh (Khan and Brush 1994).

DeLaune et al. (1981) found the same pattern in a Louisiana salt marsh, and there appears to be more C and N in the high marsh at King's Landing as well (Chapter 2). Given the spatial pattern in denitrification observed in this study, total C and N content of sediments may be more important than C:N ratio in determining the availability of organic C and remineralized NO_3 to denitrifiers.

Impact of tidal flooding

In this study, denitrification rates increased with distance from the tidal channel (Fig. 1-20). The body of literature reporting spatial patterns in denitrification rates within tidal marshes is not extensive; however, Merrill (1999) reported a similar spatial pattern for Jug Bay during the spring of 1997. Kaplan et al. (1979) measured higher denitrification rates in marsh creeks and low marsh environments than in the high marsh in a New England Salt marsh. However, creek bottoms in that marsh received large NO_3 subsidies from groundwater, to which the authors attributed the observed spatial patterns in denitrification. In Patuxent marshes during this study, denitrification rates were negatively correlated with duration of tidal inundation ($r^2 = 0.92$; Fig. 1-26).

Higher order marsh creeks are inundated 100% of the time, and even primary creeks are inundated most of the time. This contrasts sharply with high marsh environments, which are inundated least frequently and for the shortest duration of all marsh environments, sometimes receiving no tidal waters at all during the neap portion of the tidal cycle. More frequently inundated areas receive new NO_3 inputs from tidal waters more regularly, which could enhance denitrification rates. However, while providing a regular *water column* NO_3 subsidy to more inundated regions of the marsh, tidal pulsing may also create an opposing spatial pattern in *sediment* NO_3 pools from

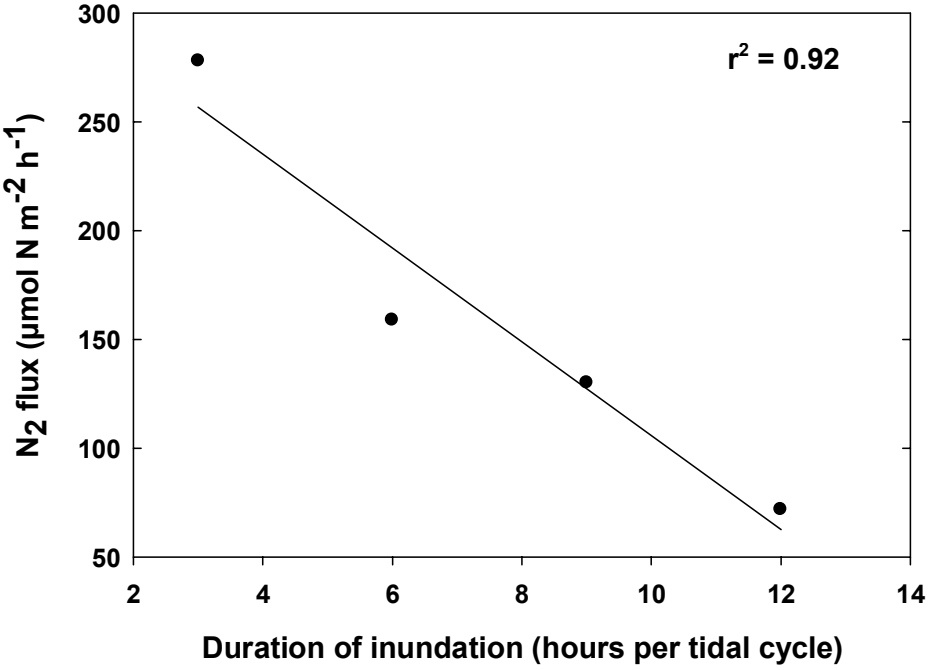


Figure 1-26. Relationship between measured denitrification rates and duration of tidal inundation in Patuxent River marshes.

nitrification by draining and aerating surface sediments. No previous studies of the relative importance of water column versus nitrified NO_3 in tidal marsh denitrification could be identified in a literature review (Greene 2005), though a positive correlation between nitrification and denitrification has been reported for salt marshes (Thompson et al. 1995). In theory, if one source of NO_3 (water column versus sediment nitrification) is sufficiently larger than the other, denitrification rates may follow the same spatial pattern as the dominant NO_3 source, assuming NO_3 availability is an important control.

Nitrification, denitrification and O_2 availability

Though denitrification is an anaerobic process, the aerobic oxidation of NH_4 to NO_3 (nitrification) can be an important source of NO_3 for denitrifiers (Vanderborght and Billen 1975; Seitzinger et al. 1984; Kemp et al. 1990). In wetland sediments, where

strong redox boundaries are spatially compressed, nitrification occurring in aerated sediments and rhizospheres can supply NO_3 to denitrifiers in adjacent anoxic sediments via diffusion (Reddy et al. 1989). Oxygen is an important control on the coupled nitrification-denitrification process, and NO_3 for denitrification has been reported to come almost exclusively from nitrification when O_2 is available (indirect denitrification) and solely from overlying water when it is not (direct denitrification; Jenkins and Kemp 1984).

Results from this study suggest a key role for nitrification in supplying NO_3 to denitrifiers in Patuxent marshes. During most routine incubations, using ambient water column NO_3, less than half of the N_2 flux from the sediments could be attributed to the observed NO_3 flux from the overlying water into the sediments (Fig. 1-27), indicating the presence of an alternate NO_3 source. Conversely, during loading experiments (high water column NO_3), most or all of the N_2 fluxes could be attributed to NO_3 losses from the water column (Fig. 1-27). These relationships indicate that while direct denitrification may dominate when water column NO_3 concentrations are very high, coupled nitrification-denitrification is likely to be the dominant pathway for denitrification at normal to low NO_3 concentrations. A strong positive relationship for nitrification and denitrification has already been established for Chesapeake Bay subtidal sediments (Kemp et al. 1990), and it follows that a similar relationship may exist in tidal marsh sediments as well.

If sediment nitrification is the dominant source of NO_3 in Patuxent marshes, then O_2 is an important (positive) control (Jenkins and Kemp 1984; Kemp et al. 1990). Therefore, areas with less frequent inundation and more plant roots/rhizomes may foster

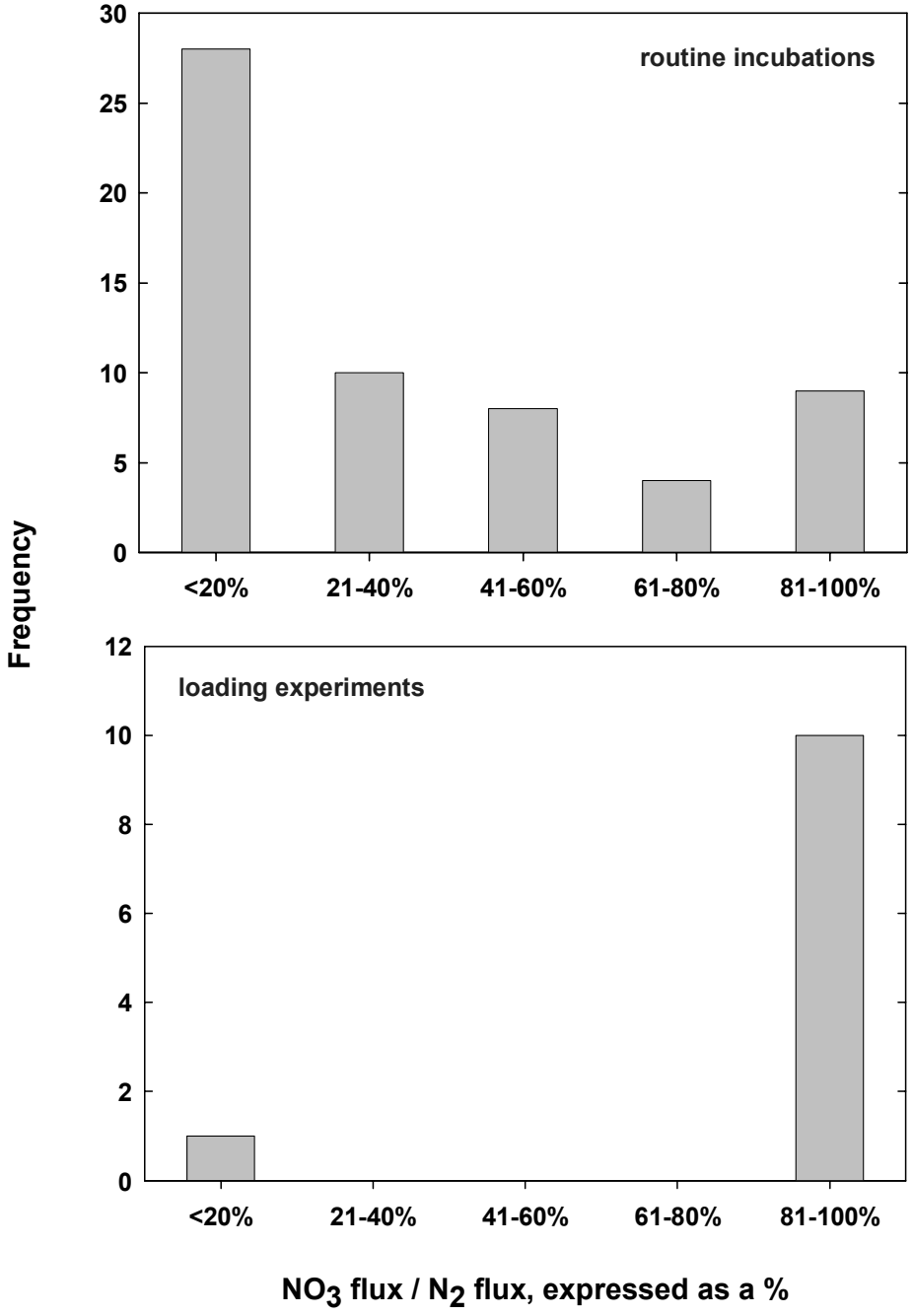


Figure 1-27. Frequency distribution of the percent of N_2 flux that could be attributed to the NO_3 flux from the water column in routine incubations and loading experiments.

more denitrification. Even though nitrification was not measured directly in this study, evidence presented here suggests that this process drives denitrification in Patuxent marshes, and controls on nitrification may therefore help to explain the observed spatial patterns in denitrification.

Temporal patterns in denitrification

The bimodal pattern in denitrification rates observed during this study suggests seasonal changes in controls. The first feature of the pattern – a general decrease in denitrification rates from April through June – is likely explained by water column NO_3 availability. The Patuxent river receives a large, terrestrially derived N pulse in late winter (Kemp and Boynton 1984; Boynton et al. 1998). Nitrate from this pulse may have supported high denitrification rates in the early spring, with rates decreasing in the following months as the riverine NO_3 supply decreased. Increasing competition for N from developing macrophyte and epiphyte communities may also have limited denitrification in the late spring/early summer (Simpson et al. 1983b).

Though the NO_3 loading experiments performed in this study were discussed initially as evidence for coupled nitrification-denitrification in Patuxent marshes, these experiments are perhaps more important as an indication that denitrification rates respond to changes in water column NO_3 concentration (i.e. availability of NO_3 limits denitrification rates; Fig. 1-25). Nitrate concentrations measured in the upper Patuxent decreased from April through the end of July in 2004 (Fig. 1-28). Given the evidence that denitrification in Patuxent marshes responds to changes in water column NO_3 concentrations, it is likely that the decreasing trend in marsh denitrification from early spring to mid summer was influenced by temporal patterns in Patuxent River NO_3

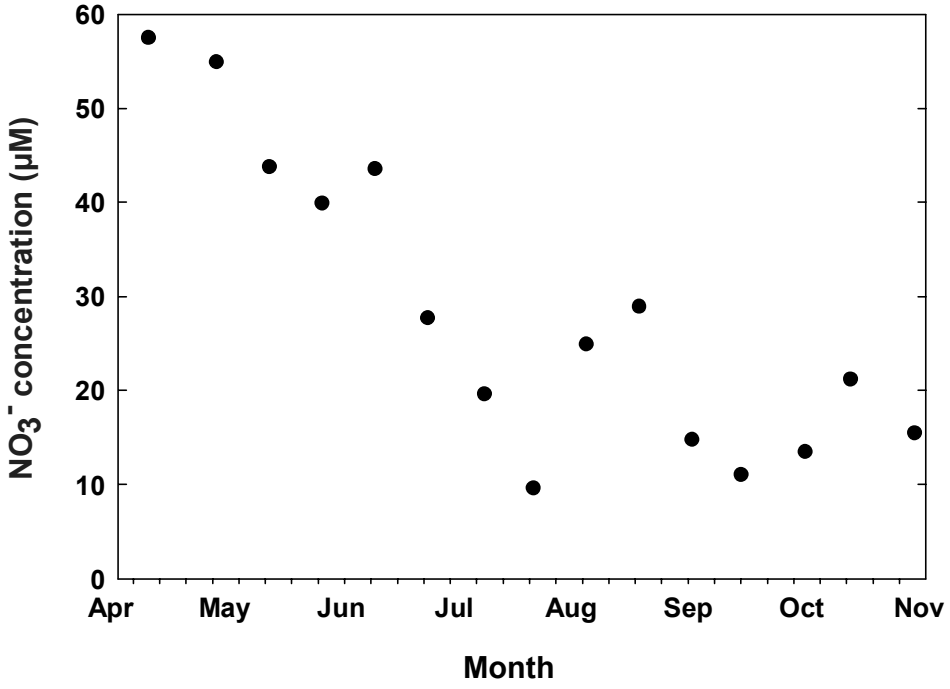


Figure 1-28. Nitrate concentrations in the Patuxent River water column at King's Landing, 2004.

concentrations. This indicates that direct denitrification may dominate during this portion of the year (Fig. 1-29a,b).

The second feature of the bimodal denitrification pattern was an increase in average denitrification rates in July. Since a corresponding increase in riverine NO_3 was not observed, this may indicate a shift from predominantly direct denitrification to more coupled nitrification-denitrification. Nutrients and organic matter from decomposition of early production could have supplied both organic substrate and NO_3 (after ammonification of organic N and subsequent nitrification) to support the observed mid-summer increase in denitrification rates (Kemp and Boynton 1984; Bowden 1986). The increased SOC observed in mid-summer in this study (Fig. 1-8b) supports this idea of augmented sediment metabolism and nutrient regeneration. After the secondary nutrient

pulse, the nutrient supply may again have been drawn down or other factors, such as decreasing temperature, may have contributed to the downward trend in denitrification rates from July through October (Fig. 1-29c,d). Though a plausible scenario, the above discussion is speculative and highlights the need for further investigations regarding sources of NO_3 for denitrification in Patuxent tidal marshes.

Previously-reported temporal patterns in Patuxent marsh denitrification

Merrill (1999) measured substantial denitrification in all marsh environments at Jug Bay in 1997. Measurements were made once during spring, summer and fall. In the spring, a spatial pattern similar to this study was found, and substantial denitrification rates were measured in all marsh environments (Table 1-5). Few data were available for the summer, and much lower rates (net N-fixation in fact) were measured in the fall (Table 1-5). To some extent, Merrill's findings appear contrary to those in this study, as substantial denitrification was observed in all environments during all months of this study. However, sampling frequency was much higher in this study (monthly, versus seasonal). Examining data from single field trips in spring, summer and fall during this study leads to the conclusion that denitrification is higher in spring than in summer and fall, much as Merrill (1999) described it.

Table 1-5. Summary of average N_2 fluxes (plus or minus standard error) measured by Merrill (1999) at Jug Bay in 1997. Fluxes are given as μmoles N m^{-2} h^{-1}. Non-interpretable data (NI), may indicate near-zero fluxes. "ND" indicates that no data were available.

	Spring	Summer	Fall
Marsh creek	-28.4	NI	ND
Low marsh	23.6 ± 17.7	33.3 ± 14.6	-8.86 ± 41.8
Mid marsh	30.8 ± 7.64	NI	-27.4 ± 15.1
High marsh	59.2 ± 23.4	NI	-22.7 ± 12.3

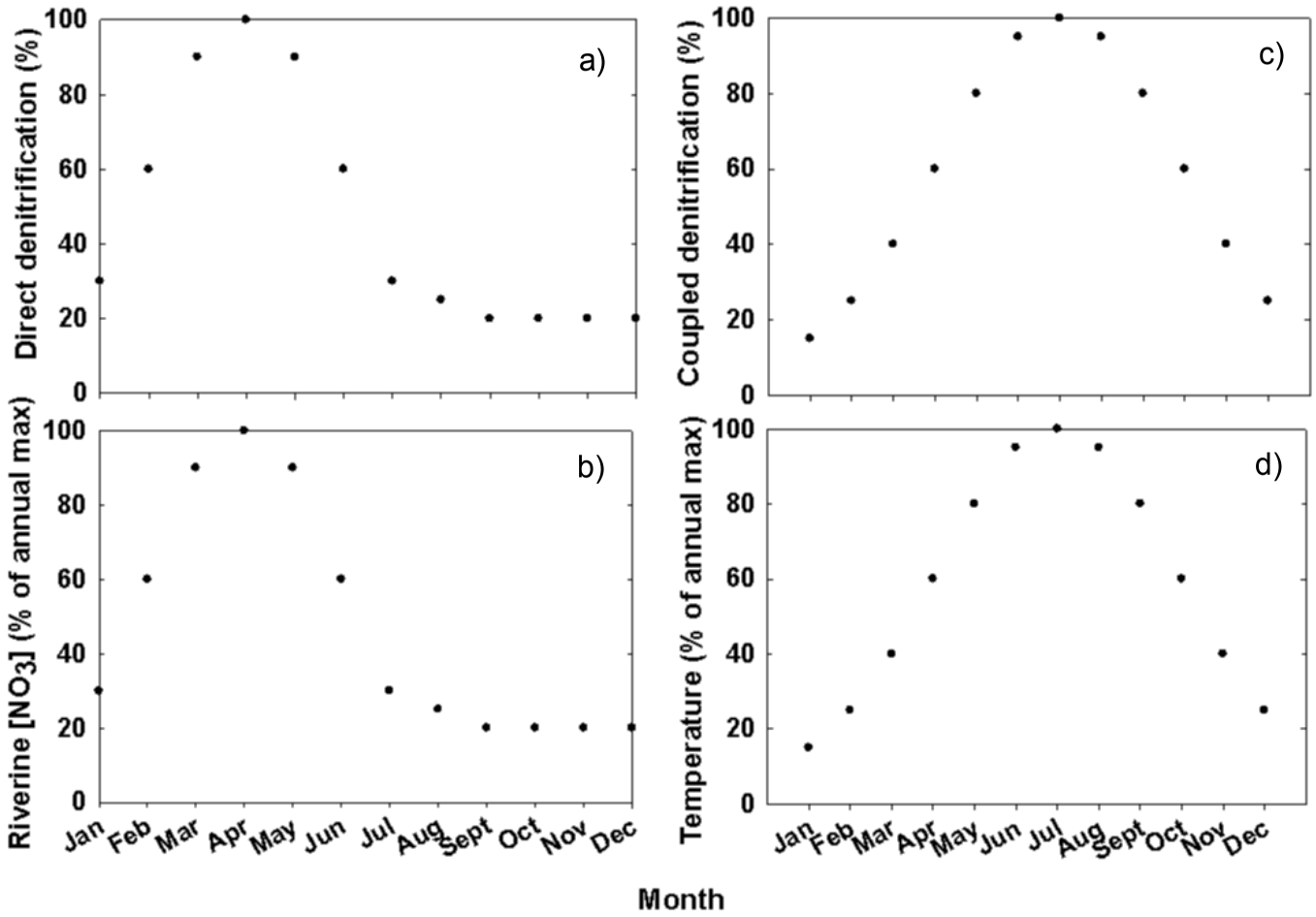


Figure 1-29. Conceptual model for environmental controls on denitrification in Patuxent marshes. Direct denitrification may be controlled by riverine NO_3 concentration (a,b), which declines from late spring to mid summer. After mid summer, coupled nitrification-denitrificationmay become dominant, and necessary metabolic processes may be more strongly controlled by temperature (c,d). The shift from direct, NO_3-controlled denitrification to coupled, temperature-controlled denitrification could produce the observed bimodal temporal pattern in denitrification rates.

Kinetics of denitrification

Spatial patterns in Patuxent marsh denitrification appear to correlate strongly with frequency of tidal inundation (negative correlation; Fig. 1-26) and to show some positive relationship with C and N availability (Chapter 2**;** further investigation would be useful), while temporal patterns correlate (positively) with NO_3 availability (Fig. 1-24). Results from NO_3 loading experiments provided more detailed information about the relationship between denitrification rates and water column NO_3 availability.

When the Michaelis-Menton equation is used to describe enzyme kinetics at the molecular level, the substrate concentration at which the reaction rate is half maximal (K_m) is an inverse indicator of enzyme affinity for that substrate. By analogy, the K_m for NO_3 being denitrified by marsh bacteria, measured at the community scale, should indicate the affinity of that community for NO_3. An important distinction between such an analysis and molecular level enzyme kinetics is that when measuring denitrification rates in sediments, the reaction rate is plotted against the substrate concentration in the overlying water rather than in the immediate vicinity of the enzymes. Therefore, the K_m generated by such analyses is an indicator of more than denitrifier affinity for NO_3; the K_m is also an indicator of physical parameters like sediment porosity and chemical parameters such as the sediment-water NO_3 gradient, all of which influence local NO_3 concentration where denitrification occurs. Thus, the K_m represents the environmental affinity for NO_3, rather than simple enzyme affinity.

