DENITRIFICATION IN URBAN BROWNFIELD WETLANDS

by

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ABSTRACT OF THE DISSERTATION

Denitrification in Urban Brownfield Ecosystems

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Wetland processes are highly spatially and temporally heterogeneous, and managers lack models relating important wetland processes to specific combinations of biological communities, flooding, and soils. Wetlands in urban settings, while having the potential to deliver ecosystem services (nutrient removal) to urban areas, pose a particular challenge in linking ecosystem processes with their environmental drivers, because urban wetlands have been little studied, and each urban system has its own unique set of altered conditions. These issues are especially true of wetlands that develop on brownfield sites, on highly modified soil materials.

My research questions were the following: (1) Where and when do the highest rates of nitrate removal occur in urban brownfield wetlands, and what are the spatio-temporal dimensions of these high rates?; (2) What are the environmental drivers of nitrate removal rates (via denitrification) in urban brownfield wetlands?; and (3) How can the spatial and temporal dimensions of nitrate removal rates be modeled and predicted to aid in restoration and management at the watershed scale?.

I utilized a combination of lab- and field-based studies to construct models designed to isolate and explain the relationship between environmental variables and soil denitrification in urban wetland environments. Whole-wetland denitrification potential was estimated through spatial interpolation of the variables mediating the highest rates of denitrification at the scale of a couple square meters. I also measured components of the nitrogen and hydrologic cycle in wetlands to construct budgets estimating the role of denitrification in removing nitrate under wet and dry conditions.

My research shows that brownfield wetlands in northern New Jersey support active populations of denitrifying bacteria and are potential sinks for nitrate in urban landscapes. Rates of nitrate consumption in the soils equaled or exceeded the rate of nitrate loading, at least from the atmosphere. Soil structure and texture, water table levels, and landscape position appear to be primary determinants of whether brownfield soils are sinks for nitrate. Modifications to hydrology that promote (1) endogenous nitrate production, particularly in low-oxygen waterlogged areas, and (2) contact between stormwater and soils with high macroporosity may augment levels of nitrate removal from brownfield wetlands.

Dedication

This dissertation is dedicated to Dr. Joan G. Ehrenfeld, a phenomenal mentor and constant source of inspiration. I hope that this document would have made you proud.

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INTRODUCTION

BACKGROUND

Wetlands are unique and important ecosystems, rich in biodiversity and valuable sources, sinks, and transformers of chemical and biological materials (Mitsch & Gosselink 2007). Due to the highly productive and diverse nature of wetland ecosystems and their proximity to large water bodies (rivers, estuaries) wetland areas are often at the epicenter of human population development and expansion. However, ecosystem services invaluable to humans are heavily compromised or lost altogether as a result of the extensive modifications required for humans to inhabit a landscape. Metropolitan development involves modification of hydrology (patterns, direction, velocity), vegetation, and soils (Paul & Meyer 2001, Ehrenfeld 2000, Ehrenfeld 2004, Ehrenfeld 2005, Walsh et al. 2005, Cutway & Ehrenfeld 2010); these are the three primary interacting factors regulating wetland function (Mitsch & Gosselink 2007). In many cases, urbanization results in the complete loss of wetlands, as areas are drained and filled for domestic or industrial construction purposes. Although little information exists about the extent of wetlands in urban areas, some studies suggest that cities have more wetland area than nearby rural areas, ostensibly due in part to wetland loss through intensive agriculture in non-urban areas (Thibault & Zipperer 1994, Ehrenfeld et al. 2011). Over 50% of the world's population lives in urban areas, and within the next 5 years, population growth will be mainly urban (UNFPA 2007). The properties, function, and regulators of function in urban wetlands in particular are therefore an area of research highly germane to ecologists and wetland managers, since this type of ecosystem appears

slated for increase in areal extent and relevance to human populations in the immediate future.

As urban areas have expanded in the United States, the importance of integrating the needs of human society with ecological system function has also increased. Restoration of ecological processes and function has always been a goal of wetland restoration ecology. It is only in recent decades, however, that focus has shifted from use of structural indicators of wetland function (e.g. plant or invertebrate community composition) to process-based (e.g. biogeochemical cycling) metrics to underpin both the design of wetlands and the evaluation of their success. Although direct quantification and modification of processes linked to ecosystems services is appealing, application of this goal is difficult. Wetland processes are highly spatially and temporally heterogeneous, and managers lack quantitative, predictive models relating wetland processes to specific combinations of biological communities, flooding patterns, and soils.

Wetlands in urban settings, while having the potential to deliver ecosystem services of high value (such as nutrient removal) to urban areas (Bolund & Hunhammar 1999), pose a particular challenge in linking ecosystem processes (such as denitrification) with their environmental drivers, mainly because urban wetlands have been little studied, and each urban system has its own unique set of altered conditions (Ehrenfeld et al. 2003). These issues are especially true of wetlands that develop on brownfield sites, on highly modified soil materials. Brownfield soils have usually formed on non-soil materials, including construction fill, under hydrogeomorphic conditions unique to highly disturbed urban areas (e.g. low areas between fill piles trapping precipitation), and with an unusual

assemblage of plant communities (e.g. combinations of urban invasive species and species planted over time by humans using the landscape). These are a class of wetlands that have received virtually no attention within the wetland science community, yet are widespread and potentially highly important to wetland and environmental management in urban regions. My dissertation research examines wetland function in highly modified brownfield wetlands, with the goal of modeling and predicting nitrate (NO_3^-) removal from surface water inputs to these wetlands.

Nitrogen (N) removal is commonly cited as a rationale behind wetland restoration projects, since wetlands have demonstrated the ability to prevent movement of excess N from upland areas into streams (Mitsch et al. 2001). The ability of wetland areas to remove nutrients from surface water is of particular importance in the northeastern United States, where atmospheric N deposition is high, and dense human populations generate high inorganic N (i.e., NO_3^-) levels in surface and ground waters (Driscoll et al. 2003, Gao et al. 2007). Increases in available nutrients in urban streams are at the forefront of research concerns within the stream ecology community (Wenger et al. 2009). Excess NO_3^- in surface waters is often transported to estuaries and coastal waters, causing eutrophication and biological perturbations such as dead zones (Mitsch et al. 2001) and invasion by exotic species (Silliman & Bertness 2004).

Denitrification is a microbial process performed by particular groups of heterotrophic bacteria that are ubiquitous in the environment; NO_3^- is used by these microbes as an electron acceptor and converted to gaseous forms, with N_2 as the final product in the reaction sequence. This process has been identified by restoration scientists as a desirable way of converting a highly biologically reactive and potential ecologically

damaging form of nitrogen (NO_3^-) to a highly inert form of nitrogen that is already pervasive in the environment (N_2). Under suboxic conditions, N_2 is the primary end product of denitrification, but denitrification can also result in release of nitrous oxide (N_2O), particularly if pH is low (which inhibits N_2O reductase), or some oxygen is present in the soil matrix (Hernandez & Mitsch 2006). The amount of N_2O produced relative to N_2 during denitrification is also higher if soil NO_3^- content is high, because NO_3^- is preferred over N_2O as an electron acceptor (Tiedje et al. 1984). Because N_2O is a potent greenhouse gas, with 310 times the heat trapping capability of CO_2 (Prather et al. 1995), a low net N_2O:N_2 ratio produced from denitrification is desirable in a wetland ecosystem serving to reduce NO_3^- from the surrounding environment. In the studies presented in chapters 1 and 2 of this dissertation, due to the denitrification measurement techniques used, N_2 and N_2O production resulting from denitrification is not differentiated (i.e., "denitrification rate" is defined as pooled N_2 and N_2O production). Chapter 3 estimates N_2O:N_2 ratios, and chapter 4 measures only N_2 production.

Quantification and prediction of where, when, and how much denitrification occurs in ecosystems has been consistently difficult for scientists, largely due to the complex set of environmental variables that control rates of denitrification, and the high level of spatial and temporal variability in controlling factors (Seitzinger et al. 2006). A recently developed paradigm attempts to conceptually integrate what we know about the factors controlling NO_3^- removal and the highly spatially and temporally dynamic nature of denitrification by focusing on "hot spots" and "hot moments" of denitrification (McClain et al. 2003). "Hot spots" are defined as "areas (or patches) that show disproportionately high reaction rates relative to the surrounding area (or matrix)" and "hot moments" are

defined as "short periods of time that show disproportionately high reaction rates relative to longer intervening time periods" (McClain et al. 2003).

NO_3^- removal via denitrification is a process mediated by three controlling factors: (1) the availability of organic carbon substrate (C); (2) the availability of NO_3^-; and (3) the presence of suboxic (<0.2 mg O_2/L) conditions (Seitzinger et al. 2006). Denitrification studies anticipate, therefore, that "hot spots" and "hot moments" are created by the intersection of these materials and conditions (Boyer et al. 2006). The dimensions and scale at which this intersection occurs in the environment have not been well-defined, however; this is largely because the mechanisms by which "primary variables" (plants, hydrology, and soils) regulate NO_3^-, C, and O_2 availability are complex and poorly understood. Although the individual effects of these "primary variables" on denitrification rates have been studied fairly extensively, there has been little work simultaneously relating plant biology, hydrologic regime, and soils with N removal function in wetlands (McClain et al. 2003, but see Pinay et al. 2007). More empirically-derived data sets at multiple spatial scales are needed to constrain the scale of "hot spots" and "hot moments" by the spatial or temporal variability of "primary variables," to accurately quantify and predict denitrification at the landscape scale (Boyer et al. 2006).

Quantifying and predicting interaction effects of "primary variables" on denitrification within a landscape is complex. Most denitrification studies cite hydrologic events (flooding, precipitation) as an important controlling factor on denitrification rates. Water flowpaths transport key materials (C, NO_3^-) through the soil surface and subsurface; intersection of these flowpaths mediates denitrification in space and time (McClain et al. 2003). Hydrology also controls the oxygen status of wetland soils, and

fluctuations between unsaturated and saturated conditions create fluctuations between nitrifying and anaerobic conditions, respectively (Richardson & Vepraskas 2001).

Although we know that hydrology is an important mediator of substrates and redox status in wetland soils, a number of variables can influence and interact with hydrologic regimes. Soil structure and texture determine water-filled pore space, which in turn influences nutrient cycling within and between soil microsites (Parkin 1987). Wetland plant communities mediate labile C and NO_3^- availability in the soil through the quantity and quality of their roots and litter; compete with microbes for NO_3^-; and influence soil moisture and oxygen status (Finzi et al 1998, Addy et al. 1999, Verchot et al. 2001). Soil temperature is also identified as playing an important role in denitrifier activity over time, but the relative importance of flooding and temperature in combination is still unclear.

It has been suggested that a combination of high temperature and moisture can lead to the highest rates of denitrification (Hernandez & Mitsch 2007) and that below a certain temperature, denitrification will not occur even under very high soil moisture conditions (Pinay et al. 2007). However, the interplay of temperature and moisture can be complex over the course of a year, and can be affected heavily by plant and soil properties at a site. Drier, aerobic soil conditions during the growing season can result in NO_3^- and C accumulation, but NO_3^- availability may be low until the end of the growing season, depending on plant uptake (Bechtold et al. 2003). In late fall, root mortality and litter can create large pools of labile carbon, but decomposition rates are influenced by N availability (Hill 1996, Rotkin-Ellman et al. 2004).

While it is likely that seasonal dynamics in temperature and in NO_3^- and C availability play a role in temporal patterns of denitrification, differences in moisture

regime can lead to large differences in seasonal denitrification dynamics between different systems and years (wet vs. dry). Quantifying and/or controlling for the relative contributions and importance of vegetation, hydrology, soil properties, and season to denitrification dynamics is challenging but necessary; this has been clearly demonstrated in studies on restored or created wetlands, where creating a "field of dreams" (all "primary variables" in the wetland system are optimized for high levels of denitrification) does not result in any measurable change in denitrification rates (Orr et al. 2007).

Urban wetlands present a unique problem when studying a process as spatially and temporally heterogeneous as denitrification. Natural wetland systems tend to be heterogeneous in soil properties and topography (Richardson & Vepraskas 2001), but most soils within a given natural wetland are derived from the same regional geologic source. Wetlands in an urban brownfield context, on the other hand, can demonstrate radical variations in textures on a much smaller scale than in natural wetlands, since fill material is often dumped (non-uniformly) at a given urban wetland site at different times and from different construction sources, leading to patches of "new" soil parent material on which soil development then proceeds (Pouyat & Effland 1999). Topography can also exhibit greater heterogeneity in an urban vs. natural wetland, due to the presence of piles of fill and massive disturbance from large machines. Due to heterogeneity in soils and topography, drainage can also demonstrate high spatial heterogeneity across an urban wetland, with areas of ponding directly adjacent to areas of high infiltration.

Vegetation community composition—which in natural wetlands is generally well-organized along allogenic gradients in distinctive, predictable zonation patterns (Mitsch & Gosselink 2007)—is highly altered and more erratic in its spatial distribution in urban

brownfield wetlands, where propagule sources may be in short supply, invasive species are often competitively dominant, and intentionally planted vegetation persists (Pickett et al. 2001). These vegetation characteristics, combined with the aforementioned alterations of soil and hydrology, hamper efforts to model and predict variability in time and space of microbial activity in urban wetlands. In order to design models for denitrification in urban brownfield wetlands, the unique spatial and temporal gradients in plants, hydrology, and soils must be defined and quantified, since they have arisen from processes and over time periods that radically differ from those found in natural wetlands.

RESEARCH QUESTIONS

I examined (1) how combinations of vegetation type, hydrologic conditions, and soil properties interact to mediate N cycling in wetland soils, and (2) how specific urban alterations may be affecting these interactions. Specifically, my research questions were:

(1) Where and when do the highest rates of NO_3^- removal occur in urban brownfield wetlands, and what are the spatial and temporal dimensions of these high rates?

(2) What are the environmental drivers (soil, hydrologic, vegetation properties) of denitrification rates in urban brownfield wetlands?