The response curve generated by NO_3 loading experiments in this study follows the classic Michaelis-Menten pattern, except that it does not pass through the origin (Fig. 1-25). Because water column NO_3 concentration is not necessarily reflective of sediment

NO_3, substantial denitrification can be observed when there is basically no NO_3 in the water column. This indicates the presence of an alternative NO_3 source, likely nitrification. Since denitrification rates near 50 μmoles m^{-2} h^{-1} were observed in both loading experiments when water column NO_3 concentrations were near zero, any discussion of kinetics must be qualified as pertaining only to *direct* denitrification from water column NO_3, where:

Direct denitrification = [Total denitrification – 50 (Coupled denitrification)].

Fitting an average response curve of direct denitrification rates from this study to the Michaelis-Menten equation yields a V_{max} of 238 μmoles N m^{-2} h^{-1} and a K_m of 93 μM NO_3 (Fig. 1-30). Whether the K_m is "high" or "low" is in some sense a relative matter, as different environments experience different ranges of ambient NO_3. Nitrate concentrations of 93 μM are at the mid to high end of the range of concentrations commonly reported for the upper Patuxent (Swarth and Peters 1993; Boynton et al. 1998), and if strictly interpreted, this K_m indicates a moderate to low affinity of marsh denitrifiers for NO_3.

Though a useful index, the K_m should be interpreted with caution since sediment nitrification appears to be important in Patuxent marshes, and since substrate (NO_3) concentrations were measured in the water column rather than in the immediate vicinity of enzymes. The amount of NO_3 actually available to denitrifiers may be more or less than what is in the water column, depending on diffusive NO_3 fluxes to the sediment and existing sediment NO_3 pools, which may vary in size. Also, even though denitrification rates measured in loading experiments were higher than rates measured for the same cores at *in situ* NO_3 concentrations, the highest of all denitrification rates observed in this

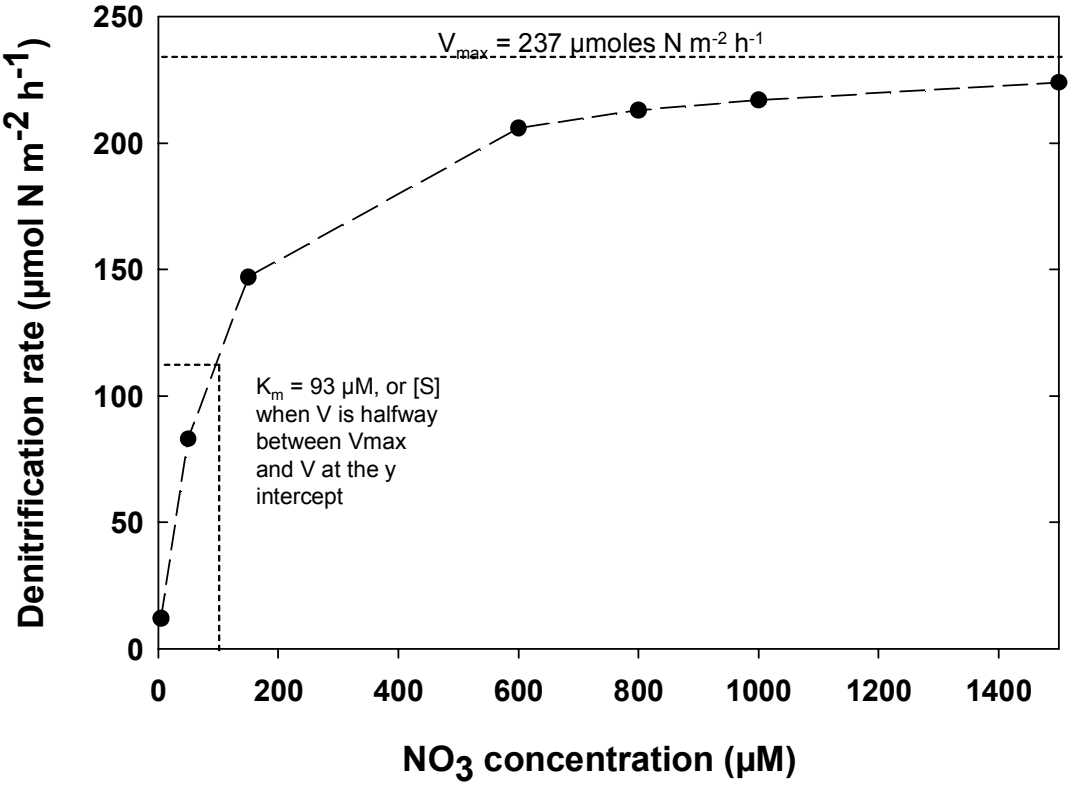


Figure 1-30. V_{max} and K_m values for direct denitrification in Patuxent marshes, suggested by response curves from loading experiments. "V" refers to denitrification rate and "V_{max}" indicates maximum predicted denitrification rate. K_m refers to the substrate (NO_3) concentration at which $V=1/2(V_{max})$.

study were generated by cores from routine incubations, at ambient NO_3 concentrations. A possible explanation is that denitrification measured during routine incubations may have occurred at the expense of sediment N pools, so loading experiments performed on fresh cores rather than on cores used in prior incubations might have yielded a higher V_{max} or different K_m. Finally, a longer equilibration period prior to incubation would allow for more diffusion of water column NO_3 amendments to the sediment. Despite limitations, the response curves generated in this study provide information regarding controls on denitrification in Patuxent marshes and the response of denitrification rates to changing levels of NO_3 in the environment.

Role of N-fixation

From the standpoint of the N economy of an estuary, N-fixation is the converse of denitrification, bringing atmospheric N_2 directly into the system for use by primary producers. To a degree, the techniques used in this study to measure denitrification already account for N-fixation in that the *net* N_2 flux between sediments and water column was measured, rather than denitrification alone. Dinitrogen fluxes measured in this study were overwhelmingly large and directed *into* the sediments. This is an indication that denitrification rates far exceed those of N-fixation in Patuxent marshes, at least in the dark. Results from dark incubations like those conducted in this study should be interpreted with some caution, however, as Currin et al. (1996) reported daytime maxima for N-fixation in a salt marsh, with almost undetectable rates at night, particularly in the spring (Currin and Paerl 1998). In addition, Kaplan et al. (1979) reported that N-fixation rates in a New England salt marsh were lower than, but of the same order of magnitude as, denitrification rates. Ultimately, a thorough investigation of tidal freshwater marsh N-fixation is needed to interpret measured N_2 fluxes, since rates reported for salt marsh N-fixation are often within one order of magnitude of typical denitrification rates (Teal et al. 1979; Wolfenden and Jones 1987; Tyler et al. 2003). It is also important to consider N-fixation when interpreting spatial and temporal patterns in marsh denitrification, as the size of the net N_2 flux from sediments can increase due to increased denitrification *or* due to decreased N-fixation, and fixation likely varies in space and time as well.

Other potential indicators of a marsh N sink

Data from this study indicate that Patuxent River tidal marshes are N sinks due to consistent, ubiquitous denitrification in marsh surface sediments and marsh creeks. Even without measuring denitrification, there is evidence that marshes remove N from tidal waters. Swarth and Peters (1993) reported consistently higher NO_3 concentrations in water flooding Jug Bay marshes than in water draining the marshes. In the South Marsh region of Jug Bay, NO_3 concentrations were reduced from 30 μM on average at high tide to 10 μM at low tide in the summer, and from 100 μM to 40 μM in winter. Nitrate concentrations in the North Marsh (slightly upstream) were reduced from 120 μM at high tide to <10 μM at low tide in the summer, and from 120 μM to ~15 μM in winter (Fig. 1-31). Simpson and Whigham (1977) reported a similar pattern in a tidal freshwater marsh in New Jersey, attributing at least some of the reductions in NO_3 concentration to plant uptake. This may be the dominant NO_3 removal mechanism during the growing season, but microbial processes (i.e. denitrification) are likely to be important as well, especially in winter and fall when plant uptake ceases. Substantial denitrification rates (~200 μmoles N m^{-2} h^{-1}) have been reported for sediments at low temperatures (0 - 6°C; Koch et al. 1992; Dong et al. 2000).

A final indication that Patuxent marshes remove and/or store N, at least temporarily, is that the ratio of O_2 uptake to NH_4 release by sediments in this study was generally far greater than the value expected when decomposition adheres to Redfield proportions (Redfield 1934). Sediment oxygen consumption is an indicator of decomposition rates, and Redfieldian decomposition of phytoplankton would yield O_2:NH_4 flux ratios near 13, with values greater than 13 suggesting an alternative fate for

N. In this study, O_2:NH_4 flux ratios ranged from 25 to 150, with few exceptions (Fig. 1-32), which suggests that remineralized N is stored or denitrified within the marsh.

Rethinking the "source vs. sink" debate

The discussion of removal of NO_3 from tidal waters by marshes evokes the great debate as to whether tidal marshes are net exporters or importers of material and energy to/from estuaries (e.g. Teal 1962; Nixon and Oviatt 1973; Stevenson et al. 1977; Nixon 1980). When system boundaries are drawn at the high tide line, this question is of great importance. Certainly, if a marsh fosters more production than a marshless stretch of estuary of the same area, it can provide material and energetic subsidies to the adjacent estuary. From a broader perspective though, it makes more sense to view tidal marshes as embedded in a watershed landscape where the marshes are a transition environment, receiving and transforming materials as they move from the surrounding land to the estuary. From this standpoint, it is somewhat irrelevant whether marshes export N to an estuary, as terrigenous N would be entering the estuary in even larger quantities without marshes present. Marshes in which more N is denitrified and buried than is fixed or eroded are net removers of N from the *system*, regardless of the direction of N flux between the marsh and estuary, and this is really the relevant question given the large anthropogenic influence on the global N cycle.

Conclusions

1. All Patuxent marsh environments (high marsh, mid marsh, low marsh and marsh creeks) denitrify at substantial rates, at least during 7 months of the year (April – October). Denitrification rates do not appear to differ significantly between tidal fresh and oligohaline Patuxent marshes.

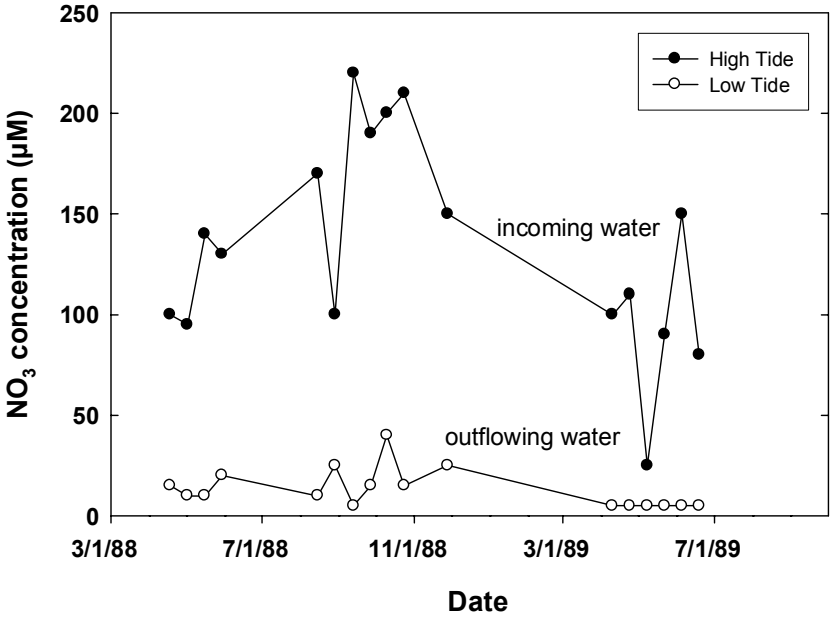


Figure 1-31. Example from the Jug Bay north marsh of lower NO_3 concentrations in tidal waters draining versus flooding the marsh (data from Swarth and Peters 1993).

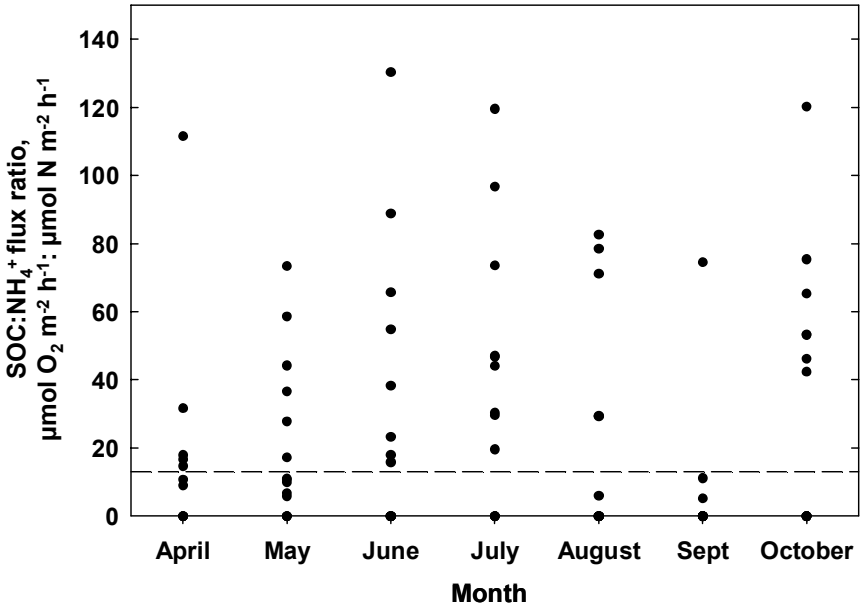


Figure 1-32. Sediment SOC:NH_4 flux ratios for Patuxent marshes. Values greater than 13 (dashed line) indicate removal or storage of N, relative to decomposition of Redfield-like organic matter. Four outliers (SOC:NH_4 > 300) were removed. Dashed line indicates stoichiometric balance (SOC:NH_4 = 13).

2. Nitrification appears to be an important, if not dominant, source of NO_3 for denitrification in Patuxent marshes (Fig. 1-27), despite the sometimes high NO_3 concentrations in waters flooding marshes.
3. Spatially, denitrification rates tend to be highest in the high marsh and decrease with distance from land. Frequency of tidal inundation (i.e. O_2 availability for nitrification) and distributions of total sediment C and N (i.e. substrate availability; Chapter 2) appear to influence this spatial pattern.
4. Denitrification rates were highest in April, declined throughout the spring, then increased in mid-summer and decreased again through the fall. This pattern may be due to a shift from direct denitrification based on allochthonous N to coupled nitrification-denitrification from N regenerated in sediments during the summer.
5. Though the water column was not necessarily the dominant source of NO_3, changes in water column NO_3 concentration elicited a substantial response in denitrification rates under experimental conditions.

CHAPTER 2:
LONG-TERM BURIAL OF NUTRIENTS IN TIDAL MARSH SEDIMENTS

INTRODUCTION

Recognition of the Patuxent River as a nutrient-overenriched system has fostered interest in managing nutrient inputs and in mechanisms, both natural and man-made, for nutrient removal (D'Elia et al. 2003). Permanent burial of particulate nutrients in river bottom sediments is a well-recognized sink in sediment-rich estuaries such as the Chesapeake Bay and its tributary rivers (Magnien et al. 1992; Boynton et al. 1995). Since recognition of the importance of subtidal nutrient burial in the Chesapeake, more attention has focused on tidal marshes as environments that may also bury substantial quantities of nutrients (Khan and Brush 1994; Merrill 1999).

Long-term burial is one of the two major internal removal mechanisms for nutrients in estuaries (the other mechanism is denitrification, which only removes N). Nutrients taken up by plants and some heterotrophs are removed on a seasonal basis, but these can be remineralized and recycled to the water column (Odum 1988; Cowan and Boynton 1996). Nitrogen and phosphorus can also be removed from the estuary in fisheries harvests and outmigration of anadromous fish (Deegan 1993), however fisheries harvests appear to account for removal of less than 10% of N inputs and less than 5% of P inputs to the Chesapeake Bay (Boynton et al. 1995). Also, nutrient losses due to outmigration of anadromous fishes may be balanced in some estuaries by nutrient inputs from inmigrating fish (Moore and Schindler 2004). Burial is by far the largest

internal sink for P and one of two major sinks for N in the Chesapeake system (Boynton et al. 1995).

Patuxent River tidal fresh and oligohaline marshes are poised particularly well to accumulate sediment and nutrients. They are the first recipients of the high "head of estuary" nutrient and sediment loads that constitute an important fraction of the load to the estuary, and thus exhibit higher accretion rates than down-estuary marshes (Brush 1984; Kearney and Ward 1986; Odum 1988; Magnien et al. 1992; Ward et al. 1998). Close to 50% of P inputs to the Patuxent are in particulate form, while N inputs are mainly dissolved and must be converted to the particulate form if burial is to occur (Magnien et al. 1992). Most particulate P enters the river as inorganic PO_4 adsorbed to iron oxide compounds, and is directly available for burial. Phosphorus is also buried due to formation of authigenic P-containing minerals (Sundby et al. 1992). The primary burial mechanism for N is incorporation in organic matter, and subsequent burial of the organic matter. High levels of primary productivity in tidal fresh marshes result in the rapid conversion of dissolved N to particulate organic forms that are available for burial at the end of the growing season.

An important caveat to the above discussion is that in order for permanent burial to occur, marshes must remain in a state of net accretion. Tidal marsh accretion is not keeping pace with sea level rise in all Chesapeake environments (Stevenson et al. 1986). Some tidal marshes on the eastern shore of the Chesapeake Bay appear to be submerging (Ward et al. 1998), while many tributary marshes (e.g. Patuxent and Choptank Rivers) appear to be accreting at sufficient rates to maintain elevation with respect to sea level (Flemer et al. 1970; Khan and Brush 1994; J. Cornwell pers. comm.). Marsh status with

respect to accretion/erosion is a pivotal factor determining nutrient burial in these environments.

Patuxent nutrient burial studies

Rates of sediment accretion and burial of N and P have been reported for Jug Bay, a tidal freshwater marsh in the upper Patuxent (Khan and Brush 1994; Table 2-1).

Table 2-1. Sediment accretion and nutrient burial rates measured in marshes at Jug Bay (tidal fresh) and King's Landing (oligohaline) during previous studies and in this study. Accretion rates are given in kg m^{-2} yr^{-1}; burial rates are given in g m^{-2} yr^{-1}.

			Jug Bay[a]	Jug Bay[b]	King's Landing[b]	King's Landing[c]
Accretion		High marsh	2.6	1.6	0.3	1.3
		Mid marsh	ND	ND	0.3	3.6
		Low marsh	3.1	5.2	3.4	5.9
Burial	N					
		High marsh	16.0 - 25.0	19.0	5.1	12.0
		Mid marsh	ND	ND	4.0	17.3
		Low marsh	9.0	22.0	31.4	32.5
	P					
		High marsh	1.1 - 2.2	1.2	0.2	1.3
		Mid marsh	ND	ND	0.3	4.8
		Low marsh	0.7	13.0	3.7	5.9

[a] Data are from Khan and Brush 1994. Accretion rates are mean values from rates derived from pollen analyses, reported for cm depth increments dated 1900 – present. Burial rates are mean values reported for the same depth increments. Burial rates are reported as ranges for the high marsh, as rates were reported to have increased substantially over the past century in this environment. Rates in the low marsh were more constant.
[b] Data are from Merrill 1999. Accretion rates were estimated via ^{210}Pb analysis.
[C] Data from this study.

Merrill (1999) also reported burial rates for King's Landing. However, accretion and burial rates for different marsh environments were based on single cores in both of the previous studies (Table 2-1). Both previous studies reported higher sediment N concentrations in the high marsh than in the low marsh, and both reported higher mass-based accretion rates for low marsh environments. These trends have also been reported by other investigators studying tidal marshes (e.g. DeLaune et al. 1981; Bricker-Urso et

al. 1989; Orson et al. 1990; Craft and Richardson 1993; Ward et al. 1998). However, while Merrill (1999) reported more burial of N and P in the low marsh, Khan and Brush (1994) calculated higher burial rates for the high marsh, citing slower decomposition and less tidal flushing of high marsh plant litter as reasons.

Burial studies such as these can provide data for estimation of the size of a system-wide nutrient sink based on relatively few measurements. Accretion rates and nutrient concentrations measured in representative sediment cores provide the data needed to calculate burial rates, and these data can be extrapolated over the entire marsh surface to estimate the size of the marsh nutrient burial sink. However, given that differences have been reported in accretion rates and sediment nutrient content between high and low marsh environments (e.g. Bricker-Urso et al. 1989; Khan and Brush 1994), additional attention to spatial patterns in these factors is needed, especially if efforts to extrapolate burial rates of N and P to whole-system spatial scales are to be made.

Dating sediments and estimating accretion

To estimate the integrated burial of nutrients by marshes, the spatial distribution of sediment accretion rates must be known. Accretion measurements have been made with a variety of techniques, all of which involve assumptions. The first accretion measurements were made by placing a visually distinctive material on the marsh surface (e.g. brick dust), above which the accumulation of sediment was measured after some number of years (e.g. Steers 1948; Stoddart et al. 1989; Wood et al. 1989). However, these estimates are subject to error due to artifactual deposition and marker washout.

The development of the ^{210}Pb isotopic dating technique introduced a new level of accuracy to the field (Krishnaswamy et al. 1971; Koide et al. 1972; Armentano and

Woodwell 1975). Lead-210 (^{210}Pb) forms in the atmosphere from the radioactive decay of ^{222}Rn, which is produced in the earth's crust. If atmospheric creation and deposition of ^{210}Pb are assumed to occur at a constant rate, the decay of ^{210}Pb in sediments (via detection of buildup of the daughter ^{210}Po) can be used to calculate sediment age at known depths and thus accretion rates (Koide et al. 1972). In the upper Patuxent, where marsh sediments have accreted largely in the past few centuries, ^{210}Pb dating is an especially appropriate technique because of its 22.3 year half-life (Brush 1984; Krishnaswamy and Lal 1978; Cornwell et al. 1996). This technique was used in both the study by Merrill (1999) and in this study to estimate accretion rates in Patuxent marshes during the past 100 years.

Other isotopes and techniques have also been used to measure sediment accretion rates, including dating with artificial radionuclides, carbon-14 (^{14}C) dating and pollen dating. Radionuclides such as ^{137}Cs were produced in the atmosphere by nuclear weapons testing in the late 1950's and early 1960's (Krishnaswami and Lal 1978), and have been used to estimate sediment accretion in salt and tidal fresh marshes (e.g. DeLaune et al. 1989; Newbauer et al. 2001), however these techniques are only useful for dating sediments that have accreted since the genesis of the nuclide (generally 50 years). Khan and Brush (1994) based their accretion rate estimates at Jug Bay on ^{14}C and pollen analyses. Carbon-14 (useful for dating on relatively long time scales due to its 5700 year half-life) was used to date the deeper sediments of cores, and pollen analysis was used to obtain dates for shallower horizons. In pollen analysis, dates are assigned to sediments at the depth of appearance or disappearance of specific pollens with known dates of introduction to or removal from a location. For example, the shallowest

sediments in which chestnut pollen is absent would be dated 1930, the approximate date of demise of the American chestnut (Brush 1989). The fact that methods other than ^{210}Pb dating have been used to estimate accretion in Patuxent marshes makes rate comparisons at once useful and difficult. There is utility in measuring processes with more than one technique, as all techniques have inherent problems, however data obtained with different techniques should be compared with caution for the same reason.

Objectives

Marsh burial of particulate N and P may be a quantitatively important sink for anthropogenic nutrients (Merrill and Cornwell 2000). In each of the marshes where denitrification was measured during this study (Chapter 1), a single previous burial study laid the groundwork suggesting that these tidal marshes are indeed important sinks for nutrients in the Patuxent system (Khan and Brush 1994, Jug Bay; Merrill 1999, King's Landing). However, there was no replication of measurements in either study, and conclusions regarding spatial patterns of nutrient burial were not the same in both cases. The objectives of this study, then, are to add to the dataset for oligohaline nutrient burial, to further understanding of spatial patterns in burial within marshes, and to synthesize the existing data on nutrient burial in Patuxent marshes so that conclusions may be drawn about the size of this internal nutrient sink at the spatial scale of the estuary. To that end, the following questions were addressed in this research effort:

1. What is the N, P and C content of high, mid and low marsh sediments in oligohaline marshes of the Patuxent River estuary?
2. At what rate are high, mid and low marsh sediments accreting?
3. What are the burial rates for N and P in oligohaline marsh sediments?

4. What spatial patterns exist in sediment nutrient content, C:N ratio and accretion and burial rates with proximity to the river channel, and how do these compare to previously reported patterns?

METHODS

Overview and method theory

Sediments for nutrient burial studies were obtained from King's Landing marsh on the Patuxent River (described in Chapter 1). Particulate N, P and C burial rates were estimated from percent N, P and C and accretion rate data for duplicate, 0.5 m sediment cores taken from low, mid and high marsh areas of King's Landing. Two 1.0 m "deep" cores were also collected for the purpose of determining *in situ* evolution of ^{210}Pb. Cores for burial studies were collected near the coring sites used for denitrification studies (Chapter 1). Concentrations of N, P and C were measured using standard analytical methods (Keefe et al. 2004), and accretion rates were estimated from ^{210}Pb radioisotope distributions with depth in sediment cores (Flynn 1968; Koide et al. 1972). Carbon concentrations were used primarily to evaluate sediment organic matter content and C:N ratios. Nitrogen, P and C concentrations (mg N, P or C g^{-1} sediment) were multiplied by accretion rates (kg m^{-2} yr^{-1}) to yield burial estimates for these elements (g N, P or C m^{-2} yr^{-1}).

To estimate accretion rates, sediments at specific depths were aged based on the radioactive decay of ^{210}Pb. The original parent of ^{210}Pb is ^{238}U. Uranium-238, through five intermediates, decays to ^{226}Ra in the earth's crust. Radium-226 decays to gaseous ^{222}Rn (half-life 3.8 days) which diffuses to the atmosphere and decays to ^{210}Pb. There is also some *in situ* decay of ^{222}Rn in the ground, which contributes a relatively constant background supply of ^{210}Pb, termed "supported ^{210}Pb."

Atmospheric ^{210}Pb binds to particles and returns to the earth's surface via both wet and dry deposition. Atmospherically-derived ^{210}Pb is termed "unsupported ^{210}Pb,"

which is the ^{210}Pb of interest for determining sediment age. Due to atmospheric deposition, ^{210}Pb is ubiquitous in soils and sediments, where it decays to ^{210}Po. For practical reasons, alpha-particle emitting isotopes like ^{210}Po are more easily measured than beta-emitting isotopes (like ^{210}Pb), so accumulation of ^{210}Po is used as a proxy for decay of ^{210}Pb. The half-life of ^{210}Pb is 22.3 years, and it takes 7 half-lives (~150 years) for the ^{210}Pb in a sample to reach near-zero activity. Thus, ^{210}Pb (^{210}Po) analyses are useful for aging sediments on a scale of ~100 years.

For cores in which the decrease in ^{210}Pb activity is log-linear with depth, a constant initial activity (also known as Constant Initial Concentration, or CIC) model can be used to calculate accretion rate (Robbins 1978). Use of this model requires the assumption of constant ^{222}Rn release to the atmosphere, constant ^{210}Pb deposition from the atmosphere, little or no bioturbation of sediments and a constant supply of particles to the estuary (Bricker-Urso et al. 1989). This final assumption is somewhat tenuous, as it has been shown that most of the sediment in the Chesapeake Bay is supplied during isolated storm events (Schubel and Hirschberg 1978), and increased sedimentation rates associated with storms have also been reported for Patuxent marshes (Khan and Brush 1994). To account for non-uniform ^{210}Pb inputs, sedimentation rates can be calculated for individual depths in a core using the Constant Rate of Supply (CRS) model (Oldfield and Appleby 1984). However, use of this model requires analysis of large numbers of core sections, which was beyond the scope of this study. Though the assumptions of the CIC model can prove problematic in attempts to precisely age sediments at fine scales, they were not unreasonable for use in this study since integrated, long-term burial

estimates were the goal. Bricker-Urso et al. (1989) reported no significant difference between accretion rates calculated by both models for cores from a tidal salt marsh.

Using the CIC model, the natural log of unsupported ^{210}Pb activity was regressed on mean cumulative mass to generate sediment accretion rates in terms of annual mass burial (g cm^{-2} yr^{-1}). Mass-based accretion rates (g cm^{-3}) for each core were divided by the average bulk density in a core to yield depth-based accretion rates (cm yr^{-1}). Regressions yielding r^2 values >0.65 ($P<0.05$) were considered significant, and the slope was then be used to determine accretion rate.

Field and laboratory techniques

To obtain sediment for aging and particulate nutrient analysis, samples were collected with a McAuley corer and cores were sectioned as follows: 2.5 cm increments to 0.2 m, 5 cm increments to 0.5 m, and 10 cm increments to 1 m. Sections were transported in capped 60 mL centrifuge tubes to the laboratory where they were weighed and then dried at 60-80^{o}C. Dry sediments were then weighed again to assure dryness and obtain a measure of dry weight, and then homogenized with a mortar and pestle. Sediment bulk density was calculated as dry sediment weight per volume, with volume determined by water displacement before samples were dried. Approximately one gram of dried, homogenized sediment was taken from selected depth increments for aging and one gram for particulate C, N and P analyses.

Selected core sections were analyzed for total C and N with an automated elemental analyzer (Exeter Analytical, Inc. CE-440 elemental analyzer; Keefe et al. 2004). Briefly, weighed sediment samples were combusted in pure O_2 to achieve a homogenous gas mixture, and differences in detector signals for N_2 and CO_2 before and

after exposure to the gas mixture were used to determine the concentrations of N and C, respectively, in the original sample. Sediments for particulate P analysis were heated in a muffled furnace at 500 ^{o}C and then particulate P was extracted from sediments in acid (Keefe et al. 2004). Liquid-phase P was quantified colorimetrically with an autoanalyzer (Technicon AutoAnalyzer II).

Selected core sections were also aged based on ^{210}Pb radioisotopes as described by Flynn (1968). Each 1.0 g sample was dosed with 1 mL of ^{209}Po as a yield tracer. Nitric (HNO_3) and hydrochloric (HCl) acids were added (10 mL each) to digest organic materials and to strip ^{210}Po from the sediments. Suspended ^{209}Po and ^{210}Po were removed from the solution by centrifugation, and the liquid supernatant was then dried overnight. Next, HCl was added and the sample evaporated to dryness twice in order to remove excess HNO_3. Finally, ^{209}Po and ^{210}Po were put back into solution with 0.1N HCl and ascorbic acid was added to prevent iron precipitation. A silver plate (17 mm x 17 mm, back side coated with paint) was added face-up to each Po solution. Beakers were heated overnight at 70^{o}C and then plates were removed and rinsed with deionized water. Activity of plated ^{209,210}Po was counted on a four channel alpha spectrometer (Tennelec TC-256).

Polonium-210 activity in decays per minute was plotted against depth and supported ^{210}Po activity was determined from the asymptote. Sediment accretion rates were estimated by regressing the natural log of unsupported ^{210}Po activity against depth and against cumulative sediment mass with depth. Accretion rates were multiplied by depth-averaged particulate N and P concentrations to yield nutrient burial estimates.

RESULTS

Accretion rates

Sediment bulk densities increased with depth in low and mid marsh cores, and from upper half-meter cores to "deep" cores (Table 2-2). Bulk densities in upper half-meter cores were similar to values previously reported for 0 to 50 cm depths. Higher bulk densities at depths >50 cm were likely due to compaction (DeLaune et al. 1981; Kearney et al. 1994). High marsh cores generally exhibited lower bulk densities, without significant depth-related changes.

Lead-210 activity decayed exponentially with depth in all cores except for one mid marsh core, which displayed almost no change with depth (Fig. 2-1). Some mixing of sediments appears to have occurred in the top 5 centimeters, but all regressions of activity on depth yielded significant slopes ($P<0.05$). Sediment accretion rates ranged from 4.0 to 17.14 mm y^{-1} (based on ^{210}Pb activity with depth), or 1.16 to 7.99 kg m^{-2} y^{-1} (based on ^{210}Pb activity with cumulative mass) (Table 2-3). These rates are similar to rates previously reported for Patuxent marshes (Khan and Brush 1994; Merrill 1999; Table 2-1). Accretion rates appear to increase with proximity to the river, with highest rates in the low marsh.

Vertical N, C and P profiles

Sediment particulate N concentrations ranged from 3.1 to 10.9 mg N g^{-1} (mean 6.4 mg N g^{-1}) in upper half-meter cores, and from 1.7 to 4.2 mg N g^{-1} (mean = 3.0 mg N g^{-1}) in deep cores. Concentrations in upper cores were significantly higher than deep core concentrations (one-tail t-test, $P<0.05$). There were changes in N concentration with both depth and distance from the river. In low and mid marsh cores, N concentration was

Table 2-2. Average bulk density for 10 cm depth intervals in cores from different marsh environments at King's Landing, an oligohaline Patuxent marsh. Mean bulk density for each marsh environment is given with standard error in parentheses.

Depth (cm)	Bulk density (g cc^{-1})		Mean bulk density (g cc^{-1})
	High marsh A	High marsh B	
0-10	0.30	0.27	
10-20	0.30	0.22	
20-30	0.28	0.25	
30-40	0.29	0.32	
40-50	0.28	0.20	
mean	0.29	0.25	0.27 (0.01)
	Mid marsh A	Mid marsh B	
0-10	0.41	0.35	
10-20	0.44	0.51	
20-30	0.43	0.49	
30-40	0.35	0.47	
40-50	0.40	0.54	
mean	0.41	0.47	0.44 (0.02)
	Low marsh A	Low marsh B	
0-10	0.22	0.30	
10-20	0.24	0.33	
20-30	0.34	0.41	
30-40	0.35	0.42	
40-50	0.33	0.40	
mean	0.29	0.37	0.33 (0.02)
	Deep core A	Deep core B	
50-60	0.64	0.48	
60-70	0.67	0.33	
70-80	0.78	0.49	
80-90	0.78	0.54	
90-100	0.61	0.49	
mean	0.69	0.47	0.58 (0.04)

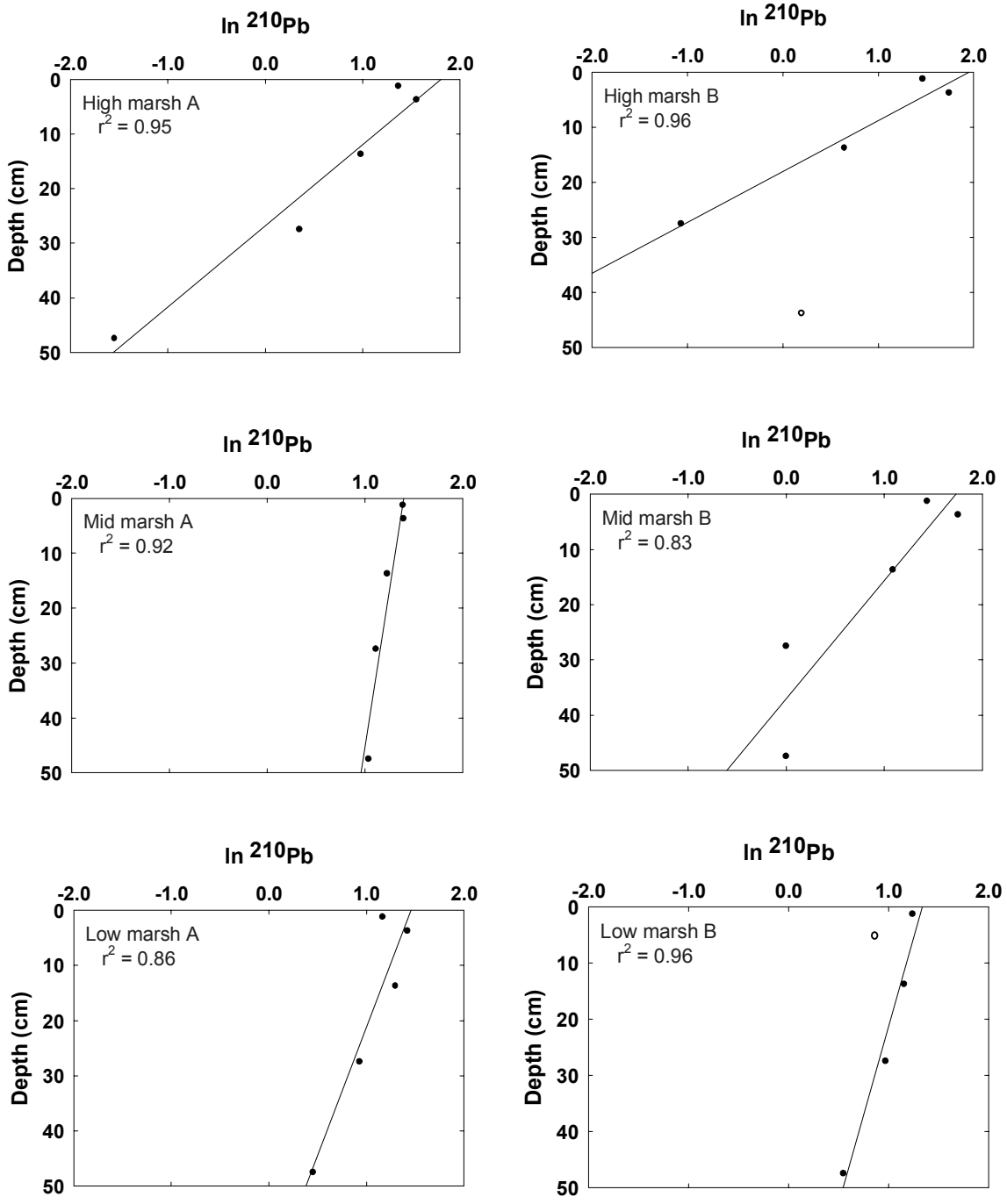


Figure 2-1. Exponential decrease of ^{210}Pb with depth in 0.5 m cores. Open symbols indicate data not included in regressions.

Table 2-3. Depth averaged concentrations, sediment accretion rates and burial rates for N, P and C in high, mid and low marsh environments in the King's Landing (oligohaline) marsh.

Location	N, P & C concentration (mg N, P or C g^{-1} sediment)			Accretion rate ($kg\ m^{-2}\ y^{-1}$)	($mm\ y^{-1}$)	Burial rate ($g\ N, P\ or\ C\ m^{-2}\ y^{-1}$)		
	N	P	C			N	P	C
High marsh A	8.54	0.92	124.26	1.16	4.00	9.94	1.07	144.63
High marsh B	9.21	0.97	137.54	1.52	4.11	13.97	1.47	208.46
Mid marsh A	--	--	--	--	--	--	--	--
Mid marsh B	4.80	1.34	63.71	3.60	7.66	17.30	4.82	229.61
Low marsh A	6.21	1.03	98.29	3.89	5.61	24.19	4.01	382.56
Low marsh B	5.10	0.98	71.37	7.99	17.14	40.77	7.86	570.60

similar and decreased with depth initially, with more stable profiles below 20cm (Fig. 2-2). Nitrogen concentrations were significantly higher in the high marsh (t-test, $P<0.05$). Nitrogen profiles tended to show increasing concentration with depth in the high marsh, and decreasing concentration with depth in mid and low marsh cores (Fig. 2-2).

Phosphorus concentrations in upper 0.5 m cores ranged from 0.5 to 3.0 mg P g^{-1} (Fig. 2-3). Mean concentrations were highest in the mid marsh and similar in low and high marsh sediments (Fig. 2-3). Differences could not be tested for statistical significance due to low sample numbers. Decreases in P concentration with depth were found in all but one upper 0.5 m core, with the sharpest declines in concentration near the surface (Fig. 2-3). The core that did not exhibit decreasing P concentration with depth was the same core that displayed anomalous trends in ^{210}Pb activity. Contrary to the decreasing trend observed with depth in upper 0.5 m cores, mean P concentrations were significantly lower in these cores (mean 1.14 mg P g^{-1}) than in deep cores (mean 1.77 mg P g^{-1}; t-test, $P<0.05$). Further investigation would be required to resolve this discrepancy, as there is no viable explanation based on existing data.

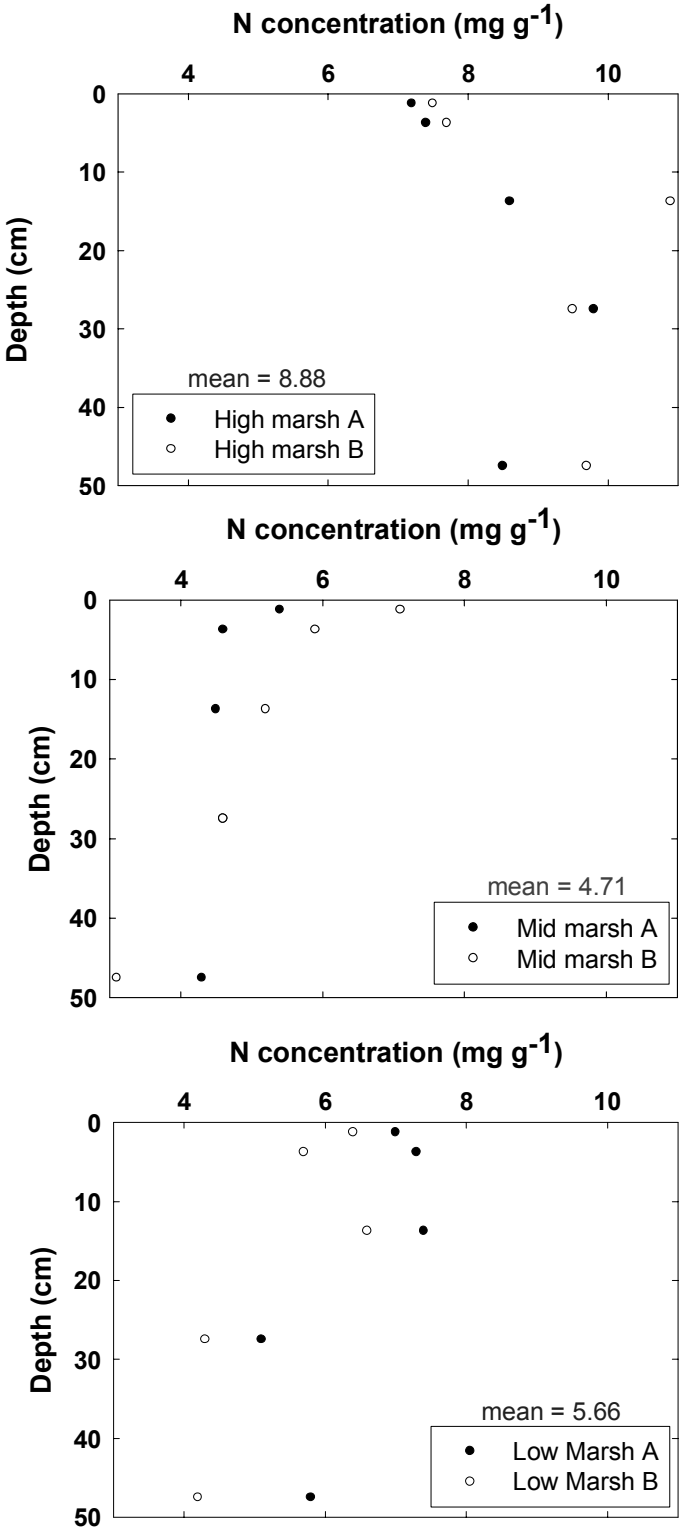


Figure 2-2. Nitrogen profiles for cores from high, mid and low marsh environments in the King's Landing marsh.