(3) Using our knowledge of the environmental drivers of denitrification, how can the spatial and temporal dimensions of high NO_3^- removal rates be modeled and predicted to aid in restoration and management at the whole-site or wetland scale?

The studies I undertook to address these objectives and the ensuing results of these studies are summarized in Table 1. In my research, I examined how the following variables influence the spatial and temporal distributions of "hot spots" and "hot moments" of NO_3^- removal from urban brownfield wetland soils in northern New Jersey:

- soil physical (texture, porosity) and chemical (% organic matter, available inorganic N) characteristics
- vegetation community types (forested vs. herbaceous)
- hydrologic conditions (topography, water retention, water table fluctuations)
- season (spring, summer, fall)

I took two approaches to predictive modeling and landscape scaling of "hot spots" and "hot moments." The first (chapters 1 and 3) utilized a combination of lab- and field-based empirical studies to construct regression models; these models were designed to isolate and explain the relationship between relatively static environmental variables (soil texture, vegetation type) and soil denitrification rates in an urban wetland environment. Using this approach, whole-watershed denitrification potential (i.e. "scaling up" of denitrification hot spots to the landscape scale) was estimated through spatial interpolation of the variables mediating the highest rates of denitrification at the scale of square meters (chapter 2). The second approach (chapter 4) involved measuring components of nitrogen and hydrologic cycling in semi-permanently flooded wetlands to construct ecosystem nitrogen budgets. These measurements were used to estimate nitrogen loading and the contribution of denitrification to inorganic nitrogen removal from these systems. This approach did not seek to isolate the individual effects of environmental variables on denitrification dynamics, but rather integrated several controlling variables into a single model applicable to a set of urban wetlands.

DISSERTATION OVERVIEW

My dissertation research took place in two different brownfield wetland systems in northern New Jersey that have been abandoned and largely unused by humans for 30–50

years. NO_3^- wet and dry deposition has been estimated to total roughly 0.03 mg N/m^2/hr at Teaneck (Ravit et al. 2006) and 0.14 mg N/m^2/hr at Liberty (Gao et al. 2007, Song & Gao 2009). In chapter 1, I present the results of a study in the Teaneck Creek watershed (Teaneck, New Jersey), in which I examined how the physical properties of different soil types (soils on fill piles, native clay soils, and flooded organic-rich soils) under the same vegetation community (*Phragmites australis*) within the watershed mediated the frequency of hot spots and hot moments of denitrification. I found that soil properties controlling soil aeration and production of endogenous NO_3^-, i.e. soil porosity and flooding, were the most important regulators of high denitrification rates in the 14 study plots. Soils in the Teaneck wetlands as a whole generally have adequate carbon and anaerobic pore space, but are limited primarily by NO_3^- availability.

Fill soils demonstrated very high denitrification rates, and had significantly more hot moments than native clay or flooded organic-rich (soil organic matter>15%) soils. Both fill and clay soils demonstrated higher denitrification rates under NO_3^- additions relative to control treatments, but fill soils responded more strongly to NO_3^- additions, implying that soils with low endogenous NO_3^- production (i.e., clay and organic-rich soils) also have less active denitrifier communities. Potential denitrification rates in fill soils were lower than potential rates measured in urban riparian soils in Maryland (Groffman et al. 2002, Groffman & Crawford 2003) and in freshwater marsh soils under the same vegetation type (*P. australis*) in the same region (Otto et al. 1999) (Table 2). However, these studies used higher concentrations of NO_3^- (100 ppm) in their additions to soils than the Teaneck study used (4 ppm) to assess denitrification activity.

Table 1. Summary of studies and experiments undertaken to address the objectives of this dissertation. Intact core denitrification rates (studies 1–3) are in mg N_2O-N/m^2/hr. Potential denitrification rates (DEA, studies 5 and 6) are in mg N_2O-N/kg/hr. Sediment denitrification rates (study 4) are in mg N_2-N/m^2/hr. Chapters 1 and 2 took place at the Teaneck site, chapter 3 took place at the Liberty site, and chapter 4 took place at both Teaneck and Liberty.

Experiment/Studies	Predictions	Outcome	Denitrification ranges
Objective 1: Where and when do the highest rates of NO_3^- removal occur in urban brownfield wetlands?			
(1) Measure denitrification rates in intact cores over three seasons in 14 quadrats characterized by different soil types, same vegetation (Ch. 1/Teaneck)	(1) rainfall stimulates denitrification by creating anoxic conditions and supplying NO_3^- (2) percent clay in a soil exhibits a positive relationship with denitrification by increasing soil water retention (3) denitrifiers are more active under higher temperatures	Flooded < Unflooded soils In unflooded soils, Low porosity < High porosity Clayey < Loamy Fill soils Fall < Spring & Summer	-0.08–0.49 (all) -0.01–0.07 (organic,flooded) -0.02–0.28 (clayey) -0.08–0.49 (fill)
(2) Measure denitrification rates in intact cores in 19 soil types, different vegetation (Ch. 2/Teaneck)	(4) denitrification highest in soils with pore structure facilitating simultaneous nitrification-denitrification	Rates highest at low elevations with high macroporosity	-1.67–2.56
(3) Measure denitrification rates in intact cores over two seasons in 5 wetlands characterized by different vegetation communities (Ch. 3/Liberty)	(5) wetlands dominated by forest vs. herbaceous vegetation demonstrate different ranges of denitrification	Low denitrification rates in all wetlands, regardless of dominant vegetation	-0.04–0.13 (herbaceous) -0.04–0.07 (forested)
(4) Measure denitrification rates in sediments of semi-permanently flooded areas during two summers (Ch. 4/Teaneck & Liberty)	(6) lowering water table increases endogenous NO_3^- production, stimulating high denitrification	Under wet vs. dry conditions: NH_4^+ production high NO_3^- production low Denitrification rate low	0.03–0.06 (Teaneck) 0.03–0.11 (Liberty)
Objective 2: What are the environmental drivers of denitrification rates in urban brownfield wetlands?			
(5) Measure DEA under enrichment of soils with NO_3^- (Ch. 1/Teaneck)	(7) denitrification limited by NO_3^- and increases in all soils with NO_3^- enrichment	Rate increases with NO_3^- additions only in soils with high endogenous NO_3^- production	0.00–0.03 (+N) 0.00-0.01 (control)
(6) Measure DEA under enrichment of soils with NO_3^- and labile carbon (Ch. 3/Liberty)	(8) denitrification limited by NO_3^- and not labile carbon	Rate increases with NO_3^- additions, no difference with labile carbon additions	0.00–0.03 (+N) 0.00–0.04 (+N, +C)

Table 1 cont.

Experiment/Studies	Predictions	Outcome	Denitrification ranges
Objective 3: How can the spatial and temporal dimensions of high NO_3^- removal rates be modeled and predicted?			
(7) Create map of soil properties and stormwater flooding areas to predict NO_3^- loading and removal (Ch. 2/Teaneck)			Not applicable
(8) Construct N budget (Ch. 4/Teaneck & Liberty)	(9) NO_3^- removal rates in semi-permanently flooded wetlands can be modeled and predicted using loading rates and sediment fluxes of NO_3^- under wet and dry conditions	NO_3^- removal is matching NO_3^- loading to sediments, but net NH_4^+ production in sediments is not matching NH_4^+ consumption	Not applicable

Table 2. Literature values of potential and actual denitrification rates measured in different wetland systems using the acetylene block method (slurry and intact core) and dissolved gas (N_2) measurements on water overlying incubating cores. Intact core and N_2 flux denitrification rates are in mg $N/m^2/hr$; potential slurry rates are in mg N_2O-N/kg/hr.

Experiment/Studies	Location	System Type	Denitrification Ranges	Measurement Type
Clement et al. 2002	Brittany, France	Mixed forest & grassland	0.08-0.16	Potential (slurry)
Gale et al. 1993	Central Florida	Natural and created wetlands	0.05-0.26 Constructed: 0.05-0.07 Natural: 0.13-0.26	Potential (slurry)
Groffman et al. 2002	Baltimore, MD	Riparian forest	0.46-2.20 Forested Reference: 0.456 Suburban: 0.586-1.66 Urban: 2.20	Potential (slurry)
Groffman & Crawford 2003	Baltimore, MD	Riparian	0.23-7.59 Forested: 2.60 Herbaceous: 3.68	Potential (slurry)
Otto et al. 1999	Tivoli North Bay, NY	Tidal freshwater marsh	15.7-19.2 *Phragmites*: 19.2	Potential (slurry)
Stander & Ehrenfeld 2009	Northern New Jersey	Urban forested wetlands	0.00–0.10	Intact core
Hanson et al. 1994	Rhode Island	Suburban forested wetland	0.05-0.43 Undeveloped: 0.01-0.19 Residential: 0.08-0.43	Intact core
Groffman & Hanson 1997	Rhode Island	Rural forested wetlands	0.01-1.54 0.06-0.38	Intact core Potential (intact core)
Hernandez & Mitsch 2007	Columbus, OH	Created wetlands	0.1-1.8	Intact core
Hopfensperger et al. 2009	Virginia	Tidal freshwater marsh	0.70-3.15	Potential (N_2 sediment flux)
Watts & Seitzinger 2000	Pinelands, New Jersey	Cedar swamps	0.00-0.04 Undisturbed: 0.00-0.59 Disturbed: 0.20-3.92	Intact core N_2 sediment flux
Hartnett & Seitzinger 2003	Raritan Bay, NJ	Estuarine	2.22-4.32	N_2 sediment flux

Although potential rates of denitrification were lower at Teaneck than in other sites on the East coast of the US, the study results do suggest that denitrifiers in fill materials are active and capable of NO_3^- removal. Ranges of actual (intact core) denitrification rates found for in this study were higher than those found for urbanized forested wetlands in northern New Jersey (Stander & Ehrenfeld 2009), and rates were much higher than those found for undisturbed cedar swamps and cedar swamps with high inorganic nitrogen loading ("disturbed") in the Pinelands of southern New Jersey using the same measurement technique (Watts & Seitzinger 2000) (Table 2). The same Pinelands study found much higher denitrification rates than those found in chapter 1 when measured using N_2 fluxes instead of the acetylene block, however, particularly in the disturbed cedar swamp (Watts & Seitzinger 2000) (Table 2). Rates of NO_3^- removal in clayey and loamy fill soils appeared to match or greatly exceed NO_3^- loading from the atmosphere. Since in this study the loamy fill and clayey sites selected received primarily atmospheric deposition and little surface or shallow groundwater (with two exceptions), the results of this study indicate that soils at the site may be serving an important role in reducing NO_3^- loading to Teaneck Creek from the atmosphere.

Chapter 2 expands on the studies in chapter 1 by using soil physical variables to estimate whole-site potential for NO_3^- removal via denitrification at the Teaneck Creek site. Soil samples were collected at 118 points and analyzed for soil organic matter and texture, interpolated maps of these soil properties were produced for the entire site, and flow paths of stormwater were digitized from aerial imagery. A subset (17%) of points was more intensively sampled to examine relationships between denitrification rates and soil water retention characteristics. This study revealed that relationships found between

porosity, denitrification rate, and NO_3^- within a small subset of plots under the same plant community (i.e., those found in chapter 1) apply to a wider range of soil types under differing plant communities across the wetland, and can be used for predicting the location of hot spots at the landscape scale. The highest denitrification rates occurred in soils located at low elevations, with high macroporosity. This study did not examine low elevation organic-rich soils, however, since based on the results of the previous study (chapter 1), organic-rich soils were assumed to be cold spots for denitrification. High potential denitrification rates corresponded with high available soil NO_3^-.

Interpolated maps revealed that roughly one third of the total site area was dominated by semi-permanently flooded organic-rich soils (i.e., cold spots); these areas coincided fairly well with known areas of flooding at the site. Almost all remaining soils at the site were loams, silt loams, sandy loams, or loamy sand. Clayey soils only made up roughly 1% of soils at the site. Spatial interpolation of soil properties related to high denitrification rates (high macroporosity, organic matter<15%, low elevation) accurately predicted most locations of denitrification hot spots and cold spots identified by the study presented in chapter 1. Hot spots corresponded to the location of stormwater channels running through the site over 31% of total channel area, indicating that soils at the site may be at least partially reducing total NO_3^- loads to the creek flowing through the site.

In chapter 3, I examined limitations to denitrification in a second brownfield wetland system, Liberty State Park (Jersey City, New Jersey). In this study, a number of small, relatively isolated precipitation-fed wetlands with different dominant vegetation communities (forested, herbaceous) and different types of fill soil (sand, gravel, coal rocks) were characterized for metrics of carbon and nitrogen cycling. I also examined

potential denitrification and respiration in a constructed wetland with finer-textured native soils at the same site. As in the Teaneck Creek wetland, soil denitrifiers at Liberty State Park were limited primarily by NO_3^- availability rather than by anaerobic pore space or carbon, dominant vegetation community did not appear to exert a strong influence in terms of relative C:N availability or denitrification rates, and soil physical properties (i.e., percent rocks) were an important factor in how much endogenous NO_3^- was produced, and therefore how much coupled nitrification-denitrification was possible in a given wetland. Although denitrification rates were lower in this system than in the Teaneck Creek site, the range was somewhat comparable to denitrification rates in cedar swamps of southern New Jersey measured using the same analytical technique (Table 2). NO_3^- additions revealed that these soils have developed active denitrifier communities, although potential denitrification rates were generally lower than literature values (Table 2). Here, as in the Teaneck Creek watershed, soils may serve an important role as sinks for NO_3^- falling on the site as atmospheric deposition.

One of the studies undertaken at the Liberty State Park site in chapter 3 addressed concerns about possible greenhouse gas implications of wetland denitrification. An intermediate product of denitrification, nitrous oxide (N_2O) is a potent greenhouse gas (Prather et al. 1995). Unremediated soils do appear to be less capable than soils in the constructed wetland of generating N_2 as the end product of denitrification (rather than N_2O). This may mean higher N_2O emissions from Liberty State Park if NO_3^- loading increases. Restored (replaced) wetland soils at the same site demonstrated tremendous potential for denitrification, and produced N_2:N_2O ratios many orders of magnitude larger

than unrestored wetlands, indicating that wetland restoration may serve a dual purpose for lessening both NO_3^- loads and N_2O emissions at the site.

My final chapter examines the role of denitrification in a whole-wetland context by constructing a budget for inorganic N using N loading calculations and denitrification measurements in largely waterlogged (organic-rich) soils at both Liberty State Park and Teaneck Creek Conservancy. The wetlands examined in this study are perhaps the most important in terms of the processing of inorganic N in both stormwater and precipitation, since these wetlands directly receive stormwater and are located in the lowest-lying areas of the site with slow drainage. In saturated soils such as this, most traditional methods of measuring denitrification rates are inaccurate (Groffman et al. 2006). I utilized pore water samplers ("peepers") and membrane inlet mass spectometry to measure N_2 and O_2 fluxes in the sediments; it is the first study to my knowledge to utilize this particular technique. Peeper samples demonstrated rapid loss of NO_3^- and simultaneous increases in N_2 at the sediment-water interface, where O_2 dropped down to very low concentrations. Sediments were generally very reduced and occasionally supported methanogenic conditions as well as high NH_4^+ production below the sediment-water interface. Loading of inorganic nitrogen via rain and stormwater was high (4–533 mg $N/m^2/d$), but large amounts of NH_4^+ were additionally created from mineralization of decomposing organic matter, leading to high fluxes of NH_4^+ out of sediment into water (2–117 mg $N/m^2/d$). Hydrology was a strong driving force of N_2 flux, since lowering of the water table allowed surface sediments to oxidize, leading to production of NO_3^- and fueling N_2 production.

Denitrification rates measured in the wetlands examined in chapter 4 were generally lower than those found using comparable measurements in tidal freshwater and deep estuarine sediments (Table 2). However, the wetland sediments do appear to be a net sink for NO_3^-. Periodic drainage of the wetlands to promote oxidation of NH_4^+ may thus be a strategy for promoting higher inorganic nitrogen removal from these sites.

CONCLUSIONS — the little wetlands that could . . .

My research shows that brownfield wetlands in northern New Jersey support active populations of denitrifying bacteria and are potential sinks for nitrate in urban landscapes, as evidenced by rates of NO_3^- consumption equaling or exceeding the rate of NO_3^- loading, at least from the atmosphere (Table 1). In brownfield sites 30–50 years old that have had time to develop persistent plant communities, organic matter is relatively high, and carbon does not appear to be limiting microbial processes. Rather, the ability of the soil to both produce and consume NO_3^- (i.e. support both anaerobic and aerobic pore space simultaneously) creates high potential for denitrification in these sites. Soil structure and texture, as well as water table levels and landscape position, appear to be the primary determinants of whether a particular brownfield soil has the potential for NO_3^- removal. Modifications to hydrology that promote conversion of NH_4^+ to NO_3^-, particularly in low-oxygen waterlogged areas, and routing of stormwater through soils with high macroporosity may augment levels of NO_3^- removal from soil.

My research also suggests that tools are available that allow for prediction and scaling of urban brownfield denitrification capacity. Two strategies were used to scale up denitrification measurements in my studies:

- scaling using soil properties across the site
- scaling using hydrologic and nitrogen budgets

Both methods appeared to be a useful means of assessing whole-wetland capacity for removal of NO_3^- entering streams and estuaries. Measurements of on a small (few meters squared) scale of soil properties and denitrification appeared to predict denitrification hotspots relatively well across an entire wetland system. Very fine-scale variations in soil properties were lost in a few cases, however, causing small areas to be mischaracterized as cold or hotspots. These results indicate the necessity of stratifying measurements carefully across time and space to adequately capture variability in N cycling and the variables driving N cycling in an urban context.

The use of nitrogen budgets also proved to be a useful way of defining when and where denitrification plays a role within a whole-wetland context. Examining individual contributions of each source of inorganic nitrogen to the wetland and measured rates of denitrification demonstrated that, although denitrification was occurring in sediments, these rates of inorganic nitrogen removal were dwarfed by the large quantities of inorganic nitrogen produced in the sediment, ostensibly by breakdown of organic matter.

Ranges of actual denitrification rates at Teaneck Creek were comparable to or higher than ranges found in other studies in New Jersey or other urbanized areas of the northeastern US. Denitrification rates at Liberty State Park were lower, but still frequently matched N loading rates from the atmosphere. These results suggest that the role of brownfield sites in a larger urban ecosystem context is an important one in terms of reducing loading of atmospheric inorganic N to urban soils and water.

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CHAPTER 1

Nitrate removal in brownfield wetlands: The role of soil properties in the creation of 'hot spots' and 'hot moments' of denitrification

ABSTRACT

The influence of hydrology and soil properties on nitrate (NO_3^-) removal via denitrification has been well-established. It is poorly understood, however, how the unique soil characteristics of brownfield wetlands contribute to or hinder denitrification. These wetlands form on non-soil materials, such as construction fill, under hydrogeomorphic conditions unique to highly disturbed urban areas. In this study, I examined denitrification rates and drivers in a watershed located on an unrestored brownfield site in New Jersey, USA. I carried out measurements of nitrogen mineralization and denitrification over 9-day sequences during three seasons under the same vegetation type (*Phragmites australis*) but in different soils (fill material, remnant marsh soils, flooded organic-rich soils) to characterize temporal variability and the role of soil properties in nitrogen cycling. Highly significant ($p<0.005$) differences were found in denitrification rates between soil types (fill material > remnant marsh soils > organic-rich flooded soils). Porosity and whether a site was inundated with water were the strongest spatial and temporal predictors of high denitrification rates, with coarse-textured, unflooded soils unexpectedly supporting the highest rates. These results suggest differences between soil types in pore-scale hydrology: soils with higher fractions of air-filled pores have more endogenous NO_3^- production, fueling high rates of denitrification. Results from a lab incubation study confirmed that denitrifiers in this system are limited by NO_3^- availability. Incubation results also suggested that denitrification in soils with

low endogenous NO_3^- production does not rapidly increase in response to exogenous NO_3^- additions.

INTRODUCTION

Due to the many functions of ecological importance provided by wetlands, these ecosystems have become the target of management schemes seeking to improve water and soil quality (Stander & Ehrenfeld 2009). Wetland processes are often highly spatially and temporally heterogeneous, however, and managers lack quantitative, predictive models relating wetland processes to specific combinations of biological communities, flooding patterns, and soils. Wetlands in urban settings, while having the potential to deliver services of high value (such as nutrient removal) (Bolund & Hunhammar 1999), pose a particular challenge in linking ecosystem processes (such as denitrification) with their environmental drivers, mainly because urban wetlands have been little studied, and each urban system has its own unique set of altered conditions (Ehrenfeld et al. 2003).

Metropolitan development increases the extent of impervious surface and thus the volume of surface runoff entering urban waterways. Geomorphic alterations such as ditching, berms, and waste dumps are also common in urban landscapes, and contribute to high variability in both elevation and water tables in urban wetlands and watersheds (Ehrenfeld 2004). The combined effect of urban hydrologic alterations results in an "urban stream syndrome," characterized by flashier hydrographs, elevated concentrations of nutrients and contaminants, altered channel morphology and stability, and reduced biotic richness (Paul & Meyer 2001, Ehrenfeld et al. 2003, Walsh et al. 2005).

The impacts of urbanization on wetland hydrology are greatly compounded by the topographic and textural variability of urban soils (De Kimpe & Morel 2000). Urban soils are composed of a mixture of materials differing from those of adjacent agricultural or forest areas (i.e., natural soils), and/or deeply modified by human activity (De Kimpe & Morel 2000). While the areal distribution of "natural" or undisturbed soil is inversely proportional to the extent of urbanization (Effland & Pouyat 1997), soils in urban landscapes are highly variable and not uniformly impacted, with "patches" of undisturbed soil interspersed in the landscape (Effland & Pouyat 1997, Pickett et al. 2008). Because urban soils are formed from heterogeneous, often non-soil materials, and have undergone highly variable times of development, the normal heterogeneity encountered within wetland soils may be greatly magnified in urban wetlands (Ehrenfeld 2004).

Brownfields are areas previously developed and now derelict, vacant, or under-utilized (Lesage et al. 2007). Although there has been much attention paid to pollutants, particularly heavy metals, within urban brownfield soils, there has been virtually no study of the function of wetlands that develop on brownfield sites. Riparian zones have a demonstrated ability to prevent movement of excess nitrogen from upland areas into streams (Hill 1996, van Breemen et al. 2002), although this ability is often compromised due to the hydrologic changes caused by urbanization (Groffman et al. 2003).

In the northeastern United States, inorganic nitrogen in atmospheric deposition and stormwater is elevated due to fossil fuel combustion, fertilizer application, and leaky sewer infrastructure (Howarth et al. 1996, Driscoll et al. 2003, Howarth 2004). Excess inorganic nitrogen in surface waters is often transported to estuaries and coastal waters, causing eutrophication and biological perturbations such as dead zones (Mitsch et al.

2001) and invasion by exotic species (Minchinton & Bertness 2003, Silliman & Bertness 2004). Denitrification, a microbial process common in wetlands, has been cited widely as a mechanism by which to reduce inorganic nitrogen in urban soils and waterways (Collins et al. 2010).

This study applied the emerging conceptual framework of "hot spots" and "hot moments" (McClain et al. 2003) for nitrate removal via denitrification in natural wetland soils to the understanding of wetlands developing on urban soils by examining patches of different soil materials across a heterogeneous urban wetland complex. NO_3^- removal via denitrification is a process mediated by three controlling factors: (1) the availability of organic carbon substrate (C); (2) the availability of NO_3^-; and (3) the presence of suboxic (<0.2 mg O_2/L) conditions (Seitzinger et al. 2006). Denitrification studies anticipate, therefore, that "hot spots" and "hot moments" are created by the intersection of these materials and conditions (Boyer et al. 2006). The dimensions and scale at which this intersection occurs in the environment has proven difficult to model and quantify, however (Groffman et al. 2009).

Denitrification rates typically display extremely high spatial and temporal variability within a landscape. This phenomenon has led to an extensive body of research exploring the location and environmental drivers of activity centers within soil (Groffman et al. 2009). A number of studies have demonstrated the influence of soil properties on denitrification rates (Groffman & Tiedje 1991, Pinay et al. 2000, Machefert & Dise 2004, Well et al. 2005, Koponen et al. 2006, Novosad & Kay 2007). Texture influences pore size and water-filled pore space of soil, which in turn influences the volume fraction of water-filled microbially habitable pores, anaerobic conditions in the soil and

denitrification rate (Groffman & Tiedje 1991, Machefert & Dise 2004, Koponen et al. 2006, Novosad & Kay 2007). Many studies linking soil physical qualities to denitrification have taken place on small temporal or spatial scales and in the laboratory (but see Groffman & Tiedje 1991, Pinay et al. 2000, Machefert & Dise 2004); the ability to "scale up" estimations of denitrification rate or potential to larger scales is therefore often unexplored. Further, measurements of disproportionately high denitrification rates relative to background variability ("hot moments" of denitrification) and/or fluctuations in explanatory variables other than moisture and temperature (such as soil NO_3^- and C content) are usually not included in analyses linking soil properties to denitrification. These approaches are thus not suitable for developing models capable of predicting very high or transient denitrification rates (Groffman et al. 2009).

This study took advantage of a freshwater wetland system (Teaneck Creek Conservancy, Bergen County) in which monospecific stands of *Phragmites australis* are located on adjacent patches of clayey, loamy (construction fill), and organic-rich (according to USDA-NRCS 2010 definition) soils. The presence of these patches enabled isolation of the effects of soil type and soil-generated differences in hydrology on the spatial and temporal distribution of "hot spots" and "hot moments" of NO_3^- removal. Rather than identify the drivers of average denitrification rates in a given location, I utilized a unique statistical analysis to isolate the most important drivers of only the highest measured denitrification rates. My goal was to use the temporal and spatial variability in denitrification within and among replicate areas within each of the three soil types to (1) define the dimensions of "hot spots" and "hot moments" in NO_3^- removal and

(2) examine soil physical properties as a primary driver of both spatial and temporal variability in such phenomena.

METHODS

Study site

The study took place in the Teaneck Creek watershed, a small (0.2 km^2) freshwater floodplain ecosystem in northeastern New Jersey (NJ) that is part of the larger Hackensack River watershed (Figure 1.1). Teaneck Creek is located in a highly urbanized (95% urban land use) setting adjacent to two major highways (the NJ Turnpike and Route 80). In the early part of the 1900s, the Creek was a low order freshwater stream system. After construction of a dam on the Hackensack River upstream of Teaneck, salt water from Newark Bay moved up into the Teaneck watershed, and the system consisted of numerous brackish tidal creeks. Following construction of a tide gate on the Hackensack River downstream of Teaneck, Teaneck Creek once again became a freshwater system.

Channelization, downcutting, and berming of the creek and dumping of clay dredge and debris in the floodplain have resulted in compaction of the upper layers of the soil profile and impeded groundwater and creek connectivity. Precipitation and stormwater are the primary hydrologic inputs for the site's wetlands. Six stormwater outfalls drain directly into Teaneck Creek and its wetlands. In addition to the stormwater inputs a local hospital is permitted to pump 100,000 gallons of groundwater per day into Teaneck Creek in order to keep the hospital basement dry (Arnold 2008).

The numerous geomorphologic, biological, and hydrologic alterations relating to development activities at the site have led to high variation in soil profile composition.