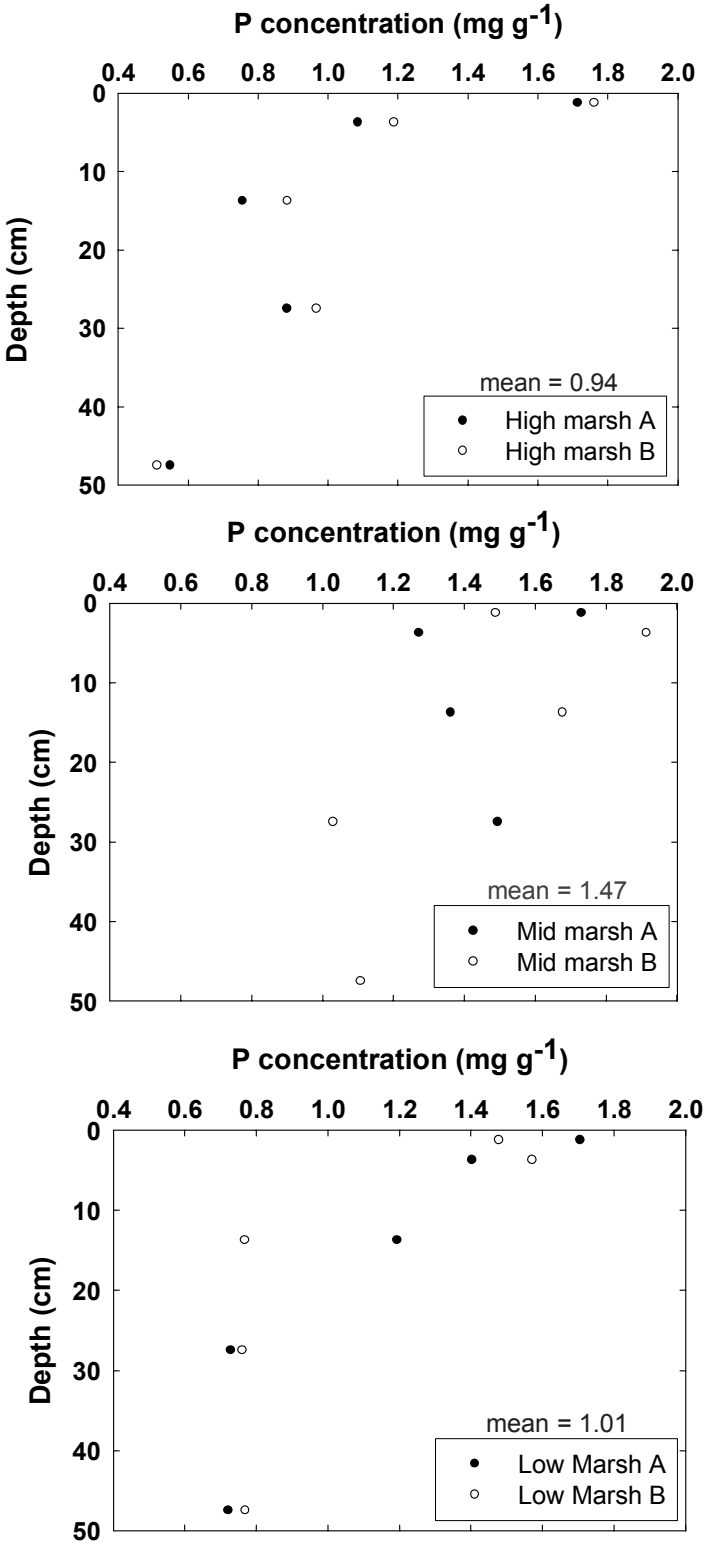


Figure 2-3. Phosphorus profiles for cores from high, mid and low marsh environments in the King's Landing marsh.

Carbon concentrations ranged from 20.2 to 173 mg C g^{-1}, with a mean of 92 mg C g^{-1} in upper 0.5 m cores and 38 mg C g^{-1} in deep cores (Fig. 2-4). Concentrations decreased in the top few centimeters of high marsh cores and then were relatively constant with depth (Fig. 2-4). Low and mid marsh C concentrations decreased and increased (respectively) to 30 cm, and then were fairly constant in both environments below 30 cm. High marsh sediments exhibited the largest C concentrations, followed by the low marsh, though differences were not significant (t-test, $P>0.05$). Carbon concentrations in general were much lower in deep cores than in the others.

Sediment C:N ratios were relatively constant in low and mid marsh cores, both vertically and with distance from land. High marsh C:N ratios increased substantially with depth (Table 2-4). There were strong differences in N:P ratio between marsh environments, with high marsh and low marsh ratios greater than mid marsh ratios by factors of 3.3 and 2, respectively (Table 2-4). In the high and low marsh, N:P ratios increased with depth, but they remained relatively constant in the mid marsh (Table 2-4).

Burial rates

Both accretion rates and nutrient concentrations were used in developing burial rate estimates. Since the range in accretion rates was larger than the range in N or P content, accretion was the dominant term in the computation. Burial rates for N ranged from 9.94 to 40.77 g N m^{-2} yr^{-1} (Table 2-3). Mid marsh N burial rates were greater than high marsh rates, and average low marsh N burial rates were 2-3 times higher on average than in any other marsh environment. Spatial variations in P burial were similar, with low marsh areas burying nearly 5 times as much P as the high marsh and ~1.25 times as

much P as the mid marsh. The range of P burial rates was 1.07 to 7.86 g P m^{-2} yr^{-1} (Table 2-3).

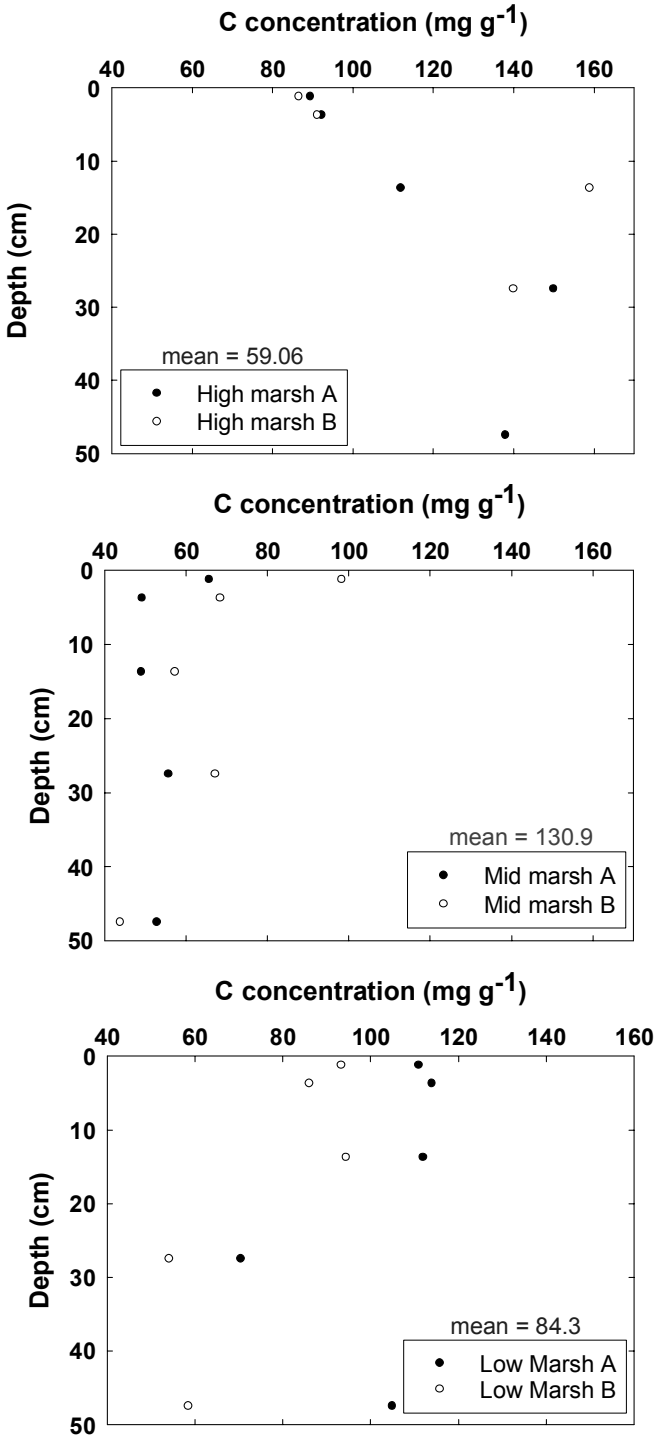


Figure 2-4. Carbon profiles for cores from high, mid and low marsh environments in the King's Landing marsh.

Table 2-4. High, mid and low marsh C:N and N:P ratios from the King's Landing (oligohaline) marsh.

Depth	High marsh		Mid marsh		Low marsh	
(cm)	C:N	N:P	C:N	N:P	C:N	N:P
1.25	12	4	13	4	15	4
3.75	12	7	11	3	15	4
13.75	14	12	11	3	15	7
27.5	15	10	13	4	13	6
47.5	17	17	13	2	16	7
mean	14	10	12	3	15	6

DISCUSSION

Spatial patterns in sediment nutrient concentration

Spatial patterns in tidal marsh nutrient burial were the result of the interaction of factors controlling both sediment accretion rates and nutrient content. Plant communities influence sediment nutrient content through their own characteristic C, N and P contents and via associated microbial and microautotrophic communities. In this study, both C and N concentrations were higher in high marsh zones than in the mid or low marsh, but C:N ratios were relatively constant among marsh environments (Figs. 2-2 and 2-4; Table 2-4). High marsh reeds and grasses (e.g. *Typha, Phragmites, Spartina* and ericaceous terrestrial plants) have high cellulose (carbon) content in stems, tend to decompose slowly and are thus prone to burial (Odum 1988; Khan and Brush 1994). Broad-leaved low marsh genera such as *Nuphar* and *Peltandra* tend towards lower C:N ratios, and litter generated by these plants tends to be more labile (Odum 1988; Traband 2003). Plant litter that is decomposed more quickly should, in theory, be less prone to burial on the marsh surface. For example, organic solids have been reported to contribute (on a mass basis) nearly twice as much to high marsh sediments as to low marsh sediments (Bricker-Urso et al. 1989), possibly due to more rapid decomposition of the more labile low marsh plants. This may explain the greater C and N content in high marsh than in low marsh sediments that appears to be characteristic of both tidal fresh and oligohaline Patuxent marshes, and of tidal marshes in general (Table 2-5). However, while there are spatial patterns in sediment C and N content, C:N ratios do not appear to differ between high and low marsh environments, or to impact nutrient burial rates in oligohaline Patuxent marshes.

Table 2-5. Comparison of N and C content in sediments from high versus low marsh environments. Values are given in mg C or N g^{-1} sediment.

Nitrogen		Carbon		
High marsh	Low marsh	High marsh	Low marsh	Reference
12 - 17	4 - 9	ND	ND	Merrill 1999
18	4	180	35	Khan and Brush 1994
9	6	156	112	DeLaune et al. 1981
7.8	6.6	139	101	DeLaune et al. 1979 (cited in Bowden 1984)
9	6	131	85	This study

Phosphorus concentrations in this study were highest in the mid marsh, which may be explained in part by the fact that particulate inputs from tidal waters are an important source of P to the marsh. Merrill (1999) found higher P concentrations with proximity to the tidal channel, and Craft and Richardson (1993) found that P content of peat in the Everglades was highest in the most frequently flooded areas of the wetlands. Craft and Richardson (1993) also found that sediment P content increased as water column P concentrations increased. To some extent, this suggests that the size of the marsh sink for P is flexible, and has the capacity to increase as P loads increase. That P concentrations in this study were not highest in the low marsh may be due to less favorable conditions for P retention in marsh environments undergoing long periods of inundation. If the environment becomes reducing, iron oxides which bind P under oxic conditions tend to dissolve, releasing P to the water column (Sundby et al. 1992).

The extent to which P is bound by iron minerals may also be affected by salinity (Froelich 1988). In reducing environments with some degree of salinity (i.e. oligohaline to euhaline marsh sediments), P liberation from oxidized iron compounds is augmented

by reduction of SO_4 and subsequent formation of reduced iron-sulfide minerals, which sequester iron and prevent further binding of P (Roden and Edmonds 1997). Thus, another possible explanation for the higher P concentrations observed in the mid marsh than in the low marsh in this study stems from the fact that in addition to more oxic conditions due to shorter periods of inundation, mid marsh environments may experience slightly lower salinities than low marsh environments, which receive comparatively more tidal water and fewer freshwater (terrestrial) inputs. More reducing conditions coupled with greater exposure to sulfur in the low marsh may contribute to lower P retention in sediments there.

Though tidal inundation can be an important source of some materials to a marsh, tidal *flushing* may also play a major role in preventing burial of organic matter. High marsh plant litter is subject to less frequent and less energetic tidal flushing than low marsh litter, adding to its tendency to accumulate on the marsh surface (Odum 1988). It has been argued that because of this, low marsh zones may act only as *seasonal* nutrient sinks, with rapid decomposition and flushing of organic matter from the low marsh preventing long-term nutrient burial (Khan and Brush 1994). Though no additional evidence to support this hypothesis could be identified in the literature, Taylor and Allanson (1995) have speculated that Odum's (1968) outwelling hypothesis is less applicable to high marsh environments than to low marsh environments, based on lower measured C export from the high marsh. With regard to nutrients though, results from this study and others tend to refute those arguments, suggesting that inorganic sediment accretion rates are more important in determining burial (i.e. nutrient retention) than

residence time of organic matter on the marsh (DeLaune et al. 1981; Merrill 1999; this study).

Spatial patterns in sediment accretion rates

Nutrient burial rates are a function of nutrient and sediment inputs to the burial environment, as well as retention of those inputs. At coarse scales (10's of kilometers), the terrigenous nature of sediment and nutrient inputs to coastal systems creates a pattern of decreasing burial with distance from land (Fig. 2-5). Within intertidal environments (10's of meters), however, proximity to tidal waters with high concentrations of suspended sediment can create the opposite pattern – increasing burial with distance from land. Accretion rates are often reported to be highest in low marsh zones due to allochthonous sediment inputs (Bricker-Urso et al. 1989; Kearney et al. 1994; Khan and Brush 1994; this study). In this study, low marsh accretion rates were 4 times as high as rates in the high marsh (Table 2-3). High-volume organic matter can add elevation to a marsh, but it is the addition of new inorganic sediment by tidal action that predominantly determines mass based accretion rates (DeLaune et al. 1989). Though N and C content of sediments is generally reported to increase landwards (DeLaune et al. 1981; Khan and Brush; this study), burial appears to follow the same spatial trends as mass based accretion (DeLaune et al. 1981; Merrill 1999; this study).

Sediment nutrient profiles

Vertical profiles of sediment particulate nutrient concentrations with depth can yield insights into biogeochemical processes and also aid in estimating the capacity of a marsh as a sink for particulate nutrients. Relatively constant N profiles with depth have often been reported and may be due to the biological role of N in plant and microbial

structural components, which are not highly labile (DeLaune et al. 1981; Bowden 1984). Nitrogen in plant litter is initially available for remineralization, denitrification and other

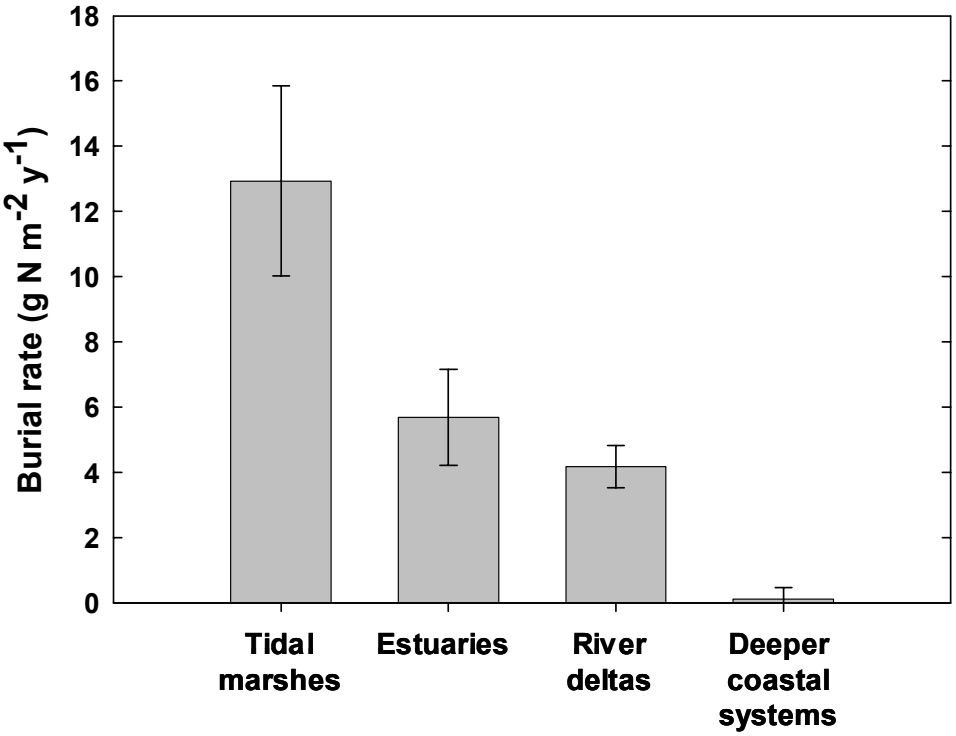


Figure 2-5. Change in average observed N burial rates with distance from land. Data are from Larsson et al. 1985; Milliman and Syvitski 1992; Boynton et al. 1995; Merrill 1999; Nixon et al. 1996 and Muzuka and Hillaire-Marcel 1999. Figure adapted from Boynton and Kemp 2005 *in press*.

pathways, but within ~7 years this material becomes sufficiently refractory that the residue is permanently retained in the sediment (White and Howes 1994). In the mid and low marsh areas sampled for this study, N concentrations decreased with depth to ~30 cm, then became relatively constant at greater depths (Fig. 2-2). This pattern suggests diagenesis in the biologically active root zone, with more permanent burial of refractory material in deeper sediments.

The initial declines observed in P concentrations with depth (Fig. 2-3) may have been due to plant and microbial uptake of labile, P-rich organic compounds in the biologically active root zone (Bowden 1984). In addition, P bound in Fe-oxide minerals may have been released in deeper, more anoxic sediments as P was released due to reduction of iron (Krom and Berner 1980). The upward diffusion of P released from Fe minerals would contribute to the observed increases in P in near-surface, more oxic regions at the top of the vertical profiles. This process has been documented in estuarine sediments, where upward migration of P produced by the remineralization of organic P and by the dissolution of iron oxides contribute to decreasing P concentrations with depth in sediments (Sundby et al. 1992).

Vertical nutrient profiles integrate many biogeochemical factors, including biological uptake and transformation of nutrients, advection and diffusion of dissolved species, initial nutrient loads to the system, and sediment accretion rates. Since these factors change on shorter timescales than those over which burial rates are calculated, it is important to consider such factors when selecting information from a nutrient profile to use in calculating burial rates. For example, in this study, P concentrations measured in the top 10 cm were roughly twice those measured at 40-50 cm depth (Fig. 2-2). By using depth-averaged P concentrations in burial calculations, it was possible to avoid large underestimates of burial due to ever-increasing loading rates, and to avoid large overestimates (especially for P) due to local diagenetic release.

Tidal marshes as long-term nutrient sinks

Contrasting views of the ecological role of tidal marshes in the terrestrial-estuarine landscape have been put forth, such that tidal marshes have been described both

as zones of outwelling (e.g. Odum 1968; Simpson et al. 1983a) and as nutrient sinks (e.g. Gosselink et al. 1973; Simpson et al. 1983a). In addition to these competing viewpoints, one of the oldest concepts in tidal marsh ecology is the idea that marshes act as transformers of nutrients and other materials, taking them up during the growing season in inorganic form, and redelivering them to the aquatic system in organic form as plant and microbial litter is flushed by tidal waters (Whigham and Simpson 1976; Heinle and Flemer 1976; Stevenson et al. 1977; Valiela et al. 1978; Simpson et al. 1983a; Wolaver et al. 1983; Baird and Winter 1992). Data from studies proscribing this view highlight the role of tidal marshes as temporary sinks, or "holding tanks," that take up nutrients at the beginning of the growing season and release them later in the year (e.g. Valiela et al. 1978; Wolaver et al. 1983). Since these nutrients would otherwise be available to phytoplankton during the growing season, this function is of special importance in eutrophied estuaries like the Chesapeake and its tributaries.