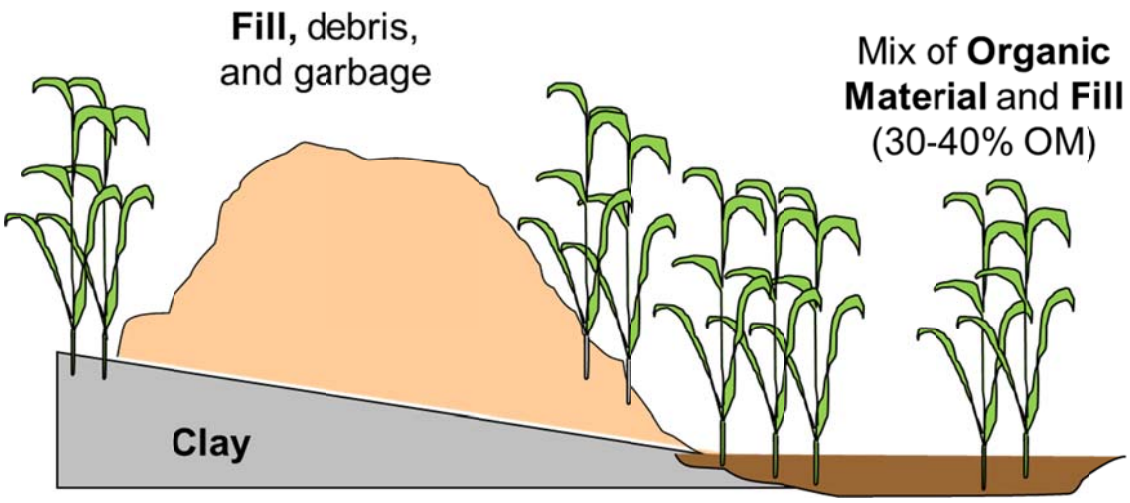

Figure 1.1. Schematic of soil profiles at Teaneck Creek Conservancy showing broad soil categories used in this study.

Broad soil categories examined in this study include clayey soil, loamy fill, and unconsolidated organic-rich soils (Figure 1.1). The areas characterized by reduced clays likely represent the original wetland soils in the site, when the area was a freshwater marsh/stream system (before dam installation). The loamy fill is from construction of the NJ turnpike in the 1950s. Fill piles additionally consist of trash deposited on the site in the 1960s; the trash is primarily domestic waste (cans, bottles, clothing, and plastic), but also includes brick, glass, concrete, roofing materials, lumber, automotive parts, and appliances (Arnold 2008). The organic-rich soils are located on what s likely former tidal channels running through the site (before tide gate construction); they are composed of a combination of slowly decomposing litter (due to the nearly constant presence of surface water) and loamy fill that has washed in via surface water flows. Although the site supports a range of vegetation communities, all soil types support large stands of the invasive grass species *Phragmites australis*; these areas were used for this study (Figure 1.2).

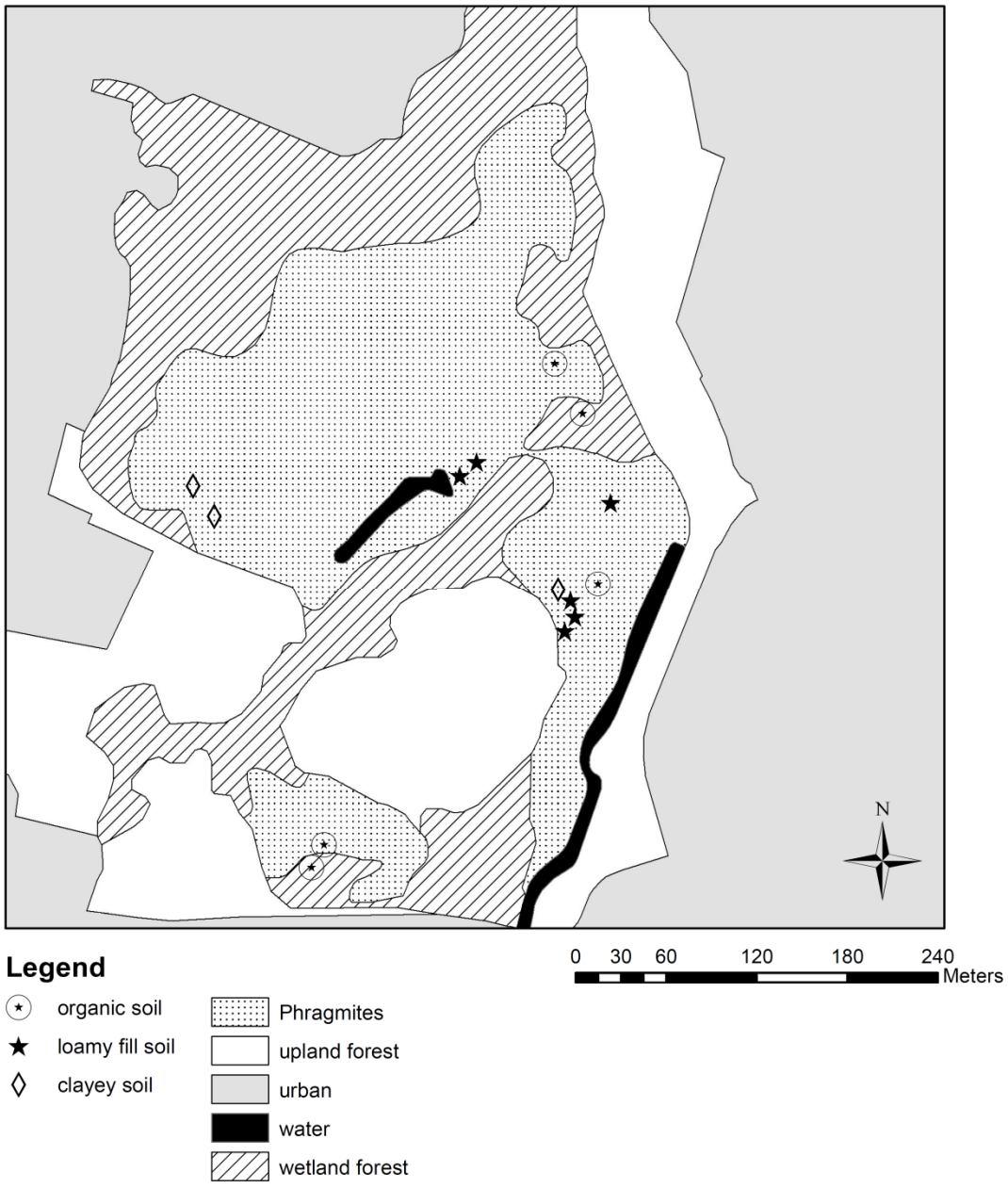

Figure 1.2. Land uses and sampling points at Teaneck Creek Conservancy used for the study. Teaneck Creek is the water body running along the eastern side of the site. Symbols represent the 14 plots used for the study; these plots were characterized by different soil textures, but all supported dense stands of *Phragmites australis*.

Identifying "hot spots" and "hot moments"

Seven patches representative of the range of soil types found in the Teaneck Creek watershed (clayey, loamy fill, organic-rich soil) were identified for sampling, and two 3 x 3 m plots (hereafter referred to as "plots") were demarcated in each patch; 14 plots total were utilized for the study (Figure 1.2). The top 20 cm of the soil profile was considered in NO_3^- removal dynamics. To identify differences in denitrification rates between soil profile types over time, soil cores were collected from each plot every day for 9 days following a rain event (>2.5 cm of precipitation). Cores were collected in 2006 in each of three seasons when temperatures were high enough for high rates of denitrification to occur: Spring (May), Summer (July), and Fall (November). A "hot moment" of N removal was thus restricted to two temporal levels: within a 9-day soil wetting and drying cycle, and within a given season.

During each season, one core 10–17 cm long and 2.5 cm wide was collected in each plot every day for 9 days using a 20x3 cm corer. These cores were used immediately for static core, acetylene-based measurements of denitrification rate (Groffman et al. 1999). Cores were transported back to the lab, sealed with gas-tight rubber stoppers, and brought back to ambient air pressure by venting with a needle. Five cc of acetylene was injected into the headspace of each core, and the headspace of the core was mixed three times with a 40 cc syringe. 5 cc of sample was collected from the headspace of each core and injected into an evacuated 9 cc gas vial 2 hours and 6 hours after injecting acetylene. Cores were maintained at room temperature (23°C) throughout the analysis, and gas samples were stored in the lab at room temperature until being analyzed for N_2O content on a Shimadzu 14A Gas Chromatograph.

Contribution of soil physical properties to denitrification dynamics

To characterize differences between soil types in hydraulic properties, the mass-based gravimetric water content of all soil cores collected during the study was determined concurrently with N processing. Water level at each site was measured during sampling; soil was considered "flooded" if water level was 5 cm below the soil surface or higher. Soil texture (percent sand, silt, and clay) and bulk density (Blake & Hartge 1986) were characterized for each plot in the middle of the study, between summer and fall sampling periods (Table 1.1). To determine bulk density, a pit was excavated at each site, and three cores (5 cm high x 4.7 cm wide) were inserted horizontally into the side of the pit. Cores were transported back to the lab, dried for one week at 105°C and weighed.

Soil texture fractions were determined using the hydrometer method (Gee & Bauder 1986). Mean particle size was calculated using soil textural fractions using the equation in Shiozawa & Campbell (1991). Particle density was also determined for all mineral soils using the pycnometer method (Blake & Hartge 1986). Particle density for the organic-rich soils was determined by taking the sum of the particle density of each constituent times its percentage contribution to the whole sample (Blake & Hartge 1986). For the organic-rich soils, the particle density of organic matter was assumed to be 1.5 g/cm^3; the particle density of mineral constituents was assumed to be 2.5 g/cm^3. The porosity of each plot was determined based on the particle density and bulk density using the equation in Blake & Hartge (1986).

Because pore structure and connectivity varied so greatly between soil types, water retention curves were simulated for each site to determine "effective air-filled pore space (AFPS)" and the water content at saturation (θ_s). The water retention curve for each site

Table 1.1. Characteristics of soils at Teaneck Creek Conservatory. Mean values over the entire study period ± 1 standard error of the mean for each parameter are reported. MPS = mean particle size, AFPS = water-filled pore space. Different letter superscripts in a given column represent a significant ($p \leq 0.05$) difference according to PROC glm (MPS, bulk density, % clay, porosity) or a repeated measures PROC mixed model (% organic matter, effective AFPS, soil NO_3^-, NH_4^+).

Soil Type	MPS (µm)	Bulk Density (g/cm^3)	% Clay	Porosity	% Organic Matter	Effective AFPS	Soil NO_3^- (µg/g soil)	Soil NH_4^+ (µg/g soil)
Clayey	3.47 ± 1.74^{A}	1.2 ± 0.07^{A}	48.11 ± 9.87^{A}	0.490 ± 0.03^{A}	7.92 ± 0.29^{A}	2.33 ± 0.16^{A}	0.59 ± 0.18^{A}	2.58 ± 0.27^{A}
Loamy Fill	24.37 ± 4.70^{B}	1.1 ± 0.04^{A}	16.80 ± 1.99^{B}	0.580 ± 0.01^{B}	11.76 ± 0.32^{A}	1.97 ± 0.07^{B}	0.18 ± 0.05^{B}	3.77 ± 0.16^{A}
Organic-Rich	26.08 ± 7.46^{B}	0.4 ± 0.05^{B}	12.67 ± 1.09^{B}	0.812 ± 0.03^{C}	16.78 ± 0.45^{B}	1.33 ± 0.07^{C}	-0.08 ± 0.03^{B}	7.33 ± 0.53^{B}

was parameterized using three different models (Rawls et al. 1983, Mayr & Jarvis 1999, and Wosten et al. 1999). The average water content (θ) predicted by all three models for each site's soil at -33, -60, -100, and -1500 kPa was then calculated. To fit water retention curves for each site, water content values over the pressure potential sequence were fed into an online program (http://swrcfit.sourceforge.net) to calculate parameters for the van Genuchten model, i.e. water content at saturation (θ_s), the residual water content (θ_r), α, and n (van Genuchten 1980, Seki 2007). Water content at the inflection point of the water retention curve was calculated using an equation from Dexter (2004):

$$\theta_p = \theta_r + (\theta_s - \theta_r) * (1 + \left(\frac{n}{n-1}\right))^{(\frac{1}{n-1})}$$

Where θ_p is water content at the inflection point. The following equation was then used to determine effective WFPS: $(\theta_s - \theta_f) / (\theta_s - \theta_p)$, where θ_f is field water content (% moisture determined each sampling day).

The redoximorphic potential and temperature of the soil in each plot was measured in the field during days 5-9 in the summer and days 1-6 in the fall concurrent with core collection using a Corning® redox combination electrode.

Contribution of organic carbon and soil nitrate to denitrification dynamics.

Percent organic matter was measured using loss on ignition on a subsample of all soil cores collected during the study (Nelson et al. 1996). To measure soil extractable nitrate and net nitrification concurrently with denitrification measurements, NH_4^+ and NO_3^- were extracted with 2 M KCl from all cores used for denitrification measurements within 24 hours of collection (Hart et al. 1994). One "incubating" core was collected concurrently with the core collected on the first day of each 9 day sampling period and immediately replaced in the ground. The "incubating" core was left in the ground for one month and

was then subjected to a KCl extraction within 24 hours of collection. The difference in NH_4^+ and NO_3^- content between "incubating" cores and cores analyzed one month prior during the 9-day sampling period were used to determine net N mineralization and nitrification rate in each soil type during each season. KCl extracts were frozen and stored until they could be analyzed for NO_3^- and NH_4^+ content using a flow injection analyzer (Hart et al. 1994).

To more closely examine the relationship between endogenous and exogenous NO_3^- inputs and denitrification rate, a lab incubation experiment was undertaken in August 2010. An 800 cm^3 volume (20x20x20 cm) of soil was collected from each of the 14 plots, and processed within 24 hours. Each sample was thoroughly mixed in a bucket and roughly 250 g was subsampled twice from the total volume. Each subsample was assigned to one of two treatments: control or experimental. All subsamples were further subsampled for percent soil moisture and a KCl extract (to determine initial NO_3^- and NH_4^+ content). Exactly 200 g of soil out of the initial 250 g subsample was then placed in a lidded 946 mL Mason Jar with either 500 mL of deionized water (control) or 500 mL of 4 ppm N-NO_3^- (KNO_3^-) solution (experimental). The headspace of each sample was evacuated and flushed 5 times using inert N_2 gas through a septum in each lid to create a sub-aerobic environment, then immediately injected with 25 cc acetylene gas. 10 cc of gas was then collected from each Mason jar after 3, 5.5, and 23 hours and analyzed for N_2O on a Shimadzu 14A GC. Mason jars were agitated by hand-swirling to loosen all gas bubbles from soil pores prior to each gas sampling.

Statistical analyses

For the field study, linear comparative models (repeated measures PROC nlmixed) were used to determine the best predictors (soil physical characteristics, soil chemical characteristics, environmental variables) of denitrification rate at each site (SAS Institute 2008). The goodness of fit of various candidate models was compared using Akaike's information criterion with a modification for finite sample sizes (AICC). PROC glm and PROC mixed were used to determine whether significant differences existed between broad soil types (clayey, loamy fill, organic-rich soil) in soil physical and chemical properties over time (SAS Institute 2008).

Denitrification rates across sites and over time within a given site had a highly skewed, non-normal distribution, with the majority of measurements near zero and a long tail to the right caused by a few very high denitrification rate measurements. I identified these "outlier" measurements as representing "hot moments" and "hot spots" of denitrification, since they were disproportionately high compared to the majority of measurements taken during the study. In order to identify the variables responsible for the highest denitrification rate measurements, denitrification rate was made into a binomial variable, based on the quartile of the data distribution (including all denitrification rate measurements taken over the entire study) into which the rate value fell. PROC nlmixed was run with soil variables predicting whether (1) the denitrification rate fell above or below the median (2nd quartile) denitrification rate (0 = below, 1 = above); or (2) the denitrification rate fell above or below the 75^{th} percentile (3rd quartile) value (0 = below, 1 = above).

For the lab incubation experiment, denitrification rates of control and experimental soils, as well as the difference in rate between both groups, were regressed (PROC glm) against soil variables. Paired t tests (PROC ttest) were used to determine whether significant differences existed between treatments.

RESULTS

Hot spots and hot moments

Overall, loamy fill soils supported the highest rates of denitrification during the study, followed by clayey soils; organic-rich soils demonstrated little to no denitrification activity (Figure 1.3). These differences between soil types (loamy fill > clayey > organic-rich) were significant over the study period according to a repeated measures analysis (PROC mixed; $p < 0.05$). Since the data distribution was highly non-normal, however, data were pooled to run an analysis on data quartiles, since non-normality violates the assumptions of a repeated measures analysis.

Periods of high denitrification activity generally occurred at the same time in clayey and loamy fill soils, although variability in rate on a given sampling day within the two soil categories was high (Figure 1.3). Soil types had significant differences in how often they demonstrated "hot moments" of denitrification: loamy fill soils had denitrification rates falling above the 3rd and 2nd quartile value significantly (PROC mixed; $p < 0.05$) more frequently than clayey soils or organic-rich soils, and clayey soils had denitrification rates falling above the 3rd and 2nd quartile value significantly more frequently than organic-rich soils (Figure 1.3). Denitrification rates across all soils ranged from -1.8 to 15.2 μg N_2O-N/kg soil/hr, with 50% of values falling below 0.15 μg

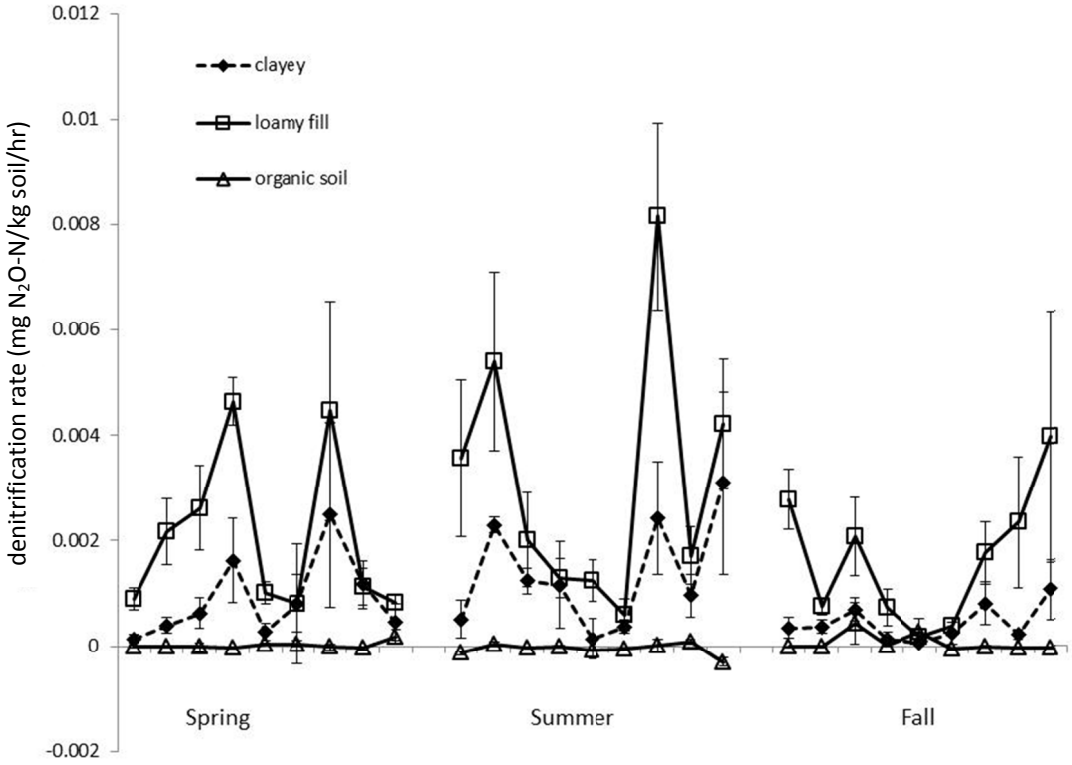

Figure 1.3. Denitrification rates in clayey, loamy fill, and organic-rich soils during the 2006 field study. Error bars represent one standard deviation from the mean value on a given day.

Table 1.2. PROC nlmixed results for temporal and spatial soil physical variables. Models predicted whether denitrification rate at a given site exceeded the 2nd quartile value or 3rd quartile value. Akaike's information criterion value (AICC) is reported as relative goodness of fit for each model. Variables with a p value of 0.15 or lower in the model are noted in the 4th column. Note temperature and redox status utilize a subset of the data used in all other models, since they were only measured during part of the study.

	Predictor(s)	**2nd quartile**	**3rd quartile**	**Significant predictors**
Spatial variables	Porosity	AICC = 283.9	AICC = 315.5	2nd: - porosity (< 0.0001) 3rd: - porosity (< 0.0001)
	Porosity, $(Porosity)^2$	AICC = **283.8**	AICC = **304.9**	2nd: - $porosity^2$ (0.15) 3rd: + porosity (0.003), - $porosity^2$ (0.001)
	MPS	AICC = 328.9	AICC = 347.4	
	% Clay	AICC = 326.8	AICC = 347.5	2nd: + clay (0.07)
	% Clay, $(\% Clay)^2$	AICC = 319.1	AICC = 338.9	2nd: + clay (0.001), - $clay^2$ (0.003) 3rd: + clay (0.002), - $clay^2$ (0.003)
Temporal variables	Effective AFPS	AICC = 330.1	AICC = 347.1	
	Effective AFPS, $(Effective\ AFPS)^2$	AICC = 330.6	AICC = 349	2nd: - AFPS (NS), + $AFPS^2$ (0.10)
	Flooding	AICC = **304.7**	AICC = **318**	2nd: - flooded (< 0.0001) 3rd: - flooded (< 0.0001)
	Temperature	AICC = 149.2	AICC = 144.2	3rd: + temperature (0.15)
	Redox status	AICC = 163.4	AICC = 157.6	2nd: + redox (0.0001)
	Season	AICC = 331.7	AICC = 349.2	
	Soil NO_3^- (same day)	AICC = 326.4	AICC = 344.3	
	Soil NO_3^- (previous day)	AICC = **303.3**	AICC = **315.5**	2nd: - soil NO_3^- (p = 0.04)
	Season, flooding, Season*flooding	AICC = 310.9	**AICC = 318.5**	2nd: - flooded (0.0005) 3rd: - flooded (< 0.0001), - Fall (0.02) , + Fall*flooded (0.03)
	Temperature, flooding, Temperature*flooding	AICC = **124.7**	AICC = **121**	2nd: - flooded (0.03) 3rd: + temp (0.02), - temp*flooded (0.07)

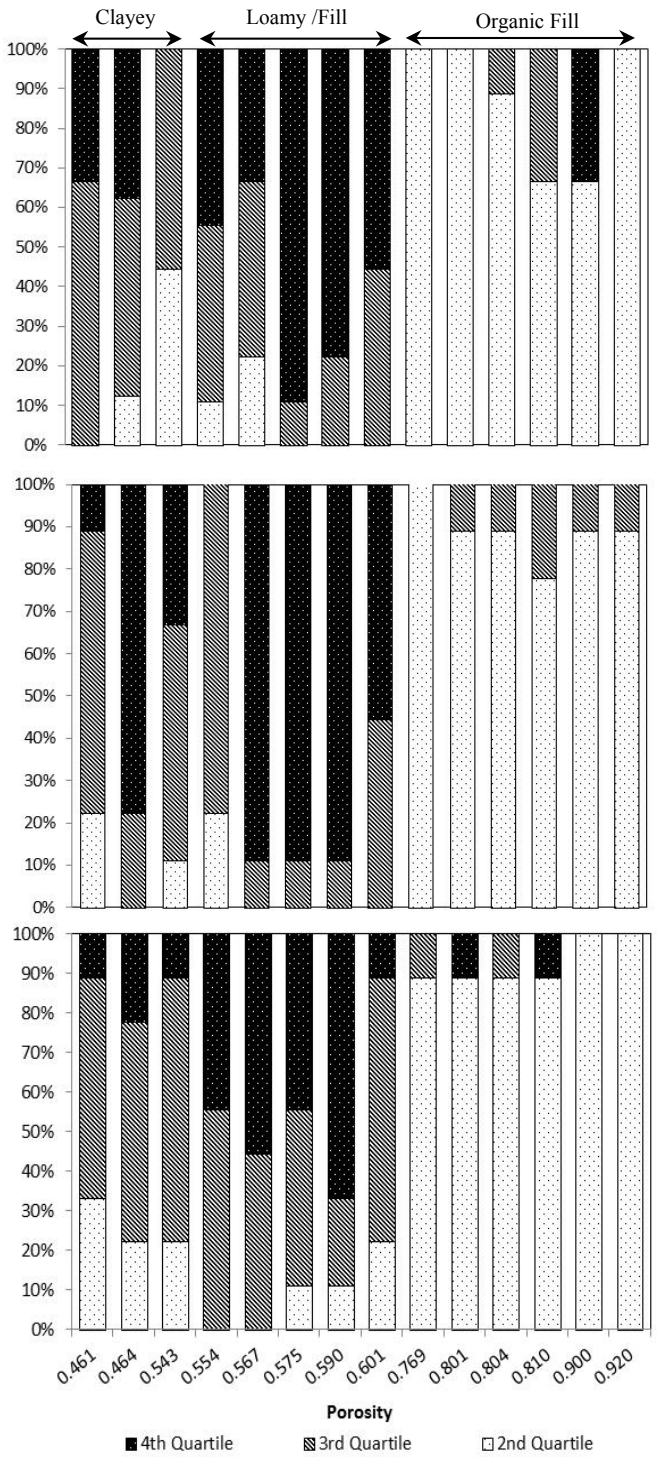

Figure 1.4. Porosity vs. denitrification quartile. Y axis is percent of denitrification rate measurements for each soil porosity (x-axis) value falling into either the 2nd, 3rd, or 4th quartile of the data distribution

N_2O-N/kg soil/hr (2nd quartile) and 75% of values falling below 1.26 μg N_2O-N/kg soil/hr (3rd quartile) (Figure 1.3).

Spatial Variables: Soil physical properties

Of all soil properties, porosity was the best predictor of whether a denitrification rate fell into the 2nd, 3rd or 4th quartile (Table 1.2). Porosity ranged from 0.45–0.55 in the clayey soils, from 0.55–0.60 in the silty fill soils, and from 0.81–0.92 in the organic fill soils (Table 1.1, Figure 1.4). Porosity demonstrated a significant negative relationship with denitrification quartile, with the highest porosity values demonstrating the least number of values exceeding the median or 3rd quartile denitrification rate. However, porosity also demonstrated a significant direct quadratic relationship with denitrification quartile (Table 1.2), indicating that soils with intermediate porosity values (i.e. loamy fill soils) had high denitrification rates most frequently (Figures 1.3 & 1.4). Percent clay also demonstrated a significant direct quadratic relationship with denitrification quartile, but yielded a higher AICC score (2nd Quartile: AICC = 319.1, 3rd Quartile: AICC = 338.9) in predicting denitrification rate quartile than the model using porosity and porosity squared as predictors (2nd Quartile: AICC = 283.8, 3rd Quartile: AICC = 304.9) (Table 1.2). Mean particle size, which was highest in loamy fill soils and lowest in clayey soils (Table 1.1), was not a significant predictor of denitrification rate quartile, and the models utilizing MPS yielded the lowest AICC values of any other spatial variables (Table 1.2).

Temporal Variables: Soil physical properties

Among temporal variables related to soil physical properties, whether soils were "flooded" or not was the best predictor of whether denitrification rate fell into the 2nd, 3rd, or 4th quartile (2nd Quartile: AICC = 304.7, 3rd Quartile: AICC = 318) (Table 1.2).

A site being "flooded" was a significant negative predictor of whether a value fell above the 2nd or 3rd quartile denitrification rate. This predictor variable did not, however, change in value much for each site over the course of the study—organic-rich soils were flooded for the duration of the study, as was one of the clayey sites; only 2 other sites rarely (1-2 instances) demonstrated flooded conditions over the course of the study.