This study provides evidence that accreting tidal marshes (e.g. Patuxent River marshes) can also play the role of *permanent* nutrient sinks, where nutrients in estuarine waters are sequestered via long-term burial in accreting marsh sediments, and are not released to the estuary. Furthermore, results from this study and others indicate that tidal marsh nutrient burial is quantitatively important. Marsh burial rates of 1.1 to 7.9 g P m^{-2} yr^{-1} are 17% to 120% of the estimated rate of P input (per unit estuarine surface area) to the Patuxent (Table 2-6). Results from this study also suggest that tidal marshes have the capacity to bury N at 16% to 66% of the rate of N input, and that N burial occurs at similar to slightly higher rates than denitrification (Table 2-6).

Table 2-6. Comparison of Patuxent marsh nutrient burial rates measured in this study to rates of nutrient input to the Patuxent River. Input data are from Boynton, unpublished data.

	N	P
Inputs ($g\ m^{-2}\ yr^{-1}$)	62.0	6.6
Marsh burial ($g\ m^{-2}\ yr^{-1}$)	9.9 - 40.8	1.1 - 7.9
Burial as % of inputs	16 - 66	17 - 120

Conclusions

1. Sediment N and C concentrations are greater in high marsh environments than in the low marsh, and P concentrations are highest in the mid marsh.
2. Sediment accretion rates increase from high to low marsh environments and appear to be the most important factor in determining burial rates for nutrients.
3. Burial rates for N and P increase with distance from land in oligohaline Patuxent marshes.
4. Nutrient concentrations and mass-based accretion rates follow similar patterns in both tidal fresh and oligohaline Patuxent marshes.
5. Average burial rates for N and P are similar in tidal fresh and oligohaline marshes; it is unclear why tidal fresh rates have been reported to follow a different trend with proximity to land than oligohaline rates (at the spatial scale of individual marshes).

CHAPTER 3:
SYNTHESIS OF TIDAL MARSH NUTRIENT REMOVAL – ECOSYSTEM AND MANAGEMENT PERSPECTIVES

INTRODUCTION

Data from this study indicate that tidal marshes have the capacity to remove substantial portions of N and P loads to the upper Patuxent River on an annual basis. In all likelihood, similar circumstances exist for other Chesapeake Bay tributaries with large and stable tidal marsh communities. Marsh nutrient removal processes are quite valuable, as indicated by the cost of nutrient reduction and removal technologies typically used by water quality management agencies. But despite marsh nutrient removal processes, anthropogenic nutrient loads continue to contribute to an altered trophic state in the Patuxent River. With respect to point sources, nutrient management in the Patuxent watershed has been aggressive and partially successful. However, non-point source nutrient loading has a much longer history and has proven more difficult to manage.

NUTRIENT LOADING IN THE PATUXENT

Historical nutrient loading

Pre-colonization and early settlement

Nutrient loads to the Patuxent River are estimated to have increased by factors of about 5 (N) and 20 (P) since precolonial days (Boynton et al. 1995). Trends in nutrient and sediment inputs to the Patuxent River can be considered in more detail during 4 periods: pre-European settlement, onset of settlement to the early 20th century, post-WWII to the 1980's, and the 1980's to the present. Prior to European settlement (mid-1600's), Native American inhabitants of the Patuxent watershed numbered in the low 1000's and practiced low-impact slash and burn agriculture (E. Chaney pers. comm.). From the onset of European settlement through the mid to late 1800's, higher-impact European farming practices were introduced and agricultural land use intensified so that by the mid-1800's, 85% of the Patuxent watershed was in agricultural land use of some type (D'Elia et al. 2003). Sediment loads to the Patuxent increased drastically during this period, as evidenced by sedimentation rates derived from dated sediment cores (Khan and Brush 1994), and by changes in the crustaceous benthic community (Cronin and Vann 2003). A particularly large increase in sediment loads likely occurred during and after the American Revolution, as tobacco markets tilted in favor of grains and more land was cleared and ploughed (Curtin et al. 2001). Elevated NO_3 and sediment losses have been reported for recent clearcuts in experimental forests (Pardo et al. 1995; Eshleman et al. 2000), and nutrient and sediment loads to the Patuxent likely increased during this period, although the elevated N loads were probably of brief duration. However,

commercial fertilizers were not yet in use, so nutrient loads probably did not increase enough to produce a substantial trophic response in the river at this point in time.

Twentieth century

In the early 20th century, urban and residential areas expanded in the Patuxent watershed and agricultural land use declined, leading to reforestation. Immediately after WWII, however, two developments led to large increases in nutrient inputs to the Patuxent River. First, population began to increase (Maryland Office of Planning 2001), and second, the fertilizer industry developed (Smil 1990). Trends in population growth lead to increases in sewage effluent (D'Elia et al. 2003), and intensification of fertilizer applications to lawns and croplands resulted in the transport of large amounts of new N and P to the Patuxent watershed. Sewage effluent is generally characterized by an N:P ratio of ~8 and a higher ratio, ~50, is common for agricultural runoff (Lee et al. 2001). Together, these inputs provide an approximately Redfieldian mixture of N and P, creating favorable conditions for elevated aquatic primary production (Fisher pers. comm.).

Evidence for changing trophic status

There are several lines of evidence to suggest that the trophic status of the Patuxent changed in concert with enhanced nutrient loading from sewage effluent and agricultural and residential/urban runoff. One of these was the observation, beginning in the early 1960's, that dissolved inorganic P (DIP) concentrations measured in the Patuxent River were increasing (Hagy et al. 1998). Phosphorus inputs are linked closely with sediment inputs, and these increased as residential and urban development occurred. Observations of increasing turbidity were also made during this period (Heinle et al. 1980). Increased turbidity may have been caused by enhanced phytoplankton

populations, by elevated terrigenous sediment inputs or, more likely, a combination of both factors.

Declining oxygen concentrations, especially in the mesohaline Patuxent, provided another line of evidence for changing trophic status of the river. Summer dissolved oxygen concentrations in certain regions of the Patuxent have consistently dropped below 1 mg l^{-1} since 1940, compared to no observations below 2 mg l^{-1} and most above 4 mg l^{-1} prior to the 1940's (Breitburg et al. 2003; D'Elia et al. 2003). Shifts in benthic ostracode community structure towards dominance by anoxia-tolerant species beginning in the mid to late 1900's also suggested low-oxygen conditions (Cronin and Vann 2003). A final indicator of changing trophic status in the Patuxent River was the loss of submerged aquatic vegetation (SAV), due to development of turbid water and of dense epiphyte communities, which began in the 1960's pursuant to increased nutrient loading to the river (Stankelis et al. 2003). Aggressive epiphyte growth has been reported to have a negative effect on the ability of SAV to remain healthy, again due to issues related to light availability (Drake et al. 2003).

1980's to the present

As phytoplankton concentrations increased and dissolved oxygen and SAV populations declined, the link between nutrient loading and Patuxent water quality became apparent. Nutrient loads to the Patuxent were derived from terrestrial point and diffuse sources, as well as from atmospheric wet and dry deposition. Point sources were primarily wastewater treatment plants (WWTP's), and diffuse (or non-point) sources included croplands, livestock facilities, forests and suburban/urban areas. During the initial period of enhanced nutrient inputs (1960's and 1970's), point sources were the

dominant source of P (60%), and were larger than any other single source of N (50%) (Hagy et al. 1998). Total dissolved concentrations of both N and P in the upper Patuxent River increased dramatically from the early 1960's to early 1980's, with a near doubling of N concentrations, and increases in P concentration by more than a factor of two (Hagy et al. 1998). During the early 1980's, P concentrations were reduced to early 1960's levels when advanced P removal technology was introduced to Patuxent WWTP's (Boynton et al. 1995). Elevated N concentrations (largely NO_3^- and NO_2^-) persisted until the early 1990's, when advanced N removal technology was introduced (D'Elia et al. 2003). An evaluation conducted in the mid-1980's indicated that atmospheric inputs were less important than terrestrial nutrient sources, contributing 13% of the TN load and 5% of the TP load (Boynton et al. 1995). However, atmospheric N loads appear to be following an increasing trend as vehicular and industrial emissions increase (Jordan et al. 1995).

Current nutrient loading

Currently, N and P loads to the upper Patuxent estuary are 4389 and 468 kg d^{-1}, respectively (W. Boynton, unpublished data). Nutrient loads are influenced by annual precipitation, land use patterns and by population size. The Patuxent watershed has seen an order of magnitude population increase in about 50 years, from less than 25,000 inhabitants in 1960 to over 500,000 at present (Maryland Office of Planning 2001). As populations grow, effluent from WWTP's and nutrition demands (i.e. agriculture) increase, both of which tend to increase nutrient inputs from the watershed. Nitrogen, P and sediment loads have all been reported to increase as the percent developed land in a watershed increases, as well as with increased cropland (Nearing et al. 1993; Smith et

al. 1993). Croplands contribute nutrients due to fertilizer application and N-fixation, and increase runoff above levels typically associated with forested lands (Beaulac and Reckhow 1982). Developed land contributes sediment during construction, nutrients due to lawn fertilization, and runoff. Runoff from paved surfaces has been reported to be 40 times higher than runoff from forested land (Chesapeake Bay Watershed Blue Ribbon Finance Panel 2004). But despite the fact that developed land now covers more area in the Patuxent watershed, croplands appear to contribute more inputs to the estuary (Jordan et al. 2003; Weller et al. 2003). Although they comprise only 10% of the watershed, croplands supply the majority of most non-point source nutrients to the Patuxent in average years, as well as the majority of nutrients from all sources in wet years (Jordan et al. 2003). It is interesting to note that agricultural land use has declined in the Patuxent watershed recently, but model-based loading estimates do not support a coincident decline in non-point nutrient inputs (Sprague et al. 2000). This indicates that there may be gaps in our understanding of land use impacts on nutrient loading, particularly with respect to agriculture.

Internal nutrient sources

In addition to terrestrial and atmospheric nutrient inputs, internal nutrient sources can become important during certain seasons (Boynton and Kemp 1985; Magnien et al. 1992; Boynton et al. 1995; Cowan and Boynton 1996). Internal recycling of nutrients tends to be largest in mesohaline regions of the Chesapeake, generally correlates with increased temperature and decreased benthic dissolved oxygen, and is also correlated with indices of the magnitude of spring bloom deposition (Cowan and Boynton 1996). The dominant pathways for nutrient remobilization are remineralization of N as NH_4

(Kemp et al. 1990) and desorption of PO_4 from sediments (Sundby et al. 1992). These processes appear to regenerate nutrients at lower N:P ratios than terrestrial and atmospheric loading ratios (Magnien et al. 1992). This may be the result of reduced N remineralization due to denitrification, or because initial P inputs are largely sediment bound, making them more susceptible to sedimentation than the primarily dissolved N inputs. Though external sources are a larger portion of the nutrient input signature during winter and spring high flow seasons, there is strong evidence that internal remobilization becomes the dominant nutrient source during the summer (W. Boynton, unpublished data). In summer, an order of magnitude more bioavailable N and P are supplied by recycling than by allochthonous inputs to the upper Patuxent estuary (Table 3-1).

Table 3-1. Relative importance of dissolved inorganic nutrient inputs from external sources versus internal recycling in the upper Patuxent estuary (W. Boynton, unpublished data). Inputs are in kg N or P d^{-1}.

	Annual		Summer		Winter	
	NH_4/DIN	PO_4	NH_4/DIN	PO_4	NH_4/DIN	PO_4
New inputs	3576	243	2541	159	4177	189
Recycle source						
Sediments	1856	309	3739	816	374	81
Macrozooplankton	1392	193	2574	356	406	ND
Total	3248	502	6313	1172	780	81

Nutrient management in the Patuxent watershed

With regard to management, a combination of circumstances has made the Patuxent unique among Chesapeake Bay tributaries. The public has recognized the presence of eutrophic conditions in the river, and there has been active scientific research and monitoring of these conditions. Also, for many years, eutrophication has been paid considerable attention by legislators, and regulatory efforts to address nutrient enrichment

have been introduced. In the late 1970's and early 1980's, scientists played a particularly large role in influencing policy, and reductions in nutrient inputs to the Patuxent as a result of regulatory policies are noticeable. However, even though a considerable degree of control has been exerted over certain nutrient sources, a substantial trophic response in river condition has yet to be reported. The Patuxent watershed is also unique in that WWTP contributions to nutrient loads have been substantial. For the mainstem Bay and many of its tributaries, diffuse nutrient sources have strongly dominated nutrient budgets, but sewage effluent played a large role in the Patuxent nutrient economy (Boynton et al. 1995). To a large degree, this is the reason that early Patuxent management efforts were so successful - point sources are simply easier to identify and treat than diffuse sources.

Early efforts (c.a. 1986) to reduce WWTP inputs focused on P removal due to the fact that P had traditionally been regarded as the primary limiting nutrient in aquatic systems (Vollenweider 1976), and because P removal techniques were more readily available and less costly. The effect of P removal was visible immediately in the form of reduced P concentrations and higher N:P ratios in Patuxent River water (D'Elia et al. 2003). However, the insistence of academics on the potential importance of N (Ryther and Dunstan 1971) and the development of a cost-effective removal process finally led to the application of Biological Nitrogen Removal (BNR) to Patuxent WWTP's beginning in 1991. The effect of BNR, as with P removal, was immediately obvious in the form of altered (lower) N:P ratios and seasonally lower N concentrations in upper Patuxent River water (Weideman and Cosgrove 1998). As a result of nutrient management, point source N inputs to the Patuxent have been cut in half and no longer

dominate the N budget, and point source P inputs have been reduced by nearly 60%, becoming only 33% of the P budget (D'Elia et al. 2003).

Though it is encouraging that N inputs to the Patuxent have been reduced during the warm portion of the year, N inputs during the winter have continued to rise. Non-point N inputs to the Patuxent may also be increasing as a result of increased anthropogenic emissions of N oxides and continued development of the Patuxent watershed. Indeed, the population in the Patuxent has grown at one of the highest rates in the U.S. (Culliton et al. 1990), and percent developed land in the watershed is increasing at a faster rate than the population (Year 2020 Panel Report 1988). The 800 pound gorilla looming in the future of nutrient management in the Patuxent is certainly non-point nutrient sources.

NATURAL SINKS FOR NITROGEN

Substantial nutrient sinks have been identified for the Chesapeake Bay and its tributaries. Both N and P are buried in subtidal sediments and removed from the Bay in fisheries harvests, and N is also removed via microbial denitrification (e.g. DeLaune et al. 1981; Deegan 1993; Cornwell et al. 1999). Subtidal denitrification is estimated to remove 31% of N inputs to the Patuxent River on a yearly basis, with burial and fishery yields removing 53% and 3%, respectively (Boynton et al. 1995). Burial of P and the fisheries harvest account for 128% and 1% of P inputs (Boynton et al. 1995).

Denitrification and nutrient burial also occur in tidal marshes. To the extent that some nutrient runoff contacts marshes prior to entering the estuary, marsh denitrification and burial have the unique quality of removing nutrients before they can contribute to phytoplankton production in estuarine waters. Another important difference between subtidal and marsh denitrification is that while the areal extent of subtidal sediments is much higher in the lower Patuxent River (making lower Patuxent nutrient sinks larger), the vast majority of marsh area occurs on the upper Patuxent, which suggests a particularly important role for tidal marshes in the nutrient economy of the upper estuary. In addition, upper Patuxent subtidal sediments tend to denitrify at higher rates than lower Patuxent sediments (Boynton et al. 1995), and coastal marshes appear to denitrify at higher median rates than subtidal sediments (Greene 2005; Table 1-1). This suggests that upper Patuxent marsh sediments may denitrify at the highest rates of any environment in the estuary. Finally, most trapping of sediment loads tends to occur in upper reaches of the Chesapeake Bay and its tributaries (Ward et al. 1998), and tidal marshes also appear to bury nutrients at higher rates than subtidal sediments (Fig. 3-1), so

upper Patuxent marshes may bury nutrients at the highest rates of any environment in the estuary.

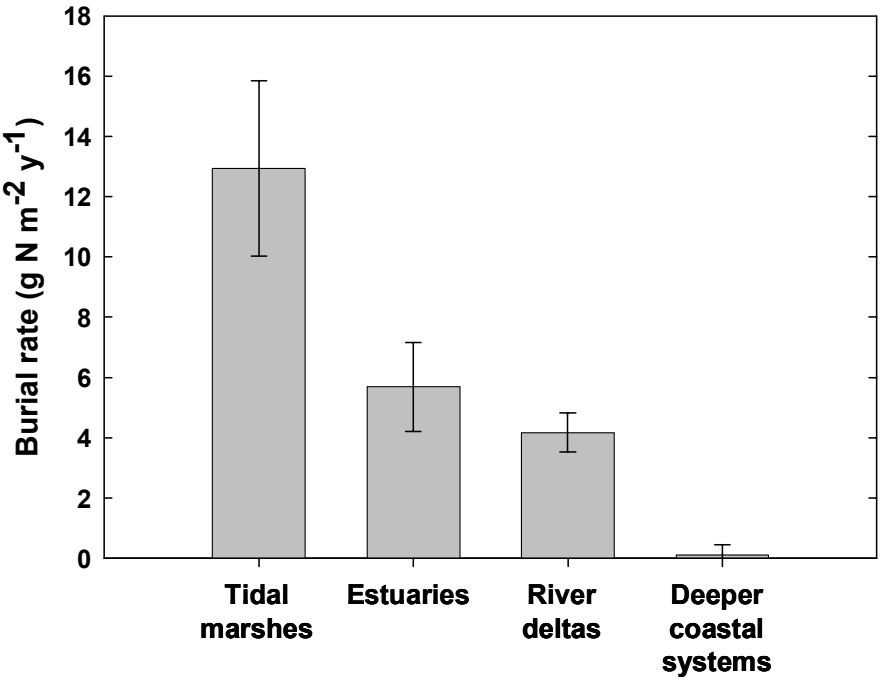


Figure 3-1. Average burial rates of particulate organic N for different coastal environments (data from Boynton, unpublished data).

Denitrification

During at least 7 months of the year, Patuxent marshes appear to denitrify at average rates of 120 μmoles N m^{-2} h^{-1}, with statistically significant spatial trends and substantial, non-linear temporal trends (Chapter 1). Measurements of denitrification are made at spatial scales orders of magnitude smaller than the landscape area covered by marshes, but these fine-scale measurements provide the only directly-measured information regarding denitrification in these systems. In order to say anything about denitrification at the landscape scale then, one of the greatest challenges in ecology must be confronted: "scaling from the miniscule to the monstrous" (Schneider 1994).

A widely used method of scaling up involves simply multiplying rates at the scale of measurement by the magnification factor necessary to arrive at the scale of interest. For example, extrapolating the grand mean of all denitrification rates measured in this study over the 25.8 km^2 of marsh in the upper Patuxent yields a daily rate of 1040 kg N d^{-1}. At this rate, tidal marsh denitrification could remove 24% of N inputs to the upper Patuxent (accounting for 80% of the "missing sink" discussed in the Introduction). But simple multiplication excludes the fractal nature of so many ecological processes (Schneider 1994). For example, a process that occurs in a rapid "burst," measured at the daily time scale, cannot simply be multiplied by 365 days to achieve a rate estimate at the annual scale. In order to extrapolate more accurately, spatial and temporal patterns should be considered.

Spatial patterns in denitrification rates measured in Patuxent marshes in this study showed some positive relationships with total sediment C and N content (Chapter 1; Table 2-5), and were negatively correlated with duration of tidal inundation ($r^2 = 0.92$; Fig. 1-26). Since the above factors vary from high to low marsh zones, accurate extrapolation of denitrification rates requires quantitative data regarding the areal extent of different marsh environments. A rigorous analysis of the areal extent of different marsh environments was beyond the scope of this study. However, educated estimates were made based on data from a visual survey of Patuxent marshes (Table 3-2). Most Patuxent marshes consist primarily of mid marsh environments, with smaller but substantial high marsh and much less low marsh and marsh creek area (Table 3-2). When extrapolating average denitrification rates, the spatial component should include weighting according to the relative areal extent of different marsh environments.

Table 3-2. Relative areal extent of high, mid and low marsh environments in oligohaline and tidal fresh regions of the Patuxent River. Data were collected during a visual survey conducted aboard the R/V Pisces during summer, 2004. Definitions of marsh environments are given in Chapter 1.

Marsh environment	Percent total marsh area
High marsh	30
Mid marsh	55
Low marsh & marsh creeks	15

Temporal patterns in denitrification rates are available for 7 months of the year, and there is evidence to suggest continued denitrification during the other 5 months. Denitrification rates were positively correlated with trends in Patuxent River NO_3 concentrations, especially from April through July (Chapter 1), which is relevant for several reasons. First, this relationship could be used for spatial extrapolation up and down river from study sites where water column NO_3 concentrations appear to vary latitudinally. Second, there are predictive implications of the NO_3-denitrification relationship, whereby substantial changes in N loads to the Patuxent could alter NO_3 concentrations, in which case denitrification rates might be predicted to change as well. Finally, temporal patterns can be used to extrapolate measured denitrification rates in time. Extrapolating on a seasonal basis may not be accurate, as certain trends in denitrification rates were expressed within a single season (i.e. sharp increases and

declines within a season). In general, denitrification rates measured in June, September and October were just over half of rates measured in April, May and July, with August rates displaying intermediate values (rates averaged across both sites; Chapter 1). Based on this pattern, Patuxent marshes appear to denitrify at rates near 170 μmoles N m^{-2} h^{-1} during 3 months of the year (April, May, July), near 90 μmoles N m^{-2} h^{-1} for another 3 months (June, September, October), and at 120 μmoles N m^{-2} h^{-1} in August.