Effective air filled pore space (AFPS) varied more within a given site than whether that site was flooded or not, and was lowest, on average, in organic-rich soils, and highest in clayey soils (Table 1.1). Water retention curves predicted higher water content in organic-rich soils than in loamy fill or clayey soils over a wide range of matric potentials (Figure 1.5). Clayey soils were predicted to retain a slightly higher water content than loamy fill soils at field capacity (-33 kPa) and drier, but the two soil types retained a similar water content at high levels of saturation (Figure 1.5). Effective AFPS alone was not a significant predictor of denitrification quartile, but AFPS did have a marginally significant quadratic relationship with whether a rate exceeded the median value (Table 2). Both models yielded a higher AICC score in predicting denitrification rate quartile than the model using flooded conditions as a predictor (Table 1.2).

Temperature and redox potential in organic-rich soils were significantly ($p < 0.05$) lower than in clay or fill soils, which were not significantly different in either variable (PROC mixed; data not shown). Unlike redox potentials in organic-rich soils (39–455 mV), redox potentials in clay and loamy fill soils were typically above the optimal range for denitrification (361–719 mV). Temperature was a marginally significant ($p = 0.15$) positive predictor of whether a denitrification rate fell into the 4th quartile of the data set, and redox potential was a significant ($p < 0.05$) positive predictor of whether

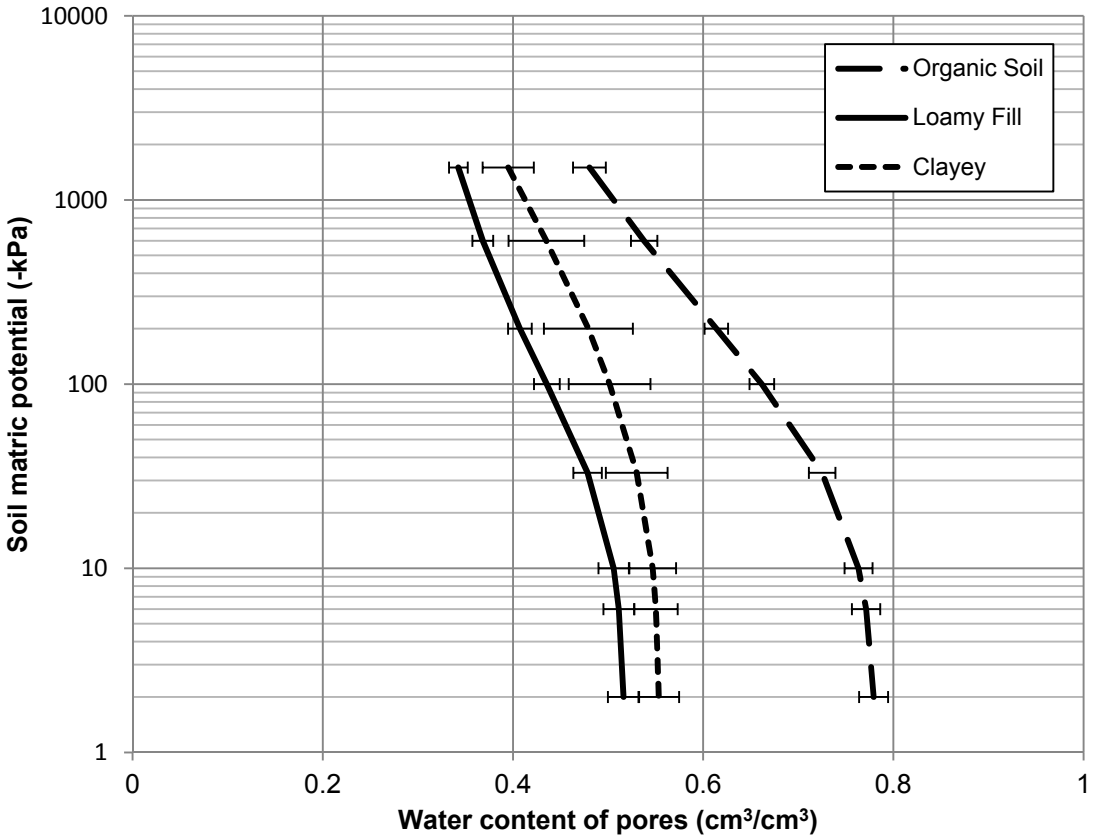

Figure 1.5. Average calculated water content contained in soil pores at various pressure potentials for organic-rich soils, loamy fill site, and clayey soils. Values were calculated using the van Genuchten (1980) equation. Error bars represent one standard error for the mean value for each soil type at each pressure potential. Note that y-axis values are negative.

denitrification rate fell above the median value (Table 1.2). Because temperature and redox potential were only measured for a subset of the study duration (days 5–9 in the summer and days 1–6 in the fall), AICC scores of models utilizing these parameters cannot be compared to the AICC scores of other models in Table 1.2. However, of the two models utilizing either temperature or redox potential as a predictor, the one utilizing temperature had lower AICC scores (Table 1.2). Adding flooding as a predictor to the model utilizing temperature substantially lowered the AICC score (Table 1.2), making the model with flooding, temperature, and flooding*temperature the best model of those utilizing temperature and redox data. Temperature had a significant ($p < 0.05$) positive

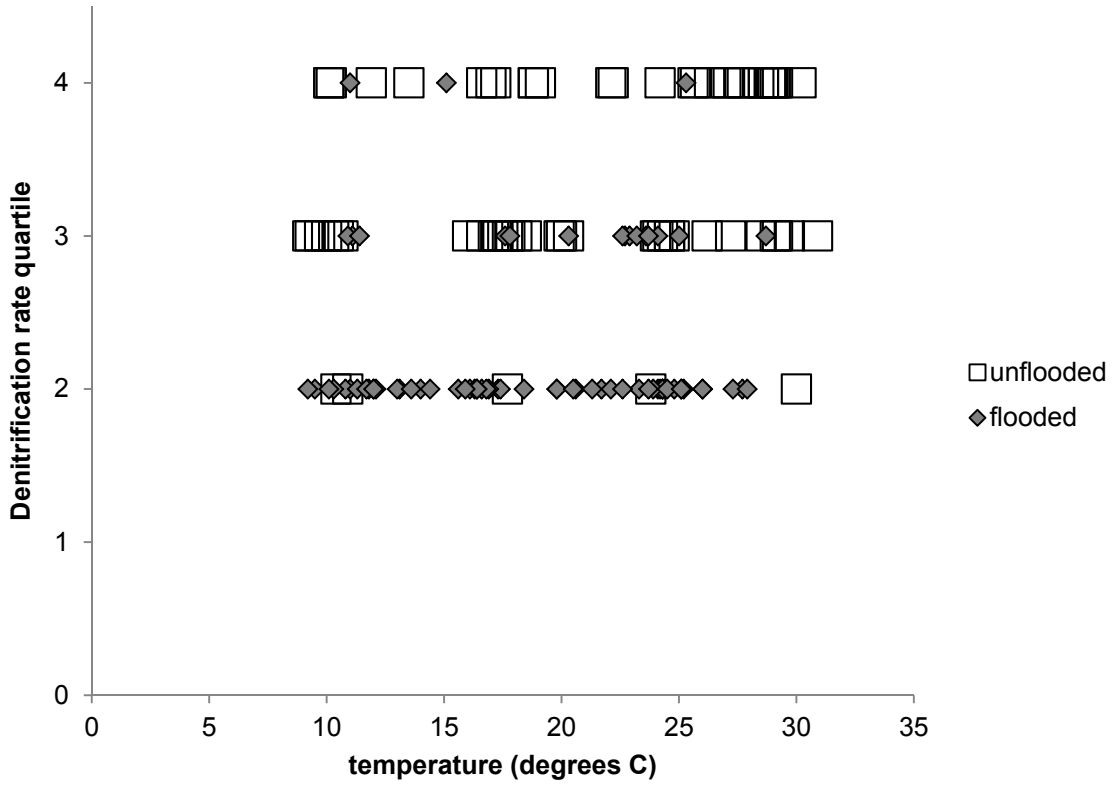

Figure 1.6. Temperature vs. denitrification rate quartile. Each point represents a single denitrification rate measurement.

effect, and temperature*flooding had a marginally significant ($p = 0.07$) negative effect, on whether denitrification rate fell above the 3rd quartile value (Table 1.2). This relationship was due to the fact that denitrification rates at flooded sites rarely fell into the 3rd quartile of the data, despite occasionally experiencing high temperatures (Figure 1.6).

The model utilizing season as a predictor of denitrification did not have a high relative AICC score (Table 1.2), and season was not a significant predictor of denitrification rate quartile. However, when season and flooding were both used as predictors in the same model, the AICC score was substantially lowered and was comparable in value to the model utilizing only flooding as a predictor for whether a

value exceeded the 3rd quartile denitrification rate (Table 1.2). In the latter model, denitrification rates fell into the 3rd quartile significantly ($p < 0.05$) fewer times in Fall (Table 1.2). However, as with the model utilizing temperature and flooding as predictors, the model with season and flooding demonstrated a significant positive Fall*flooding effect on whether a denitrification rate exceeded the 3rd quartile value (Table 1.2); this is likely due to the fact that a few flooded sites demonstrated a few "hot moments" of denitrification in the Fall, and not in any other season (Figure 1.4).

Contribution of organic carbon and nitrate to dentrification dynamics

Organic matter content was significantly ($p < 0.05$) higher in the organic-rich soils than in the loamy fill or clayey soils (Table 1.1). NO_3^- content of the soil was significantly higher in clayey soils than in loamy fill or organic-rich soils, and organic-rich soils had significantly higher NH_4^+ than loamy fill or clayey soils (Table 1.1). NO_3^- was not a significant predictor of denitrification quartile, and the model utilizing NO_3^- had relatively low AICC scores (2nd Quartile: AICC = 326.6; 3rd Quartile: AICC = 344.3). However, a model utilizing NO_3^- content of the soil the day prior to each denitrification measurement yielded comparable AICC scores to the model utilizing soil flooding as a predictor (2nd Quartile: AICC = 303.3; 3rd Quartile: AICC = 315.5). In this model, soil NO_3^- was a significant negative predictor of whether denitrification rate the following day would fall above the 2nd quartile value (Table 1.2).

NO_3^- additions did significantly increase denitrification rate in the loamy fill soils, but not in organic or clayey soils (Figure 1.7). Denitrification rates were non-normally distributed; the natural log of denitrification rate was therefore used for all subsequent statistical analyses. Initial soil NO_3^- was not significantly different between control and

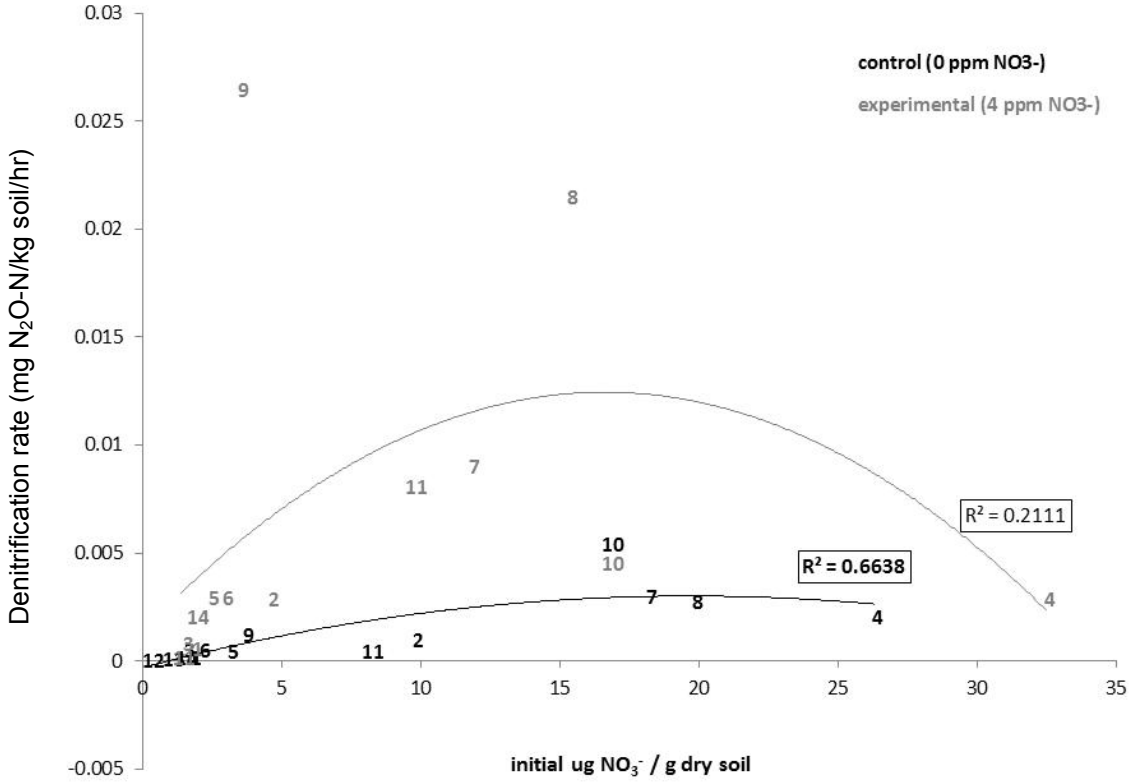

Figure 1.7. Potential denitrification rate versus soil NO_3^- (experimental, gray color) or without (control, black color) 4 ppm NO_3^- added to the soil. Sites 1-6 are organic-rich soils, sites 7-11 are loamy fill soils, sites 12-14 are clayey soils. R-squared and p values apply to analyses performed using ln(denitrification rate), since denitrification rate was non-normally distributed.

Table 1.3. PROC glm results for Teaneck incubation study. The outcome variable for all models was ln |experimental denitrification rate - control denitrification rate|

Predictor	**R-square (p-value)**
Average initial NO_3^-	0.0386 (p = 0.50)
Average initial NO_3^-, (Average initial NO_3^-)^2	**0.2821** (p = 0.16)
Porosity, (Porosity)^2	0.1291 (p = 0.47)
Clay, (Clay)^2	0.0696 (p = 0.67)

experimental treatments (paired t test: t=-0.65, p >> 0.05). Initial soil NO_3^- demonstrated a significant ($p < 0.05$) direct quadratic relationship with ln(denitrification rate) in control treatments (Figure 1.7). In experimental treatments, ln(denitrification rate) demonstrated a weaker, but still significant, quadratic relationship with initial soil NO_3^-; several loamy fill sites had denitrification rates much higher than would be predicted by initial soil NO_3^- content, however (Figure 1.7). NO_3^- and NO_3^- squared also generated the best model predicting ln |experimental - control denitrification| (Table 1.3).

DISCUSSION

This study found large differences in denitrification dynamics between brownfield soil types, and provides important evidence that differences in variables associated with soil texture are a source of patchiness in denitrification within urban wetlands. Further, this study constrained the dimensions of "hot spots" in a brownfield wetland context as "hot spots" were defined in space by the dimensions of fill piles within the site. In natural wetlands, hydrogeomorphic setting can be a key determinant of denitrification "hot spots" (Nelson et al. 1995, Clement et al. 2002). My findings identify a useful new paradigm for predicting where high denitrification occurs in an urban brownfield wetland context, since this type of wetland does not exhibit classically predictable patterns in hydrogeomorphic settings, but instead reflects a pattern of random dumping and earth movement. These results suggest that brownfield restoration projects aiming for higher levels of denitrification within wetlands must carefully consider texture and flooding of wetland soils and fill materials in their design.

"Hot moments" appeared to be constrained by NO_3^- availability and temperature: high temperatures and soil characteristics facilitating nitrification promoted the highest

levels of denitrification. Minor daily fluctuations in soil water content were not found to be a significant determinant of denitrification "hot moments," but flooding (i.e., long-term presence of standing water) was found to inhibit denitrification activity.

I defined any denitrification rate above the 3rd quartile value as "hot"; denitrification rates above the 2nd quartile value are higher than 50% of measured rates, but do not necessarily represent extreme events. Only two variables from the field study (soil NO_3^- and redox potential) predicted whether a denitrification rate fell above or below the 2nd quartile value but not whether a rate fell above the 3rd quartile value. These variables will be discussed in the context of promoting a "high" denitrification rate.

Key factors controlling hot spots and moments of denitrification: Nitrate limitations

"Hot spots" of denitrification at the study site appeared to be most heavily influenced by where conditions were optimized for simultaneous denitrification (anaerobic) and NO_3^- production (aerobic). Porosity and percent clay were the best predictors of *in situ* denitrification rate quartile; in soils with no standing water, less clay and higher porosity meant more denitrification rates falling in the upper quartiles of the data distribution. Soils with lower percent clay also retained less water over a range of simulated soil matric potentials relative to soils with higher clay content, or soils with high percent organic matter. The sites with high percent organic matter also had standing water for most of the study, and denitrification rates were uniformly low. These findings suggest that a higher percent of aerated pores at a given soil moisture content means higher denitrification activity. Effective air-filled pore space (AFPS) was not found to be a significant predictor of denitrification rate quartile, but AFPS was significantly highest, on average, in clayey soils and significantly lowest on average in organic-rich soils. The

poor relationship between AFPS and denitrification quartile may be due to the fact that soil moisture did not fluctuate very much at any given site over the course of the study, while denitrification varied considerably within a given site.

Past research has found that denitrification is negligible or on the low end of a range of measurements below a threshold of 60% water-filled pore space (WFPS). Above this threshold, denitrification is positively correlated with soil water content (Aulakh & Rennie 1985, Grundmann & Rolston 1987, Groffman & Tiedje 1991, Parsons et al. 1991, Pinay et al. 2000) and percent clay (Groffman & Tiedje 1991) or clay + silt (Pinay et al. 2000), among other variables. In this study, WFPS (calculated using the formula used in Pinay et al. 2000, data not shown) exceeded 60% over half the time in all site types over the course of the study, but measures of soil water content were not significant predictors of denitrification rate. Further, organic and clayey soils, which exceeded 60% WFPS for around 87% of the study exhibited lower denitrification rates than loamy fill soils, which exceeded 60% WFPS roughly 65% of the time. Percent clay in this study was significantly negatively correlated with denitrification "hot spots."

My results, seemingly inconsistent with the results of past studies, may be due to the fact that in the aforementioned studies, ambient soil NO_3^- was in abundant supply due to deliberate soil fertilization (Aulakh & Rennie 1985, Grundmann & Rolston 1987, Parsons et al. 1991) or endogenous net NO_3^- production rates were 10-100 times higher than those found in this study (Groffman & Tiedje 1989, Pinay et al. 2000). Therefore, denitrifier communities in these studies may not have been as limited by NO_3^-, and aerobic soil pore space (which is negatively related to soil water and clay content) was therefore not as crucial for maintaining high denitrification rates in these studies. Further, none of the

studies above utilized soils that were classified as pure clay; they typically had low percent clay and were classified as loam or silt soils. Diffusion of NO_3^- to denitrifiers can be limited in well-aggregated soils, even if NO_3^- concentrations are high (Myrold & Tiedje 1985); this phenomenon was likely occurring in several of the clayey sites, where NO_3^- in the soil was on average high relative to the other sites (Table 1.1) but denitrification rate was low. The significant negative relationship between previous day soil NO_3^- and whether a denitrification rate exceeded the median rate value was likely due to the high soil NO_3^- concentrations at clayey soil sites (Table 1.2). Porosity of clayey soils was significantly lower than that of fill soils; this is unusual for soils of this texture. Low porosity may imply a higher tortuosity value for the medium (Tremblay et al. 2005) and slower diffusion of NO_3^- from aerobic to anaerobic pores.

Study results are similar to those of Hefting et al. (2004), who found that average water table levels were a primary determinant of nitrogen dynamics, and that high silt + clay percentages had a significant positive correlation with denitrification rates only when groundwater table levels were below -30 cm (Hefting et al. 2004). In my study, water table level ("flooding") was the second best predictor of denitrification quartile after porosity (Table 1.2). Flooding was considered a temporal variable, but most sites were either flooded or unflooded for the entirety of the study. In unflooded soils, less clay and higher porosity meant more denitrification rates falling in the upper quartiles of the data distribution. In sites with standing water, denitrification rates were uniformly low—rates rarely exceeded either the 2nd or 3rd quartile value. Flooded sites (which in nearly all cases were the organic-rich soil sites) had significantly higher levels of NH_4^+ than other sites (Table 1.1), low levels of NO_3^- (Table 1.1), and very low rates of

denitrification (Table 1.2, Figure 1.3). Hefting et al. (2004) found very similar results for sites with water tables above -10 cm. Excepting a site with high allochthonous NO_3^- input, they surmised that the major end product of nitrogen mineralization under water tables above -10 cm was NH_4^+, and the rate-limiting step for denitrification was nitrification (Hefting et al 2004). Interestingly, I found in the lab incubation experiment that additions of NO_3^- to the organic-rich soils at concentrations comparable to NO_3^- concentrations in stormwater entering Teaneck (4 ppm) did not substantially increase denitrification rate, even after 23 hours (Figure 1.7). Flooded organic-rich soils at this site do not appear to support active denitrifier populations that can quickly respond to NO_3^- loading events.

In the Hefting et al. (2004) study, water table levels between -10 and -30 cm from the soil surface were the conditions under which the highest denitrification rates occurred due to the co-existence of aerobic (nitrifying) and anaerobic (denitrifying) hotspots within the soil profile. Although I did not record water levels deeper than -20 cm at any of the loamy fill sites save for a few instances, the soil water content was likely high enough at these sites to create a similar co-existence of aerobic and anaerobic hotspots within the soil profile. In clayey soils, both aerobic and anaerobic pores likely exist (since high NO_3^- and denitrification did occur in these soils), but are not well-connected enough to facilitate high denitrification. As with the organic-rich soils, denitrification in the clayey soils did not substantially increase in response to NO_3^- additions during the incubation experiment (Figure 1.7), despite the fact that the soils were made into slurries, lessening the influence of diffusion in the soil pore matrix (Myrold & Tiedje 1985). It appears,

therefore, that like the organic-rich soils, clayey soils support less abundant active denitrifier populations than loamy fill soils due to low availability of substrate.

Effect of season and temperature on denitrification

"Hot moments" in this wetland system varied with season, but did not occur on the time scale of my 9-day sampling periods within each season during which no marked wetting and drying cycles took place. Instead, high rates of denitrification occurred over period of 1-2 days, and the soils with the highest individual measurements of denitrification had the greatest variability in denitrification rate. Variability in denitrification rates observed at the scale of an entire soil core may be tied to the degree of small scale (microsite) variability and/or discontinuity in required denitrification reactants (low O_2, NO_3^-, C) within that core (Parkin 1987). It is unclear, however, how the coincidence of these reactants is facilitated on a day-to-day basis within fill soils.

In unflooded soils, denitrification "hot moments" occurred more frequently during spring and summer than in fall and temperature was a significant predictor of "hot moments" even within seasons (Figure 1.4, Figure 1.6, Table 1.2). Interestingly, organic-rich soil sites demonstrated their only "hot moments" in the fall, and not in the spring or summer. Although none of the predictor variables appeared to be substantially different during or immediately prior to these "moments," the fall sampling was preceded by a rain event at least twice as large as those preceding the spring and summer samplings. It is possible that exogenous NO_3^- in stormwater accelerated denitrification rates in these soils after 3–4 days of incubation, when denitrifier communities had a chance to grow.

Distinct seasonal patterns in denitrification have been found by other studies in comparable climatic regions, with pulses of activity in the spring and fall (Hanson et al.

1994, Nelson et al. 1995); however, high rates of denitrification have also been found in the winter (Haycock & Pinay 1993, Pinay et al. 1993), and summer (Hanson et al. 1994, Hernandez & Mitsch 2007). All studies cite hydrologic events (flooding, precipitation) as an important controlling factor on denitrification rates, and soil temperature is also identified as playing an important role, but the relative importance of the two variables in combination has not been elucidated. It has been suggested that a combination of high temperature and moisture can lead to the highest rates of denitrification (Hernandez & Mitsch 2007) and that below a certain temperature, denitrification will not occur even under very high soil moisture conditions (Pinay et al. 2007). My study found a different trend, where under very high moisture conditions, temperature increases did not make a difference; at intermediate moisture levels, temperature had a strong positive effect on denitrification and denitrification "hot moments" (Figure 1.6).

Intact core denitrification rates in the loamy fill soils were higher than those found in studies of native forested wetland soils in New Jersey (Zhu & Ehrenfeld 1999, Stander & Ehrenfeld 2009), and much higher than those found for cedar swamps in the Pinelands of southern New Jersey (Watts & Seitzinger 2000). Potential denitrification rates of soils were much lower than potential rates measured in native freshwater marsh soils under the same vegetation type (*P. australis*) in the same region (Otto et al. 1999). Potential denitrification rates for loamy fill and clayey soils in this study were also lower than those found for riparian soils in Baltimore, MD (Groffman et al. 2002, Groffman & Crawford 2003). The lower potential rates in my study are likely due to the fact that I used much lower concentrations of NO_3^- for my study than in the others (4 ppm instead of 100 ppm). However, my study possibly more closely mimicked the rates that one may

find in the field under flooding, since I selected a concentration at the high end of what might be found in surface water at Teaneck. Despite the low values of potential denitrification as compared to other studies of urban wetlands, the significant response of soils to NO_3^- additions versus control treatments did demonstrate that denitrifiers at the site are capable of higher rates of activity under NO_3^- additions.

Clayey soils supported denitrification rates comparable to forested wetland soils in northern New Jersey (Stander & Ehrenfeld 2009). Denitrification rates in all soils, but especially in clayey and loamy fill soils (range of all measurements: -0.08–0.49 mg N_2O-$N/m^2/hr$), matched or exceeded estimated NO_3^- wet and dry deposition (roughly 0.03 $mg/m^2/hr$) at Teaneck (Ravit et al. 2006), indicating that soils at the site may be an important sink for atmospheric NO_3^-.

CONCLUSIONS

This study is the first, to my knowledge, to examine denitrification rates in unmitigated fill materials on a brownfield site. Soil physical properties were highly heterogeneous over the extent of the site, and these properties influenced which soils supported the highest rates of denitrification. Soils in the Teaneck wetland site as a whole generally have adequate carbon and anaerobic pore space, but their denitrification capacity is limited primarily by NO_3^- availability. The loamy fill soils appear to have optimal structure for supporting simultaneous nitrification and denitrification, and therefore supported the highest rates of denitrification. My results suggests that denitrifiers in fill materials are active and capable of high NO_3^- removal; this brownfield site and brownfield sites as a whole may therefore serve an important role in NO_3^- removal from urban stormwater, potentially performing better than native soils. Further

research should determine just how fill materials can be chosen and/or managed to maximize their denitrification potential.

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CHAPTER 2

Soil texture and water retention as spatial predictors of denitrification in urban wetlands

ABSTRACT

Urban wetlands potentially play an important role in nitrate (NO_3^-) removal from stormwater, but the intersection of soil properties optimal for NO_3^- removal with nitrogen loads from the atmosphere and surface water is key to this function. NO_3^- removal via the microbial process of denitrification was examined in an urban brownfield wetland in New Jersey, USA. Soil samples were collected at 118 points and analyzed for soil organic matter and texture fractions. Maps of these soil properties were interpolated across the entire site, and flow paths of stormwater and nearby low-lying areas through the site were digitized from aerial imagery. A subset (17%) of points was more intensively sampled to examine relationships between denitrification rates and soil water retention characteristics. Denitrification, potential denitrification, available inorganic nitrogen, and water retention curves were characterized for this subset of soils. The highest denitrification rates occurred in soils located at low elevations, with high macroporosity. High potential denitrification rates corresponded with high available soil NO_3^-. Spatial interpolation of soil properties related to high denitrification rates accurately predicted most locations of denitrification hot spots and cold spots. These hotspots corresponded to the location of stormwater channels running through the site over 31% of total channel area, indicating that soils at the site may be at least partially reducing total NO_3^- loads to the creek flowing through the site. These results show that soil physical properties can be

used for predicting the location of potential hot spots of denitrification at the landscape scale.