Denitrification rates were not measured in winter in this study, but there is evidence that denitrification does occur in Patuxent marshes during winter months. Heterotrophic processes generally exhibit temperature-dependence, and a strong positive relationship was observed between sediment oxygen consumption and temperature in Patuxent marshes from April through October (Chapter 1; Fig. 1-9). However, temperature alone did not appear to control denitrification in Patuxent marshes during the 7 months of this study, as the highest monthly rate for denitrification occurred in the coldest month (April, 9^{o}C). In addition, substantial denitrification rates have been reported for Chesapeake subtidal sediments in winter (J. Cornwell pers. comm.) and for other systems at near-zero temperatures (Greene 2005). Measurements of winter denitrification rates in Patuxent marshes are clearly needed. However, for the purpose of this extrapolation, winter rates can be assumed to occur at 12 μmoles N m^{-2} h^{-1} (10% of the mean April-October rate).

Estimation of annual Patuxent marsh denitrification based on observed spatial and temporal patterns was accomplished with the following summation:

$$\text{Denitrification (kg N)} = W + \sum_{i=1} [(0.3H_i + 0.55M_i + 0.15L_i)*A*D_i*k]$$

Where W = winter marsh denitrification, in kg (95.8, derived from an assumed hourly rate of 12 μmoles N m^{-2} h^{-1}),

H_i = high marsh denitrification rate for the i^{th} month, in µmoles N m^{-2} h^{-1},

M_i = mid marsh denitrification rate for the i^{th} month, in µmoles N m^{-2} h^{-1},

L_i = low marsh denitrification rate for the i^{th} month, in µmoles N m^{-2} h^{-1},

i = month, April (1) through October (7),

A = upper Patuxent marsh area (25.8 km^2),

D_i = number of days in the i^{th} month, and

k = constant, to convert rates in µmoles m^{-2} h^{-1} to rates in kg km^{-2} d^{-1} (0.336).

After weighting of measured rates based on observed spatial and temporal patterns, Patuxent marshes were estimated to remove 3.52 x 10^5 kg N yr^{-1}, or 964 kg N d^{-1}, which is 22% of total N inputs to the upper estuary (Table 3-3). This estimate is slightly lower than the estimate made without spatial and temporal weighting of measured rates. That the weighted estimate is lower than the non-weighted estimate is to be expected, as rates were assumed to be quite low for 5 months of the year in the weighted calculation. That the weighted estimate is not *very much* lower than the unweighted estimate can be attributed to the fact that higher rates were measured in environments which comprise a greater portion of the marsh surface.

Nutrient burial

Applying the areal weighting scheme previously discussed for marsh environments, this study indicates that Patuxent marshes bury N and P at average rates of 18 g N m^{-2} yr^{-1} and 4 g P m^{-2} yr^{-1}. Though there is likely a seasonal component to nutrient burial, this is already accounted for since accretion rate calculations are made at the annual timescale and integrate the contributions of all months of the year. Data collected by Merrill (1999) indicated similar rates for N and P burial at King's Landing

(21.4 and 3.76 g N and P yr^{-1}). At Jug Bay, Khan and Brush (1994) reported similar burial rates for the high marsh, but lower rates for the low marsh. Extrapolating the areal-weighted burial estimates from this study, upper Patuxent marshes were estimated to remove 4.64 x 10^5 kg N yr^{-1} and 1.03 x 10^5 kg P yr^{-1}. This accounts for nearly 30% of N inputs to the upper Patuxent (98% of the "missing N sink" described in the Introduction) and 60% of P inputs to the entire Patuxent (Table 3-3).

Table 3-3. Rates of N and P loading to the upper Patuxent estuary, with estimates of N and P removal based on measurements made in this study. The estuarine surface area is 26.0 km^2 and total marsh surface area is 25.8 km^2 (used in computation of areal rates).

	kg d^{-1}		kg yr^{-1}		g m^{-2} yr^{-1}	
	N	**P**	**N**	**P**	**N**	**P**
Load[a]	4389	468	1.6 x 10^6	1.7 x 10^5	62	7
Burial[b]	1271 (29)[c]	282 (60)	4.6 x 10^5	1.0 x 10^5	18	4
Denitrification[b]	964 (22)	--	3.5 x 10^5	--	14	--

[a] Estimate of current N loads to the upper Patuxent estuary are from Boynton, unpublished data. Rates were given by Boynton in kg N d^{-1}.
[b] Estimate based on measurements made in this study. Denitrification measurements made in μmoles N m^{-2} h^{-1}; burial measurements made in g N or P m^{-2} yr^{-1}.
[c] Burial and denitrification rates are given in parentheses as % of N or P load to the upper Patuxent estuary.

Future studies

One avenue for future work to facilitate more accurate spatial extrapolation of nutrient removal rates would be to examine relationships between nutrient removal processes and specific plant communities. If strong enough correlations were found, a measurement tool, in some ways analogous to measuring oceanic primary production by satellite, could be developed. More specifically, areal extent of specific plant communities in all Patuxent marshes could be quantified with aerial photographs and GIS. Nutrient removal rates associated with each plant community could then be summed according to the total area of each community, just as primary production

associated with ocean surface color can be summed according to the total number of pixels of each color in a satellite photograph. This summation procedure eliminates some of the error associated with multiplying fine-scale rates by large magnification factors.

Resilience of marsh nutrient removal mechanisms

In the face of increasingly intense anthropogenic nutrient inputs, it is important to consider how removal mechanisms (both man-made and natural) will respond to changing nutrient loads. Data from this study suggest that marsh denitrification rates respond to Patuxent River NO_3 concentrations during portions of the year (April through June), and that denitrification in general exhibits a positive response to elevated NO_3 in the water column (Chapter 1; Fig. 1-25). This does not necessarily indicate that marsh denitrification will counteract increased N inputs, as total N inputs have been reported to increase without associated increases in NO_3-N inputs (Jordan et al. 2003). Also, though denitrification rates appear to increase in concert with water column NO_3 concentrations, rates only appear to increase in *proportion* to NO_3 to concentrations around 150 μM, after which denitrification rates approach an asymptote (Chapter 1). Despite these caveats regarding the capacity of Patuxent marshes to offset increased N inputs, the size of the marsh denitrification sink could be expected to increase if NO_3 loading were to increase.

It has been demonstrated that P burial increases as concentrations of P in river water increase (Craft and Richardson 1993), so the size of the P sink, like that of the N sink, might also be expected to increase as loading increases. Marsh nutrient burial is tenuous, however, as it is dependent on continuous accretion of marsh sediments relative to sea level changes. If Patuxent marshes (due to reduced sediment inputs, rising sea

level, or other factors) do not continue to accrete, the marsh nutrient sink may diminish, disappear, or even become a source of nutrients if substantial erosion begins to occur.

VALUING TIDAL MARSH NUTRIENT REMOVAL

Cost of nutrient control

The Patuxent watershed is an illustration of successful point source nutrient management, and this example suggests that there is hope for controlling point source nutrient inputs to other Chesapeake Bay tributaries, even in the face of burgeoning populations. Due to successful point source nutrient control measures, however, non-point sources now dominate nutrient inputs to the Patuxent and much of the Chesapeake. Human activity that contributes to the diffuse nutrient supply is increasing not only due to population growth and increased demand for food, but also due to the rising *intensity* of this activity. For example, in the Chesapeake basin, population increased by 8% during the past decade while impervious surface area increased by 41% and vehicle miles traveled rose 26% (Chesapeake Bay Watershed Blue Ribbon Finance Panel 2004). The future of nutrient management in the Patuxent and the entire Chesapeake basin clearly rests in dealing with non-point source nutrients and with the human activities that produce them.

Several efforts to restore the Chesapeake Bay and its tributaries to a less-impacted state are presently underway. By 2004, nutrient reduction technology of some sort had been applied to 55% of the flow from all Chesapeake wastewater facilities; phytase additions to poultry feed led to 16% P reductions in poultry litter; nutrient management plans were prepared for 85, 45 and 40% of croplands in Maryland, Pennsylvania and Virginia, respectively; and limited conservation tillage and cover cropping practices were being used on a number of farms (Chesapeake Bay Commission 2004). A $19 billion price tag has been placed on restoring the Chesapeake Bay to a less-impacted state, and

the bulk of these funds have been allocated to improving water quality (Chesapeake Bay Commission 2004). To this end, the cost-effectiveness of various nutrient and sediment reduction strategies has been assessed (Table 3-4).

Largely because of examples like the Patuxent, WWTP upgrades are listed as the nutrient reduction strategy carrying the highest degree of confidence for consistent, long-term nutrient reductions (Chesapeake Bay Commission 2004). State of the art nutrient reduction technologies allow N and P reductions to 2 and 0.1 mg L^{-1} respectively, and 3 mg L^{-1} is considered a widely-attainable goal for nitrogen. Though all facilities would not likely strive for the 3 mg L^{-1} standard initially, substantial reductions could be achieved for N and P using less advanced technologies. Other cost-effective nutrient control strategies include adjusting feed formulation for poultry and livestock to reduce N and P in excreta; continuation of traditional nutrient management, which is the most widespread management practice currently in use and includes prescriptions for timing of fertilizer application and other best management practices; enhanced nutrient management, which encourages fertilizer application based on typical, rather than ideal growing conditions; conservation tillage practices (which could provide 100% of the estimated sediment reduction needs in the Chesapeake); and cover crops, both early and late season (Chesapeake Bay Commission 2004).

Valuing ecosystem (marsh) nutrient control

Valuing ecosystem services like nutrient removal by tidal marshes is an inherently difficult undertaking because no ecosystem has ever produced a bill for services rendered (e.g. Turner et al. 1993; Costanza 1999). Constructed wetlands for wastewater

Table 3-4. Estimated annual load reductions and costs associated with the six most cost-effective nutrient management strategies for the Chesapeake Bay (data from Chesapeake Bay Commission 2004).

Strategy	Reduction potential (kg x 10^6) N	Cost per kg ($) N	Reduction potential (kg x 10^6) P	Cost per kg ($) P
Wastewater treatment plant upgrades*	15.91	18.83	1.36	162.80
Diet and feed adjustments**	ND	ND	0.10	-6.60
Traditional nutrient management	6.18	3.65	0.36	62.17
Enhanced nutrient management	10.77	9.70	0.36	210.74
Conservation tillage***,#	5.45	3.45	1.18	0.00
Late cover crops***,#	6.90	7.70	0.10	0.00
Early cover crops***,#	3.68	5.13	0.10	0.00
Total	48.89		3.57	

ND = no data were available

*Point source management strategy. All other strategies are for non-point source nutrients.

**There are potential net savings of \$6.60 kg^{-1} since reduced P inputs would lower the cost of feed; not evaluated for N.

***Implementation is the same for both N and P, so after strategies are put in place for N management, P management is essentially free.

#These techniques have the added benefit of sediment removal, at 1.68 million tons for conservation tillage and 0.11 million tons each for late and early cover crops; all benefits accrue at no additional cost after the strategies are implemented for N removal

treatment constitute a group of wetlands to which traditional economics are more easily applied. During the past 30 years, constructed wetlands have become a frequent option chosen in waste management due to the appeal and potentially lower costs of natural technology (Kadlec and Knight 1996). The costs of treatment wetlands are incurred overwhelmingly in the installation phase, and wetlands that remain operational long enough (>20 years) are generally a less-expensive waste treatment option than traditional technologies serving the same purpose (Steer et al. 2003). Costs and benefits are more easily evaluated for treatment wetlands than for natural wetlands, as there are construction costs associated with treatment wetlands, as well as technological analogues. Another important distinction between treatment and natural wetlands is that treatment wetlands are often designed only to deal with point source nutrients, whereas natural wetlands receive (and can remove) diffuse inputs as well. There are no installation or operational costs associated with natural wetlands, and there is no equivalent technology for removal of non-point source nutrients (though there are strategies for *reduction* of non-point nutrient discharge).

The cost associated with removal of N and P by WWTP's provides a simple indicator of the value of point source nutrient removal. The cost illustrates, in a loose sense, societal willingness-to-pay for nutrient removal, and can thus be used as a proxy for value. The costs of advanced N and P removal technologies are incurred primarily during the installation/addition phase, rather than during day-to-day operations, so it is these initial costs which provide the best indicator of value. The cost of upgrading Chesapeake basin WWTP's to incorporate advanced nutrient reduction measures has been estimated at \$18.83 and \$162.80 kg^{-1} for N and P, respectively (Table 3-4).

Considering only the cost of point source nutrient removal technology, and the fact that upper Patuxent marshes remove 8.14 and 1.03 kg x 10^5 N and P yr^{-1}, respectively, tidal marsh nutrient removal in the upper Patuxent could be valued at $32 million, annually (Table 3-5).

Table 3-5. Valuation of nutrient removal by upper Patuxent marshes based on the cost of point source nutrient removal and on the weighted average cost of non-point source nutrient reduction (Chesapeake Bay Commission 2004; this study).

	Non-Point Source Nutrients	Point Source Nutrients
Cost/value of nutrient removal ($ kg^{-1} N, $ kg^{-1} P)	6.60, 44.80	18.80, 162.80
Nutrient removal by upper Patuxent marshes (kg N yr^{-1} x 10^6,kg N yr^{-1} x 10^6)	8.1, 1.0	8.1, 1.0
Value of upper Patuxent marsh nutrient removal ($ yr^{-1} x 10^6)	10	32

Tidal marsh nutrient removal is perhaps more appropriately valued based on the cost of non-point source nutrient management. There are five strategies currently under consideration for non-point source nutrient management in the Chesapeake basin (Table 3-6). Management strategies under serious consideration by policy organizations indicate that the most economical non-point nutrient reduction options for the Chesapeake and its tributaries range in cost from $3.45 to $9.70 kg^{-1} for N removal and from -$6.62 to +$210.74 kg^{-1} for P removal. At the scale of the entire Chesapeake basin, total potential for non-point N and P removal using the five most cost-effective strategies is 32.98 x 10^6 kg N yr^{-1} and 2.20 x 10^6 kg P yr^{-1} (Table 3-6). Using the average cost of non-point nutrient reduction strategies, weighted according to reduction potential ($6.61 kg^{-1} N and $44.76 kg^{-1} P), tidal marsh nutrient removal in the upper Patuxent can be valued at $10 million per year (Table 3-5).

Valuation of nutrient removal by tidal marshes, using the costs of technological alternatives as indicators, suggests a range of values for Patuxent marsh nutrient removal services. Which value to use, and even the legitimacy of techniques employed to derive these values, are always in question when traditional economics are applied to nature. Whatever the price tag one wishes to place on marsh nutrient removal, this study demonstrates that tidal marshes perform services for which Chesapeake basin legislators and their constituents are willing to pay. Moreover, marshes provide these services to an ecologically significant extent, at no cost. In a synthesis of current knowledge on the history and ecological impacts of eutrophication in the Chesapeake Bay, Kemp et al. (2005) wrote, "It is ironic that many of the Bay's tidal marshes, which arose in the 18th century as a consequence of eroding agricultural lands, have become effective buffers reducing sediment and nutrient loads from watershed to estuary." Perhaps "ironic" is too negative a word, at least at this stage of the nutrient story, for the Patuxent River basin.

Table 3-6. Estimated annual load reductions and costs associated with the five most cost-effective non-point nutrient management strategies for the Chesapeake Bay (Chesapeake Bay Commission 2004).

	Nitrogen				Phosphorus			
Strategy	Reduction potential (kg x 10^6)	Cost per kg ($)	Fraction of total reduction potential (kg)	Weighted Cost per kg ($)	Reduction potential (kg x 10^6) P	Cost per kg ($) P	Fraction of total reduction potential (kg)	Weighted Cost per kg ($)
Diet and feed adjustments	ND	ND	--	--	0.10	-6.60	0.05	-0.30
Traditional nutrient management	6.18	3.65	0.19	0.68	0.36	62.17	0.17	10.26
Enhanced nutrient management	10.77	9.70	0.33	3.17	0.36	210.74	0.17	34.79
Conservation tillage	5.45	3.45	0.17	0.57	1.18	0.00	0.53	0.00
Late cover crops	6.90	7.70	0.21	1.61	0.10	0.00	0.04	0.00
Early cover crops	3.68	5.13	0.11	0.57	0.10	0.00	0.04	0.00
Total	32.98			6.61	2.20			44.76

APPENDIX:
NUTRIENT (NO_3, NH_4, PO_4), O_2 AND N_2 FLUXES FOR ALL MARSH ENVIRONMENTS AT JUG BAY AND KING'S LANDING MARSHES, APRIL – OCTOBER, 2004

NH_4 fluxes measured at Jug Bay and King's Landing marshes, in all marsh and marsh creek environments, April through October, 2004. Fluxes are given in µmoles N m^{-2} h^{-1}. "NI" indicates non-interpretable fluxes; "ND" indicates that no data were collected. Some data are mean values for replicate cores collected in a single location; these are marked with an asterisk "*".

Month		Jug Bay marsh surface	King's Landing marsh surface		Jug Bay marsh creek		King's Landing marsh creek	Jug Bay avg. control	King's Landing avg. control
1 (April)	Low marsh	NI	227	Head	NI	Main	79		
	Mid marsh	-6*	-118*	Middle	206*	Secondary	156	NI	-107
	High marsh	-53	ND	Mouth	164	Primary	NI (near 0)		
2 (May)	Low marsh	56	NI (near 0)	Head	345	Main	119		
	Mid marsh	186*	90*	Middle	487*	Secondary	0*	62	0
	High marsh	176	ND	Mouth	648	Primary	89		
3 (June)	Low marsh	158	NI	Head	516	Main	111		
	Mid marsh	113*	0*	Middle	305	Secondary	26	7	15
	High marsh	211	13	Mouth	410	Primary	32		
4 (July)	Low marsh	58	64	Head	145	Main	36		
	Mid marsh	104*	7	Middle	272	Secondary	75	0	0
	High marsh	NI	0	Mouth	221	Primary	93		
5 (Aug)	Low marsh	272	0	Head	162	Main	45		
	Mid marsh	-1*	0*	Middle	563	Secondary	NI	-6	0
	High marsh	-37	0	Mouth	129	Primary	59		
6 (Sept)	Low marsh	0	0	Head	ND	Main	496		
	Mid marsh	0*	9*	Middle	128	Secondary	ND	54	0
	High marsh	0	ND	Mouth	ND	Primary	ND		
7 (Oct)	Low marsh	59*	0	Head	20	Main	31		
	Mid marsh	0	-24	Middle	35	Secondary	ND	-12	-11
	High marsh	NI (near 0)	17*	Mouth	41	Primary	ND		

NO_3 fluxes measured at Jug Bay and King's Landing marshes, in all marsh and marsh creek environments, April through October, 2004. Fluxes are given in µmoles N m^{-2} h^{-1}. "NI" indicates non-interpretable fluxes; "ND" indicates that no data were collected. Some data are mean values for replicate cores collected in a single location; these are marked with an asterisk "*".

Month		Jug Bay marsh surface	King's Landing marsh surface		Jug Bay marsh creek		King's Landing marsh creek	Jug Bay avg. control	King's Landing avg. control
1 (April)	Low marsh	-65	-155	Head	-73	Main	-57		
	Mid marsh	-155*	8*	Middle	-129*	Secondary	-92	NI	0
	High marsh	-3	ND	Mouth	-94	Primary	-88		
2 (May)	Low marsh	8	-40	Head	zero or NI	Main	-80		
	Mid marsh	-21*	-147*	Middle	-15*	Secondary	-71*	-8	NI (near 0)
	High marsh	-48	-78	Mouth	-11	Primary	-75		
3 (June)	Low marsh	-16	-32	Head	-29	Main	-184		
	Mid marsh	-16*	8*	Middle	-28	Secondary	-19	-3	8
	High marsh	NI (near 0)	-6	Mouth	-46	Primary	-21		
4 (July)	Low marsh	NI	NI	Head	-14	Main	-106		
	Mid marsh	-18*	NI (near 0)	Middle	-21	Secondary	-111	-14	NI (near 0)
	High marsh	-54	NI	Mouth	-17	Primary	-23		
5 (Aug)	Low marsh	13	NI	Head	10	Main	-88		
	Mid marsh	NI (near 0)*	-47*	Middle	NI (near 0)	Secondary	-276	2	NI/-50.53
	High marsh	NI (near 0)	-30	Mouth	-7	Primary	-73		
6 (Sept)	Low marsh	NI	-25	Head	ND	Main	0		
	Mid marsh	NI*	-17*	Middle	NI	Secondary	ND	NI	-7
	High marsh	ND	ND	Mouth	ND	Primary	ND		
7 (Oct)	Low marsh	-65*	NI (near 0)	Head	NI	Main	0		
	Mid marsh	-142	-34	Middle	-31	Secondary	ND	NI (near 0)	0
	High marsh	-82	-29*	Mouth	-42	Primary	ND		

PO_4 fluxes measured at Jug Bay and King's Landing marshes, in all marsh and marsh creek environments, April through October, 2004. Fluxes are given in µmoles P m^{-2} h^{-1}. "NI" indicates non-interpretable fluxes; "ND" indicates that no data were collected. Some data are mean values for replicate cores collected in a single location; these are marked with an asterisk "*".

Month		Jug Bay marsh surface	King's Landing marsh surface		Jug Bay marsh creek		King's Landing marsh creek	Jug Bay avg. control	King's Landing avg. control
1 (April)	Low marsh	NI	0	Head	0	Main	0		
	Mid marsh	NI*	-1*	Middle	0*	Secondary	2	NI	-7
	High marsh	0	ND	Mouth	NI	Primary	0		
2 (May)	Low marsh	8	6	Head	NI	Main	7		
	Mid marsh	NI*	8*	Middle	NI*	Secondary	38*	NI	-7
	High marsh	14	0	Mouth	5	Primary	3		
3 (June)	Low marsh	0	4	Head	2	Main	20		
	Mid marsh	2*	0*	Middle	0	Secondary	15	0	-2
	High marsh	16	0	Mouth	7	Primary	-4		
4 (July)	Low marsh	31	0	Head	10	Main	0		
	Mid marsh	7*	0	Middle	NI	Secondary	21	4	0
	High marsh	23	0	Mouth	NI	Primary	10		
5 (Aug)	Low marsh	NI	-19	Head	-9	Main	0		
	Mid marsh	3*	5*	Middle	-7	Secondary	30	-20	-9
	High marsh	-26	1	Mouth	5	Primary	7		
6 (Sept)	Low marsh	NI	-5	Head	ND	Main	2		
	Mid marsh	5*	1*	Middle	NI	Secondary	ND	6	-5
	High marsh	ND	ND	Mouth	ND	Primary	ND		
7 (Oct)	Low marsh	0*	NI/0	Head	NI	Main	NI/0		
	Mid marsh	-5	-4	Middle	NI	Secondary	ND	-4	-3
	High marsh	NI	-6*	Mouth	-5	Primary	ND		

O_2 fluxes measured at Jug Bay and King's Landing marshes, in all marsh and marsh creek environments, April through October, 2004. Fluxes are given in µmoles O_2 m^{-2} h^{-1}. "NI" indicates non-interpretable fluxes; "ND" indicates that no data were collected. Some data are mean values for replicate cores collected in a single location; these are marked with an asterisk "*".

Month		Jug Bay marsh surface	King's Landing marsh surface		Jug Bay marsh creek		King's Landing marsh creek	Jug Bay avg. control	King's Landing avg. control
1 (April)	Low marsh	-1170	-1215	Head	-1429	Main	-1243		
	Mid marsh	-1667*	-1571*	Middle	-1282*	Secondary	-1293	-84	-390
	High marsh	-841	ND	Mouth	-1203	Primary	-1502		
2 (May)	Low marsh	-2128	-684	Head	-1119	Main	-1652		
	Mid marsh	-2218*	-2766*	Middle	-2643*	Secondary	NI/0*	-858	-286
	High marsh	-3888	ND	Mouth	-3139	Primary	-766		
3 (June)	Low marsh	-2482	-744	Head	-4070	Main	-3047		
	Mid marsh	-1797*	-1448*	Middle	-2305	Secondary	-1724	-561	-289
	High marsh	NI (large)	-2047	Mouth	-3676	Primary	-1043		
4 (July)	Low marsh	-2387	-1505	Head	-3400	Main	-2137		
	Mid marsh	-2710*	-1906	Middle	-1217	Secondary	-3629	-449	-263
	High marsh	-3962	-5177	Mouth	-2165	Primary	-1379		
5 (Aug)	Low marsh	-2293	-2103	Head	-2378	Main	-1587		
	Mid marsh	-4224*	-2276*	Middle	-1667	Secondary	-5293	-411	-230
	High marsh	-3870	-1258	Mouth	-1888	Primary	-2418		
6 (Sept)	Low marsh	-1511	-2291	Head	ND	Main	-1276		
	Mid marsh	-2799*	-1910*	Middle	-950	Secondary	ND	-372	-409
	High marsh	ND	ND	Mouth	ND	Primary	ND		
7 (Oct)	Low marsh	-1425*	-749	Head	-470	Main	-1004		
	Mid marsh	-4525	-1109	Middle	-516	Secondary	ND	-253	-116
	High marsh	-1703	-2055*	Mouth	-1100	Primary	ND		

N_2 fluxes measured at Jug Bay and King's Landing marshes, in all marsh and marsh creek environments, April through October, 2004. Fluxes are given in µmoles N m^{-2} h^{-1}. "NI" indicates non-interpretable fluxes; "ND" indicates that no data were collected. Some data are mean values for replicate cores collected in a single location; these are marked with an asterisk "*".

Month		Jug Bay marsh surface	King's Landing marsh surface		Jug Bay marsh creek		King's Landing marsh creek	Jug Bay avg. control	King's Landing avg. control
1 (April)	Low marsh	251	243	Head	181	Main	245	121	92
	Mid marsh	211*	184*	Middle	131*	Secondary	165		
	High marsh	96	ND	Mouth	130	Primary	170		
2 (May)	Low marsh	175	127	Head	0	Main	NI/177	16	0 or NI
	Mid marsh	0*	389*	Middle	41*	Secondary	0*		
	High marsh	470	ND	Mouth	118	Primary	50		
3 (June)	Low marsh	195	70	Head	36	Main	212	56	-1
	Mid marsh	76*	137*	Middle	NI or 0	Secondary	141		
	High marsh	26	NI	Mouth	NI	Primary	76		
4 (July)	Low marsh	217	138	Head	118	Main	86	0	NI
	Mid marsh	130*	104	Middle	NI	Secondary	78		
	High marsh	282	846	Mouth	-62	Primary	72		
5 (Aug)	Low marsh	-116	217	Head	0	Main	0	-41	0
	Mid marsh	215*	213*	Middle	54	Secondary	221		
	High marsh	512	0	Mouth	-159	Primary	81		
6 (Sept)	Low marsh	50*	NI	Head	ND	Main	-99		
	Mid marsh	148	106*	Middle	107	Secondary	nd	189	-103
	High marsh	ND	nd	Mouth	ND	Primary	nd		
7 (Oct)	Low marsh	109*	16	Head	0	Main	0		
	Mid marsh	135	176	Middle	NI	Secondary	nd		
	High marsh	143	126*	Mouth	33	Primary	nd	40	0

REFERENCES

An, S. and S.B. Joye. 2001. Enhancement of coupled nitrification-denitrification by benthic photosynthesis in shallow estuarine sediments. Limnology & Oceanography **46:** 62-74.

Anderson, I., C. Tobias, B. Neikirk and R. Wetzel. 1997. Development of a process-based nitrogen mass balance model for a Virginia (USA) *Spartina alterniflora* salt marsh: Implications for net DIN flux. Marine Ecology Progress Series **159:** 13-27.

Armentano, T.V. and G.M. Woodwell. 1975. Sedimentation rates in a Long Island marsh determined by 210Pb dating. Limnology & Oceanography **20:** 452-255.

Bachand, P. and A.J. Horne. 2000. Denitrification in constructed free-water surface wetlands: I. Very high nitrate removal rates in a macrocosm study. Ecological Engineering **14:** 9-15.

Bailey, E. 2005. Measurements of nutrient and oxygen fluxes in estuarine and coastal marine sediments: literature review and data report, p. 13. University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory.

Baird, D. and P.D. Winter. 1992. Flux of inorganic nutrients and particulate carbon between a *Spartina maritima* salt marsh and the Swartkops Estuary, Eastern Cape. Southern African journal of aquatic sciences **18:** 64-73.

Baird, D. and R. Ulanowicz. 1989. The seasonal dynamics of the Chesapeake Bay ecosystem. Ecological Monographs **59:** 329-364.

Beaulac, M.N. and K.H. Reckhow. 1982. An examination of land use-nutrient export relationships. Water Resources Bulletin **18:** 1013-1024.

Bowden, W.B. 1984. Nitrogen and phosphorus in the sediments of a tidal freshwater marsh in Massachusetts. Estuaries **7:** 108-118.

---. 1986. Nitrification, nitrate reduction and nitrogen immobilization in a tidal freshwater marsh sediment. Ecology **67:** 88-99.

Boynton, W.R. and W.M. Kemp. 1985. Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. Marine Ecology Progress Series **23:** 45-55.

Boynton, W.B., J.H. Garber, R. Summers and W.M. Kemp. 1995. Inputs, transformations and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. Estuaries **18:** 285-314.

Boynton, W.R., F.M. Rohland and J.M. Frank. 1998. Sediment oxygen and nutrient exchanges (SONE) program: 1997 Patuxent River study. *In* W.R. and F.M. Rohland Boynton [ed.], Maryland Chesapeake Bay Water Quality Monitoring Program Ecosystem Processes Component. Level One Report No. 15. Interpretive Report. Maryland Department of Natural Resources, Annapolis, Maryland.

Boynton, W.R. and W.M. Kemp. 2005. Nitrogen in estuaries. *In* D. Capone, D. Bronk, M. Mulholland and E. Carpenter [ed.], Nitrogen in the marine environment, 2nd Ed. Academic Press, New York *in press*.

Breitburg, D. 2002. Effects of hypoxia, and the balance between hypoxia and enrichment, on coastal fishes and fisheries. Estuaries **25:** 767-781.

Breitburg, D.L., A. Adamack, K.A. Rose, S.E. Kolesar, M.B. Decker, J.E. Purcell, J.E. Keister and J.H. Cowan Jr. 2003. The pattern and influence of low dissolved oxygen in the Patuxent River, a seasonally hypoxic estuary. Estuaries **26:** 280-297.

Brettar, I. and G. Rheinheimer. 1992. Influence of carbon availability on denitrification in the central Baltic Sea. Limnology & Oceanography **37:** 1146-1163.

Bricker, S.B., C.G. Clement, D.E. Pirhalla, S.P. Orlando and D.R.G. Farrow. 1999. National estuarine eutrophication assessment: effects of nutrient enrichment in the nation's estuaries. National Oceanic and Atmospheric Association. 87 p.

Bricker-Urso, S., S.W. Nixon, J.K. Cochran, JK, D.J. Hirschberg and C. Hunt. 1989. Accretion rates and sediment accumulation in Rhode Island salt marshes. Estuaries **12:** 300-317.

Brush, G.S. 1984. Patterns of recent sediment accumulation in Chesapeake Bay (Virginia-Maryland, U.S.A.) tributaries. Chemical Geology **44:** 227-242.

---. 1989. Rates and patterns of estuarine sediment accumulation. Limnology and Oceanography **7:** 1235-1246.

Brush, G.S. and W.B. Hilgartner. 2000. Paleoecology of submerged macrophytes in the upper Chesapeake Bay. Ecological Monographs **70:** 645-667.

Caddy, J.F. 1993. Toward a comparative evaluation of human impacts on fishery ecosystems of enclosed and semi-enclosed seas. Reviews in Fisheries Science **1:** 57-95.

Caffrey, J.M. and W.M. Kemp. 1992. Influence of the submersed plant, *Potamogeton perfoliatus*, on nitrogen cycling in estuarine sediments. Limnology & Oceanography **37:** 1483-1495.

Castro, M.S., C.T. Driscoll, T.E. Jordan, W.G. Reay, W.R. Boynton, S.P. Seitzinger, R.V. Styles, and J.E. Cable. 2001. Contribution of atmospheric deposition to the total nitrogen loads to thirty four estuaries on the Atlantic and Gulf coasts of the United States., p. 77-106. *In* R.M. Valigura et al. [ed.], Nitrogen Loading in Coastal Water Bodies: an Atmospheric Perspective. American Geophysical Union, Washington D.C.

Castro, M.S., C.T. Driscoll, T.E. Jordan, W.G. Reay and W.R. Boynton. 2003. Sources of nitrogen to estuaries in the United States. Estuaries **26:** 803-814.

Chaney, E. 2005. Personal communication regarding the history of population of the Patuxent watershed.

Chesapeake Bay Watershed Blue Ribbon Finance Panel. 2004. Saving a national treasure: financing the cleanup of the Chesapeake Bay, p. 40. Chesapeake Bay Program.

Chesapeake Bay Commission. 2004. Cost-effective strategies for the Bay, p. 20. Chesapeake Bay Commission. Annapolis, Maryland.

Cloern, J.E. 2001. Our evolving conceptual model of the coastal eutrophication problem. Marine Ecology Progress Series **210:** 223-253.

Cornwell, J.C. and P.A. Sampou. 1995. Environmental controls on iron sulfide mineral formation in a coastal plain estuary, p. 224-242. *In* M.A. Vairavamurthy and M.A. Schoonen [ed.], Geochemical Transformations of Sedimentary Sulfur. American Chemical Society.

Cornwell, J.C., D.J. Conley, M. Owens and J.C. Stevenson. 1996. A sediment chronology of the eutrophication of Chesapeake Bay. Estuaries **19:** 488-499.

Cornwell, J.C., W.M. Kemp and T.M. Kana. 1999. Denitrification in coastal ecosystems: methods, environmental controls, and ecosystem level controls, a review. Aquatic Ecology **33:** 41-54.

Costanza, R. 1999. The ecological, economic, and social importance of the oceans. Ecological Economics **31:** 199-213.

Cowan, J.L. and W.R. Boynton. 1996. Sediment-water oxygen and nutrient exchanges along the longitudinal axis of Chesapeake Bay: Seasonal patterns, controlling factors and ecological significance. Estuaries **19:** 562-580.

Craft, C.B. and C.J. Richardson. 1993. Peat accretion and N,P and organic accumulation in nutrient-enriched and unenriched Everglades peatlands. Ecological Applications **3:** 446-458.

Cronin, W.B. and D.W. Pritchard. 1975. Additional statistics on the dimensions of the Chesapeake Bay and its tributaries: cross-section widths and segment volumes per meter depth. CBI Spec. Rep. 42. Johns Hopkins University. Baltimore, Maryland. 475 p.

Cronin, T.M. and C.D. Vann. 2003. The sedimentary record of climatic and anthropogenic influence on the Patuxent Estuary and Chesapeake Bay ecosystems. Estuaries **26:** 196-209.

Culliton, T.J., M.A. Warren, T.R. Goodspeed, D.G. Remer, C.M. Blackwell and J.J. McDonough III. 1990. 50 years of population change along the nation's coasts, 1960-2010. National Oceanic and Atmospheric Administration, Strategic Assessment Branch, Rockville, MD. 41 p.

Currin, C.A., S.B. Joye and H.W. Paerl. 1996. Diel rates of N2-fixation and denitrification in a transplanted *Spartina alterniflora* marsh: implications for N-flux dynamics. Estuarine, Coastal and Shelf Science **42:** 597-616.

Currin, C.A. and H.W. Paerl. 1998. Epiphytic nitrogen fixation associated with standing dead shoots of smooth cordgrass, *Spartina alterniflora*. Estuaries **21:** 108-117.

Curtin, P.D., G.S. Brush and G.W. Fisher. 2001. Discovering the Chesapeake: history of an ecosystem. The Johns Hopkins University Press.

D'Elia, C.F., J.G. Sanders and W.R. Boynton. 1986. Nutrient enrichment studies in a coastal plain estuary: phytoplankton growth in large-scale, continuous cultures. Canadian Journal of Fisheries and Aquatic Sciences **43:** 397-406.

D'Elia, C.F., W.R. Boynton and J.G. Sanders. 2003. A watershed perspective on nutrient enrichment, science and policy in the Patuxent River, Maryland: 1960-2000. Estuaries **26:** 171-185.

Dauer, D.M., J.A. Ranasinge and S.B. Weisberg. 2000. Relationships between benthic community condition, water quality, sediment quality, nutrient loads, and land use patterns in Chesapeake Bay. Estuaries **23:** 80-96.

De Leiva Moreno, J.I., V.N. Agostini, J.F. Caddy and F. Carocci. 2000. Is the pelagic-demersal ratio from fishery landings a useful proxy for nutrient availability? A preliminary data exploration for the semi-enclosed seas around Europe. ICES Journal of Marine Science **57:** 1091-1102.

Deegan, L.A. 1993. Nutrient and energy transport between estuaries and coastal marine ecosystems by fish migration. Canadian Journal of Fisheries and Aquatic Sciences **50:** 74-79.

DeFries, R. 1986. Effects of land-use history on sedimentation in the Potomac estuary, p. 23. U.S. Geological Survey. Water-Supply Pap. 2234-K. 23 p.

DeLaune, R.D., C.N. Reddy and W.H. Patrick Jr. 1981. Accumulation of plant nutrients and heavy metals through sedimentation processes and accretion in a Louisiana salt marsh. Estuaries **4:** 328-334.

Diaz, R. and R. Rosenberg. 1995. Marine benthic hypoxia: a review of its ecological effects and the behavioral responses of benthic macrofauna. Oceanogr. Mar. Biol. Ann. Rev. **33:** 245-303.

Dong, L.F., D.C. Thornton, D.B. Nedwell, and G.J. Underwood. 2000. Denitrification in sediments of the River Colne estuary, England. Marine Ecology Progress Series **203:** 109-122.

Drake, L.A., F.C. Dobbs and R.C. Zimmerman. 2003. Effects of epiphyte load on optical properties and photosynthetic potential of the seagrasses *Thalassia testudinum* Banks ex Koenig and *Zostera marina L*. Limnology & Oceanography **48:** 456-463.

Eshleman, K.N., R.H. Gardner, S.W. Seagle, N.M. Castro, D.A. Fiscus, J.R. Webb, J.N. Galloway, F.A. Deviney and A.T. Herlihy. 2000. Effects of disturbance on nitrogen export from forested lands of the Chesapeake Bay watershed. Environmental Monitoring and Assessment **63:** 187-197.

Eyre, B.D., S. Rysgaard, T. Dalsgaard and P.B. Christensen. 2002. Comparison of isotope pairing and N sub(2):Ar methods for measuring sediment denitrification - assumptions, modifications, and implications. Estuaries **25:** 1077-1087.

Fisher, T.R., A.B. Gustafson, K. Sellner, R. Lacouture, L.W. Haas, R.L. Wetzel, R. Magnien, D. Everitt, B. Michaels and R. Karrh. 1999. Spatial and temporal variation of resource limitation in Chesapeake Bay. Marine Biology **133:** 763-778.

Fisher, T.R., J.D. Hagy III, W.R. Boynton and M.R. Williams. 2005. Cultural eutrophication in the Choptank and Patuxent estuaries of Chesapeake Bay. Limnology & Oceanography *in press*.

Fisher, T.R., M. Williams, G. Radcliffe, W.R. Boynton, S. Greene, W.M. Kemp, J. Testa, R. Hood, K. Eshleman, D. Fiscus, C. Cerco and S-C. Kim. 2005. Evaluation of an integrated modeling system of watershed and estuarine ecology for management of the Patuxent basin. Maryland Department of the Environment. 70 p.

Flemer, D.A., D. Heyward Hamilton, C.W. Keefe and J.A. Mihursky. 1970. Final report to Office of Water Resources Research on the effects of thermal loading and water quality on estuarine primary production. University of Maryland Natural Resources Institute, Chesapeake Biological Laboratory, Solomons, Maryland. 217 p.

Flynn, W.W. 1968. The determination of low levels of polonium-210 in environmental materials. Analytica Chimica Acta **43:** 221-227.

Froelich, P.N. 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: a primer on the phosphate buffer mechanism. Limnology & Oceanography **33:** 649-668.

Gosselink, J.G., E.P. Odum and R.M. Pope. 1973. The value of the tidal marsh. Louisiana State Univ. Agricult. Mech. Coll. Cent. Wetland Resour. Sea Grant Program, Baton Rouge, Louisiana. 34 p.

Gottschalk, L.C. 1945. Effects of soil erosion on navigation in upper Chesapeake Bay. Geographical Revue **35:** 219-237.

Greene, S.E. 2005. Measurements of denitrification in aquatic ecosystems: literature review and data report. University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, Solomons, Maryland. 29 p.

Hagy, J.D. III, W.R. Boynton and M.M. Weir. 1998. Estimating nitrogen and phosphorus loads for Patuxent River, 1960-1977, p. 184-211. *In* W.R. Boynton and F.M. Rohland [ed.], Chesapeake Bay Water Quality Monitoring Program Ecosystem Processes Component: Level One Report. No.15 Interpretive Report. University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, Solomons, MD.

Hagy, J.D., W.R. Boynton, C.W. Keefe and K.V. Wood. 2004. Hypoxia in Chesapeake Bay, 1950-2001: long-term change in relation to nutrient loading and river flow. Estuaries **27:** 634-658.

Haramis, M. 1997. The effect of nutria (*Myocastor coypus*) on marsh loss in the lower Eastern Shore of Maryland: an exclosure study. U.S. Geological Survey, Biological Resource Division, Patuxent Wildlife Research Center, Laurel, Maryland.

Heinle, D.R. and D.A. Flemer. 1976. Flows of materials between poorly flooded tidal marshes and an estuary. Marine Biology **35:** 359-373.

Heinle, D.R., C.F. D'Elia, J.L. Taft, J.S. Wilson, M. Cole-Jones, A.B. Caplins and L.E. Cronin. 1980. Historical review of water quality and climatic data from Chesapeake Bay with emphasis on effects of enrichment. Grant # R806189010. USEPA Chesapeake Bay Program Final Report. Publication No. 84. Chesapeake Research Consortium, Inc., Annapolis, Maryland.

Heywood, M.A. 1977. The effects of nutrient enrichment on the decomposition of *Spartina cynosuroides* and *Peltandra virginica*. Master's Thesis. University of Virginia.

Howell, P. and D. Simpson. 1994. Abundance of marine resources in relation to dissolved oxygen in Long Island Sound. Estuaries **17:** 394-402.

Hutchinson, G.E. 1969. Eutrophication, past and present., *In* Eutrophication: Causes, Consequences, and Correctives; Proceedings of a Symposium. National Academy of Sciences.

Jenkins, M.C. and W.M. Kemp. 1984. The coupling of nitrification and denitrification in two estuarine sediments. Limnology & Oceanography **29:** 609-619.

Jones, J.C. and J.D. Reynolds. 1999. Costs of egg ventilation for male common gobies breeding in conditions of low dissolved oxygen. Animal Behaviour **57:** 181-188.

Jordan, T.E., D.L. Correll, D.E. Weller and N.M. Goff. 1995. Temporal variation in precipitation chemistry on the shore of the Chesapeake Bay. Water, Air and Soil Pollution **83:** 263-284.

Jordan, T.E., D.E. Weller, and D.L. Correll. 2003. Sources of Nutrient Inputs to the Patuxent River Estuary. Estuaries **26:** 226-243.

Joye, S.B. and H.W. Paerl. 1993. Contemporaneous nitrogen fixation and denitrification in intertidal microbial mats: Rapid response to runoff events. Marine Ecology Progress Series **94:** 267-274.

Joye, S.B. and J.T. Hollibaugh. 1995. Influence of sulfide inhibition of nitrification on nitrogen regeneration in sediments. Science **270:** 623-625.

Kadlec, R.H. and R.L. Knight. 1996. Treatment wetlands. Lewis Publishers, Boca Raton, Florida. 893 p.

Kana, T.M, C. Darkangelo, M.D. Hunt, J.B. Oldham, G.E. Bennett and J.C. Cornwell. 1994. Membrane Inlet Mass Spectrometer for rapid high-precision determination of N2, O2 and Ar in environmental water samples. Analytical Chemistry **66:** 4166-4170.

Kana, T.M., M.B. Sullivan, J.C. Cornwell, and K.M. Groszkowski. 1998. Denitrification in estuarine sediments determined by membrane inlet mass spectrometry. Limnology & Oceanography **43:** 334-339.

Kaplan, W., I. Valiela, and J.M. Teal. 1979. Denitrification in a salt marsh ecosystem. Limnology & Oceanography **24:** 726-734.

Kearney, M.S. and L.G. Ward. 1986. Accretion rates in brackish marshes of a Chesapeake Bay estuarine tributary. Geo-Marine Letters **6:** 41-49.

Kearney, M.S., J.C. Stevenson and L.G. Ward. 1994. Spatial and temporal changes in marsh vertical accretion rates at Monie Bay: implications for sea-level rise. Journal of Coastal Research **10:** 1010-1020.

Keefe, C.W., K.L. Blodnikar, W.R. Boynton, C.A. Clark, J.M. Frank, N.L. Kaumeyer, M.M. and K.V. Wood Weir, C.F. Zimmerman. 2004. Nutrient Analytical Services Laboratory standard operating procedures. University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory.

Kemp, W.M. and W.R. Boynton. 1984. Spatial and temporal coupling of nutrient inputs to estuarine primary production: the role of particulate transport and decomposition. Bulletin of Marine Science **35:** 522-535.

Kemp, W.M., P. Sampou, J. Caffrey and M. Mayer. 1990. Ammonium recycling versus denitrification in Chesapeake Bay sediments. Limnology & Oceanography **35:** 1545-1563.

Kemp, W.M., W. Boynton, J. Adolf, D. Boesch, W. Boicourt, G. Brush, J. Cornwell, T. Fisher, P. Glibert, J. Hagy, L. Harding, E. Houde, D. Kimmel, W. Miller, R. Newell, M. Roman, E. Smith and J.C. Stevenson. 2005. Eutrophication of Chesapeake Bay: historical trends and ecological interactions. Marine Ecology Progress Series *in press*.

Khan, H. and G.S. Brush. 1994. Nutrient and metal accumulation in a freshwater tidal marsh. Estuaries **17:** 345-360.

Koch, M.S., E. Maltby, G.A. Oliver and S.A. Bakker. 1992. Factors controlling denitrification rates of tidal mudflats and fringing salt marshes in south-west England. Estuarine, Coastal and Shelf Science **34:** 471-485.

Koide, M., A. Soutar and E.D. Goldberg. 1972. Marine geochronology with 210Pb. Earth and Planetary Science Letters **14:** 442-446.

Krishnaswamy, S., D. Lal, J.M. Martin and M. Meybeck. 1971. Geochronology of lake sediments. Earth and Planetary Science Letters **11:** 407-414.

Krishnaswamy, S. and D. Lal. 1978. Radionuclide limnochronology, p. 153-177. *In* A. Lerman [ed.], Lakes: Chemistry, Geology, Physics. Springer Verlag.

Krom, M.D. and R.A. Berner. 1980. Adsorbtion of phosphate in anoxic marine sediments. Limnology & Oceanography **25:** 797-806.

---. 1981. The diagenesis of phosphorus in a nearshore marine sediment. Geochimica et Cosmochimica Acta **45:** 207-216.

Lee, K-Y., T.R. Fisher and E. Rochelle-Newall. 2001. Modeling the hydrochemistry of the Choptank River basin using GWLF and Arc/Info: 2. Model validation and application. Biogeochemistry **56:** 311-348.

Magnien, R.E., R.M. Summers and K.G. Sellner. 1992. External nutrient sources, internal nutrient pools, and phytoplankton production in Chesapeake Bay. Estuaries **15:** 497-516.

Maryland Office of Planning. 2001. Patuxent watershed land use data. Maryland Department of Planning, Baltimore, Maryland.

Merrill, J.Z. 1999. Tidal freshwater marshes as nutrient sinks: particulate nutrient burial and denitrification. Dissertation. University of Maryland, College Park, Maryland.

Merrill, J.Z. and J.C. Cornwell. 2000. The role of oligohaline marshes in estuarine nutrient cycling, p. 425-441. *In* M.P. Weinstein and D.A. Kreeger [ed.], Concepts and Controversies in Tidal Marsh Ecology. Kluwer Academic Publishers.

Mitsch, W.J. and S.E. Jorgensen. 2004. Ecological Engineering and Ecosystem Restoration. John Wiley & Sons, Inc., New York, New York. 411 p.

Moore, J.W. and D.E. Schindler. 2004. Nutrient export from freshwater ecosystems by anadromous sockeye salmon (*Oncorhynchus nerka*). Canadian Journal of Fisheries and Aquatic Sciences **61:** 1582-1589.

Mortimer, C.H. 1941. The exchange of dissolved substances between mud and water in lakes. J. Ecology **29:** 280-329.

National Academy of Sciences. 1969. Eutrophication: Causes, Consequences, Correctives. Proceedings of an International Symposium on Eutrophication, University of Wisconsin, 1967., Washington, DC: NAS Printing and Publishing Office. 661 p.

National Estuarine Research Reserve System. 2004. Jug Bay - Chesapeake Bay, MD, Tidal Range. National Oceanic and Atmospheric Administration. Accessed 11/15/05. http://nerrs.noaa.gov/ChesapeakeBayMD/Tidal2.html.

Nearing, M.A., R.M. Risse and L.F. Rogers. 1993. Estimating daily nutrient fluxes to a large piedmont reservoir from limited tributary data. Journal of Environmental Quality **22:** 666-671.

Neckles, H.A., R.L. Wetzel and R.J. Orth. 1993. Relative effects of nutrient enrichment and grazing on epiphyte-macrophyte (*Zostera marina L.*) dynamics. Oecologia **93:** 285-295.

Neubauer, S.C., I.C. Anderson, J.A. Constantine and S.A. Kuehl. 2001. Sediment deposition and accretion in a mid-Atlantic (U.S.A.) tidal freshwater marsh. Estuarine, Coastal and Shelf Science **54:** 713-727.

Nielsen, S.L., K. Sand-Jensen, J. Borum and O. Geertz-Hansen. 2002. Phytoplankton, nutrients and transparency in Danish coastal waters. Estuaries **25:** 930-937.

Nixon, S. W. and C.A. Oviatt. 1973. Ecology of a New England salt marsh. Ecological Monographs **43:** 463-498.

Nixon, S.W. 1980. Between coastal marshes and coastal waters: a review of twenty years of speculation and research on the role of salt marshes in estuarine productivity and water chemistry, p. 437-525. *In* Estuarine and wetland processes with emphasis on modeling. Proceedings of workshop on wetland and estuarine processes and water quality modeling, New Orleans, Louisiana, June 18-20, 1979. Plenum Publishing Corp., New York, New York.

---. 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia **41:** 199-219.

Nixon, S. W. and B.A. Buckley. 2002. A strikingly rich zone - nutrient enrichment and secondary production in coastal marine ecosystems. Estuaries **25:** 782-796.

Odum, W.E. 1968. A research challenge: evaluating the productivity of coastal and estuarine water, Proceedings of the 2nd Sea Grant Conference, University of Rhode Island, Kingston, Rhode Island. p. 63-64.

Odum, W.E. and M.A. Heywood. 1977. Decomposition of intertidal freshwater marsh plants, p. 297. *In* R.E. Good, D.F. Whigham and R.L. Simpson [ed.], Freshwater Marshes: Present Status, Future Needs. Academic Press, Inc., New Brunswick, New Jersey.

Odum, W.E. 1988. Comparative Ecology of Tidal Freshwater and Salt Marshes. Annual Review of Ecology and Systematics **19:** 147-176.

Ohle, W. 1955. Die Ursachen der rasanten Seeneutrophierung. Verh. Intern. Ver. Limnol. **12:** 373-382.

Oldfield, F. and J.P. Appleby. 1984. Empirical testing of super(210)Pb-dating models for lake sediments, p. 93-124. *In* E.Y. and J.G. Lund Haworth [ed.], Lake Sediments and Environmental History. University of Minnesota Press.

Orson, R.A., R.L. Simpson and R.E. Good. 1990. Rates of sediment accumulation in a tidal freshwater marsh. Journal of Sedimentary Petrology **60:** 859-869.

Pardo, L.H., C.T. Driscoll and G.E. Likens. 1995. Patterns of nitrate loss from a chronosequence of clear-cut watersheds. Water, Air and Soil Pollution **85:** 1659-1664.

Porter, E.T., J.C. Cornwell and L.P. Sanford. 2004. Effect of oysters *Crassostrea virginica* and bottom shear velocity on benthic-pelagic coupling and estuarine water quality. Marine Ecology Progress Series **271:** 61-75.

Reddy, K.R., W.H. Patrick and C.W. Lindau Jr. 1989. Nitrification-denitrification at the plant root-sediment interface in wetlands. Limnology & Oceanography **34:** 1004-1013.

Redfield, A.C. 1934. On the proportions of organic derivatives in sea water and their relation to the composition of plankton, p. 176-192. *In* R.J. Daniel [ed.], James Johnstone Memorial Volume. University Press of Liverpool.

Reshetiloff, K., Ed. 1995. Chesapeake Bay: introduction to an ecosystem. US Environmental Protection Agency, Chesapeake Bay Program. Accessed April 26, 2005. http://web.gmu.edu/bios/.

Robbins, J.A. 1978. Geochemical and geophysical applications of radioactive lead, p. 285-405. *In* J.O. Nraigu [ed.], The Biogeochemistry of Lead in the Environment. Elsevier.

Roden, E. E. and J.W. Edmonds. 1997. Phosphate mobilization in iron-rich anaerobic sediments: microbial Fe (III) oxide reduction versus iron-sulfide formation. Archiv fur Hydrobiologie **139:** 347-378.

Rodhe, W. 1969. Crystallization of eutrophication concepts in northern Europe, Eutrophication: Causes, Consequences, and Correctives: Proceedings of a Symposium. National Academy of Sciences, Washington D.C.

Ryther, J.H. and W.M. Dunstan. 1971. Nitrogen, phosphorus, and eutrophication in the coastal marine environment. Science **171:** 1008-1013.

Ryther, J.H., W.M. Dunstan, K.R. Tenore and J.E. Huguenin. 1972. Controlled eutrophication - increasing food production from the sea by recycling human wastes. Bioscience **22:** 144-152.

Santschi, P., P. Hoehener, G. Benoit and M. Buchholtz-ten Brink. 1990. Chemical processes at the sediment-water interface. Marine Chemistry **30:** 269-315.

Schindler, D.W. 1981. Studies of eutrophication in lakes and their relevance to the estuarine environment, p. 71-82. *In* B.J. Neilson and L.E. Cronin [eds.], Estuaries and Nutrients. Humana Press.

Schubel, J.R. and D.J. Hirschberg. 1978. Estuarine graveyards, climatic change, and the importance of the estuarine environment, p. 285-303. *In* M.L. Wiley [ed.], Estuarine Interactions. Academic Press, Inc.

Seitzinger, S.P., S.W. Nixon and M.E. Pilson. 1984. Denitrification and nitrous oxide production in a coastal marine ecosystem. Limnology & Oceanography **29:** 73-83.

Seitzinger, S.P. 1988. Denitrification in freshwater and coastal marine systems: ecological and geochemical significance. Limnology & Oceanography **33:** 702-724.

Seitzinger, S.P., L.P. Nielsen, J. Caffrey and P.B. Christensen. 1993. Denitrification measurements in aquatic sediments: a comparison of three methods. Biogeochemistry **23:** 147-167.

Short, F.T., D.M. Burdick and J.E. Kaldy III. 1995. Mesocosm experiments quantify the effects of eutrophication on eelgrass, *Zostera marina*. Limnology & Oceanography **40:** 740-749.

Simpson, R.L. and D.F. Whigham. 1977. Seasonal patterns of nutrient movement in a freshwater tidal marsh, p. 297. *In* D.F. Whigham and R.L. Simpson R.E. Good [ed.], Freshwater marshes: present status, future needs. Academic Press, Inc.

Simpson, R.L., R.E. Good, R. Walker and B.R. Frasco. 1983a. The role of Delaware River freshwater tidal wetlands in the retention of nutrients and heavy metals. Journal of Environmental Quality **12:** 41-48.

Simpson, R.L., R.E. Good, M.A. Leck and D.F. Whigham. 1983b. The ecology of freshwater tidal wetlands. Bioscience **33:** 255-259.

Smil, V. 1990. Nitrogen and Phosphorus, p. 423 - 436. *In* B. L. Turner [ed.], The Earth as Transformed by Human Action. Cambridge University Press.

Smith, S.V. 1984. Phosphorus versus nitrogen limitation in the marine environment. Limnology and Oceanography **29:** 1149-1160.

Smith, R.A., R.B. Alexander and K.J. Lanfear. 1993. Stream water quality in the conterminous United States - status and trends on selected indicators during the 1980's. U.S. Geological Survey Water-Supply Paper 2400. U.S. Geological Survey, Reston, Virginia.

Sprague, L.A., M.J. Langland, S.E. Yochum, R.E. Edwards, J.D. Blomquist, S.W. Phillips, G.W. Shenk and S.D. Preston. 2000. Factors affecting nutrient trends in major rivers of the Chesapeake Bay watershed. Water Resources Investigations Report 00-4218. United States Geological Survey, Virginia.

Stankelis, R.M., M.D. Naylor and W.R. Boynton. 2003. Submerged aquatic vegetation in the mesohaline region of the Patuxent Estuary: past, present and future status. Estuaries **26:** 186-195.

Steer, D., T. Aseltyne and L. Fraser. 2003. Life-cycle economic model of small treatment wetlands for domestic wastewater disposal. Ecological Economics **44:** 359-369.

Steers, J.A. 1948. Twelve years' measurement of accretion on Norfolk salt marshes. Geological Magazine **85:** 163-166.

Stevenson, J.C., D.R. Heinle, D.A. Flemer, R.J. Small, R.A. Rowland, and J.F. Ustach. 1977. Nutrient exchanges between brackish water marshes and the estuary. *In* M. Wiley [ed.], Estuarine Processes. Academic Press.

Stevenson, J.C., L.G. Ward and M.S. Kearney. 1986. Vertical accretion in marshes with varying rates of sea level rise, p. 241-259. *In* D.A. Wolfe [ed.], Estuarine Variability. Academic Press, Inc.

Stoddart, D.R, D.J. Reed and J.R. French. 1989. Understanding salt-marsh accretion, Scolt Head Island, Norfolk, England. Estuaries **12:** 228-236.

Sundby, B., C. Gobeil, N. Silverberg and A. Mucci. 1992. The phosphorus cycle in marine sediments. Limnology & Oceanography **37:** 1129-1145.

Swarth, C. and D. Peters. 1993. Water quality and nutrient dynamics of Jug Bay on the Patuxent River 1987-1992, p. 110. Jug Bay Wetlands Sanctuary.

Tappin, A.D. 2002. An examination of the fluxes of nitrogen and phosphorus in temperate and tropical estuaries: current estimates and uncertainties. Estuarine, Coastal and Shelf Science **55:** 885-901.

Taylor, D.I. and B.R. Allanson. 1995. Organic carbon fluxes between a high marsh and estuary, and the inapplicability of the Outwelling Hypothesis. Marine Ecology Progress Series **120:** 263-270.

Teal, J.M. 1962. Energy flow in the salt marsh ecosystem of Georgia. Ecology **43:** 614-624.

Teal, J.M., I. Valiela and D. Berlo. 1979. Nitrogen fixation by rhizosphere and free-living bacteria in salt marsh sediments. Limnology & Oceanography **24:** 126-132.

Thompson, S.P., H.W. Paerl and M.C. Go. 1995. Seasonal patterns of nitrification and denitrification in a natural and a restored salt marsh. Estuaries **18:** 399-408.

Todd, J. and B. Josephson. 1996. The design of living technologies for waste treatment. Ecological Engineering **6:** 109-136.

Traband, J. 2003. Removal of wastewater nitrogen and phosphorus by an oligohaline marsh. Master's Thesis. University of Maryland. College Park, Maryland.

Turner, R.K., D. Pearce and I. Bateman. 1993. Environmental economics. The Johns Hopkins University Press.

Tyler, A.C., T.A. Mastronicola and K.J. McGlathery. 2003. Nitrogen fixation and nitrogen limitation of primary production along a natural marsh chronosequence. Oceologia **136:** 431-438.

Valiela, I., M.L. Cole, J. McClelland, J. Hauxwell and J. Cebrian. 2000. Role of salt marshes as part of coastal landscapes, p. 23-38. *In* M.P. Weinstein and P.A. Kreeger [ed.], Concepts and Controversies in Tidal Marsh Ecology. Kluwer Academic Publishers.

Vanderborght, J.P. and G. Billen. 1975. Vertical distribution of nitrate concentration in interstitial water of marine sediments with nitrification and denitrification. Limnology & Oceanography **20:** 953-961.

Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger and D.G. Tilman. 1997. Human alteration of the global nitrogen cycle: sources and consequences. Ecological Applications **7:** 737-750.

Vollenweider, R.A. 1976. Advances in defining critical loading levels for phosphorus in lake eutrophication. Mem. Ist. Ital. Idrobiol. **33:** 53-83.

Ward, L.G., M.S. Kearney and J.C. Stevenson. 1998. Variations in sedimentary environments and accretionary patterns in estuarine marshes undergoing rapid submergence, Chesapeake Bay. Marine Geology **151:** 111-134.

Webb, A.P. and B.D. Eyre. 2004. Effect of natural populations of burrowing thalassinidean shrimp on sediment irrigation, benthic metabolism, nutrient fluxes and denitrification. Marine Ecology Progress Series **268:** 205-220.

Weideman, A. and A. Cosgrove. 1998. Chesapeake Bay watershed model application and calculations of nutrient and sediment loading. Appendix F: Point source loadings. USEPA Chesapeake Bay Program, Annapolis, Maryland.

Weller, D.E., T.E. Jordan, D.L. Correll and Z.J. Liu. 2003. Effects of land-use change on nutrient discharges from the Patuxent River watershed. Estuaries **26:** 244-266.

Whigham, D.F. and R.L. Simpson. 1976. The potential use of tidal marshes in the management of water quality in the Delaware River. *In* J. Tourbier and R.R. Pierson [ed.], Biological Control of Water Pollution. University of Pennsylvania Press, Philadelphia, PA.

White, D.S. and B.L. Howes. 1994. Long-term super(15)N-nitrogen retention in the vegetated sediments of a New England salt marsh. Limnology & Oceanography **39:** 1878-1892.

Williams, M.R., T.R. Fisher, W.R. Boynton, C.F. Cerco, M.W. Kemp, K.N. Eshleman, S.-C. Kim, R.R. Hood, D.A. Fiscus, and G.R. Radcliffe. 2005. An integrated modeling system for management of the Patuxent River estuary and basin, Maryland, USA. International Journal of Remote Sensing *in press*.

Wolaver, T.G., J.C. Zieman, R. Wetzel and K.L. Webb. 1983. Tidal exchange of nitrogen and phosphorus between a mesohaline vegetated marsh and the surrounding estuary in the lower Chesapeake Bay. Estuarine, Coastal and Shelf Science **16:** 321-332.

Wolfenden, J. and K. Jones. 1987. Seasonal variation of in situ nitrogen fixation (C sub(2)H sub(2) reduction) in an expanding marsh of *Spartina anglica*. Journal of Ecology **25:** 1011-1021.

Wood, M.E., J.T. Kelley and D.F. Belknap. 1989. Patterns of sediment accumulation in the tidal marshes of Maine. Estuaries **12:** 237-246.

Zehr, J.P. and B.B. Ward. 2002. Nitrogen cycling in the ocean: new perspectives on processes and paradigms. Applied and Environmental Microbiology **68:** 1015-1024.

Year 2020 Panel Report. 1988. Population growth and development in the Chesapeake Bay Watershed to the year 2020. A Report to the Chesapeake Executive Council. Chesapeake Bay Commission, Annapolis, Maryland.

Zumft, W.G. 1997. Cell biology and molecular basis of denitrification. Microbiology and Molecular Biology Reviews **61:** 533-616.