INTRODUCTION

Planning and decision-making for human-induced ecological change can be improved by generating reliable forecasts of ecosystem state, ecosystem services, and natural capital (Clark et al. 2001). Urbanization is a major aspect of global change: over 50% of the world's population lives in urban areas, and within the next five years, population growth will be mainly urban (US Census 2010). There is a great need for understanding and managing the wide range of "services" that can be provided by the natural and semi-natural ecosystem components with urban landscapes.

Soils can potentially provide a number of important ecosystem services to urban landscapes; however, urban soil mapping and the use of urban soil mapping to determine ecological functions within cities are relatively new areas of research (De Kimpe & Morel 2000). The spatial positioning of soils with particular properties in relation to different types of urban land use can be important in determining how effectively they process pollutants (Pouyat et al. 2008). There is particular uncertainty about soils in urban brownfields, which are composed of a mixture of materials differing from those of natural soils and/or deeply modified by human activity (De Kimpe & Morel 2000).

Studies examining urban and rural sites in a variety of metropolitan areas have found significant effects of the urban environment on soil nitrogen and carbon pools and storage, but these effects vary considerably across the urban landscape due to patchiness of land use, vegetation, and soil types (Sawa et al. 2010). The ability of soils to retain and/or reduce nutrients is particularly important in coastal urban areas due to concerns

about nutrient loading and eutrophication in nearby estuaries (Paul & Meyer 2001, Ehrenfeld et al. 2003, Walsh et al. 2005, Paerl et al. 2006). The pervasiveness of brownfield sites in urban areas and increasing interest in wetland restoration as a means of reducing nitrate (NO_3^-, the most common and mobile form of reactive nitrogen) in urban runoff means that we need better estimates of whole-site NO_3^- removal potential in urban watersheds.

Denitrification is an anaerobic microbial process that converts NO_3^- into nitrogen gases. This process is common in floodplain soils and capable of removing large amounts of NO_3^- from the environment. Methods do not currently exist for making direct measurements of denitrification at the scale of watersheds, and scaling up denitrification rates from individual measurements of field soils can prove challenging due to high variability in measurements (Seitzinger et al. 2006). Denitrification is regulated by a complex set of environmental variables that are also highly variable over space and time; this further complicates estimates of denitrification over large areas (Boyer et al. 2006).

The purpose of this study was (1) to identify the soil physical characteristics that best predict high NO_3^- removal via denitrification within a small wetland complex on a former brownfield site, and (2) use the spatial positioning of these characteristics relative to the location of stormwater flow to estimate whole-site potential for NO_3^- removal. Previous research has shown that denitrification is tightly coupled to nitrification in soils at the study site (chapter 1). Nitrification is an aerobic process and denitrification occurs under anaerobic conditions; it appears therefore that relatively well-drained coarse-textured (sandy or silty loam) soils with adequate moisture were shown to support the highest levels of denitrification at the site (chapter 1). The high porosity and low tortuosity in

coarser soils at the site appear to facilitate the existence of and exchange between pores supporting NO_3^- creation via nitrification and pores supporting NO_3^- removal via denitrification. Soils with high clay content and low porosity appear to lack adequate exchange to couple nitrification and denitrification. Soils located in positions of the site that are very dry (around or over 3.5 m above sea level) or very wet (1–2 m above sea level) appear to be too aerobic to support denitrification or too anaerobic to support nitrification, respectively.

I expected that the highest denitrification rates would be found in areas with water retention characteristics facilitating simultaneous nitrification and denitrification within the soil matrix. I therefore hypothesized that soils with high macroporosity, intermediate water-holding capacity and pore size, and intermediate elevations would demonstrate the highest rates of denitrification in the site. Potential denitrification rates are measured in slurries under anaerobic conditions, where soil structure plays less of a role in mediating the redox status of pores and delivery of NO_3^- to denitrifiers. I expected that potential denitrification rates would be mediated less by soil structure and more by NO_3^- availability and overall size and activity of the denitrifier community. I therefore hypothesized that the highest potential denitrification rates would occur at intermediate NO_3^- concentrations, since very anaerobic soils have low NO_3^- production and therefore low denitrifier activity and populations, and very aerobic soils have high NO_3^- production, but bacterial populations have little need to produce denitrifying enzymes. Lastly, I expected that stormwater flowpaths mainly intersected with low elevation areas that are semi-permanently flooded, and therefore too anaerobic to support denitrification activity.

MATERIALS AND METHODS

Site Description

The study took place in the Teaneck Creek wetland complex, a small (0.2 km^2) freshwater floodplain ecosystem in northeastern New Jersey (NJ) that is part of the larger Hackensack River watershed (Figure 2.1). Teaneck Creek is a former brownfield area, with soils ranging from clays to pure sand and gravel due to the varied history of land use at the site. In the late 1800s, the Creek was a low order freshwater stream system, and based on profile data, soils were dominated by reduced clay soils. Modifications to the site started as early as 1899, when a trolley line was constructed through the site; the line lasted through 1938 (Arnold 2008). From 1926–1957, parts of the site were used for commercial and residential buildings, and starting in the early 1950s, wetlands were filled with clay dredge from nearby Overpeck Creek, raising elevations near the creek (Arnold 2008). Large parts of the site were used as a staging and disposal area for clay dredge and construction debris materials (concrete, gravel, loam material) during construction of the New Jersey Turnpike and Interstate 80 in the 1960s (Figure 2.2). Materials deposited on the site in the 1960s consisted primarily of domestic waste (e.g., cans & bottles, clothing, plastic), construction debris (e.g., brick, glass, concrete, roofing materials, lumber), and industrial waste (e.g., automotive parts, appliances) (Arnold 2008). From 2001 forward, when the land was taken over by Teaneck Creek Conservancy, large amounts of surface debris (automotive parts, construction materials, household appliances) have been removed from the site; however, trash, debris and dredge materials in the soil have remained largely undisturbed (Arnold 2008).

Figure 2.1. The Teaneck Creek Conservancy wetland site in 2007. Outlines in photo on right represent different land use areas digitized from a 1966 photograph (see Figure 2.2). Dashed white lines delineate the transects used for choosing sampling locations for characterization of soil properties in 2007; white circles and blue triangles are the actual sample locations along the transects. Blue triangles were also sampled for the denitrification and water retention study in 2009. Red stars are sample locations from sampling in 2005-06 and described in chapters 1 and 4. Organic matter and soil texture data from the red star sites were used for the analyses in this chapter.

ID	Landuse
1	Bare soil
2	Trolley track
3	Dark soil, herbaceous vegetation
4	Buildings
5	Light soil, herbaceous vegetation
6	Forested
7	Ditch

Figure 2.2. The Teaneck Creek Conservancy wetland site in 1966. Outlines in photo on left represent different land use areas digitized from a 1966 photograph. Numbers correspond to land uses identified from the photograph, described in the table on the right.

The location and movement of standing water through the site has also changed substantially since the late 1890s. The site has remained at a lower elevation than the surrounding landscape, but the deposition of dredge and other materials has resulted in areas within the site that are drier than they were historically; i.e. they rarely support standing water. The stream has been channelized and re-routed into the eastern side of the site. As a result, some areas that were previously characterized by anaerobic, waterlogged soils are now aerobic and well-drained. The numerous geomorphologic, biological, and hydrologic alterations at the site have led to high variation in soil profile composition at very small spatial scales.

Soil Physical Characteristics

Soil samples were collected during three days in the summer of 2007 from 118 points at Teaneck. Eight transects were designed to traverse the site in a west to east direction, and two points at each elevation were identified within each transect. Elevation data was obtained from a 2 ft digital elevation model of the site (B2A SURVSAT 2003). Mid-sections of a few of the transects were not accessible due to excessive flooding at the time of sampling or very dense and tangled vegetation covering large mounds of debris (Figure 2.1).

3.5 to 7.5 L of soil was collected from the top 10 cm of the profile at each point using shovels. Within 24 h of collection, 7 to 10 g of each sample was analyzed for gravimetric moisture content by drying at 105°C for 48 h. Percent organic matter of each subsample was then measured using loss on ignition at 450 °C for 4 h (Nelson et al. 1996). The remainder of each sample was air-dried in the laboratory for two weeks.

90 of the original 118 samples were run for particle size analysis; organic-rich soils (≥20% organic matter) were not run for this analysis. To measure percent composition of textural fractions, 100 g of dry soil was combusted with 30% hydrogen peroxide to remove organic matter, and 50 g of dry soil was used for quantifying 11 texture fractions using a modified version of the pipette method outlined in Gee & Bauder (2006). For each sample, 100 mL of 0.5% sodium hexametaphosphate solution was combined with 50 g of sample, blended for five minutes, and then poured into a 1 L graduated cylinder through a 0.053 mm sieve. The sieve was rinsed with denionized water while being held over the graduated cylinder until the water leaving the sieve ran clear; the volume of solution in the cylinder was then brought up to 1 L with deionized water. The material remaining on the sieve was rinsed into a ceramic crucible, dried at 105°C for 48 h, and used for analysis of sand and gravel fractions. Clay and silt particles were suspended in solution by plunging a rubber stopper through the solution three times. Samples were then hand pipetted from the graduated cylinder at a depth of 10 cm after 4:36 min, 51:12 min, and 7:40:49 h, to collect particles <20, <5, and <2 μm, respectively (Gee & Bauder 2006). Pipetted solutions were placed in ceramic crucibles, dried at 105°C for 48 h, then weighed. Sand fractions were determined by running the dried samples collected in the 0.053 mm sieve through a sieve tower in the following order: 2; 1; 0.7; 0.5; 0.25; 0.1; 0.053 mm. Any material on the 2 mm sieve was considered gravel and not included in the total weight when determining all other texture fractions. Any material retrieved from the bottom of the sieve tower was considered unanalyzed silt and clay. If the latter constituted ≥10% of the total sample weight, the sample was re-analyzed for texture using the same method.

Nitrogen Removal

In the summer of 2009, samples were collected on two different days (in August and in September, respectively) to characterize denitrification rates and inorganic nitrogen content. Soil moisture did not differ, on average, between the two sampling dates (data not shown); precipitation at the site totaled approximately 0 cm (August sampling) and 2 cm (September sampling) during the 7 d period prior to each collection date. 19 sample sites were selected from the original 118 sample sites to represent the range of textures found at the site, from loamy sand (83% sand, 13% silt, 0% clay) to silt loam (20% sand, 60% silt, 15% clay) to silty clay loam (7% sand, 59% silt, 34% clay). Intact cores were collected from the field using a 20x3 cm corer and analyzed for denitrification rate using the acetylene block method immediately upon returning to the lab (less than 8 h) using procedures outlined in Groffman et al. (1999). The cores were made airtight with rubber stoppers. Gas samples were taken at 2 and 6 h using a syringe and stored in evacuated glass tubes at 23°C until they could be analyzed for N_2O by electron capture gas chromatography. Samples were stored (less than 24 h) at 4°C between denitrification analysis and analysis for extractable NO_3^- and NH_4^+, gravimetric moisture content, and soil organic matter using procedures modified from Robertson et al. (1999). Soil samples were hand sorted and mixed, and held at field moisture for extracting NO_3^- and NH_4^+. Soil moisture content was determined by drying soil at 105°C for 48 h. Soil moisture was not used for subsequent soil mapping, however, since soils were collected over 2–3 days while several rain events took place. Soil organic matter content was determined by loss on ignition at 450°C for 4 h. Available soil NO_3^- and NH_4^+ contents in soil were

determined by extraction of 10 g of soil with 2M KCl followed by colorimetric analysis with an Omnion Lachat Quickchem 8000 (Lachat Instruments, Loveland, CO).

For the September collection date, denitrification rate was measured on intact cores and potential denitrification rate was measured with soil slurries. Replicate cores were collected at each sample site on the same date. Intact core denitrification rate was measured on one set of replicate cores in the lab within 8 h of collection using the methods described above. The second set of replicate cores were stored at 4°C for one week, and then used to measure potential denitrification rate. Potential denitrification rate was measured in the following manner: soil core samples were brought to room temperature, hand sorted and mixed, and subsampled for determination of extractable NO_3^-, extractable NH_4^+, gravimetric moisture content, and percent organic matter using the methods described above. Soils were also sub-sampled for 25 g of soil and combined with 25 mL of DI water to make slurries. Slurries of each sample were replicated whenever possible; in a few cases, when soil quantity was insufficient, 10–15 g of soil was used with an equal weight of DI water for a duplicate slurry sample. Slurries were placed in airtight vials, and the headspace was made anaerobic by evacuating and flushing vials 5 times with N_2 gas. After the 5th evacuation, the headspace was brought to ambient pressure with N_2 gas. 10 cc of acetylene gas was injected into each vial, and slurries were placed on a rotating table. 10 cc of headspace was sampled after 30 and after 90 min using a syringe. Samples were stored in evacuated glass tubes at 23°C until they could be analyzed for N_2O by electron capture gas chromatography.

Water Retention Curves

Water retention curves were generated for soils at 18 of the 19 sites used in the denitrification analysis by collecting several intact cores from each site in 2009. Cores were analyzed for water content at pressure potentials ranging from -1 to -50 cm using the hanging water column method. Soil cores (3 cm in height and 5.4 cm in diameter) were collected (in duplicate) from the field and saturated overnight before being placed on saturated double-layered filter paper (Whatman #3) in sealed chambers in a hanging water column system. The replicate sample from one of the sites (site 11) was damaged during transportation to the laboratory, and was thus not analyzed. Soil cores were placed in a sequence of pressure potentials in the following order: -5 cm (for 6 h), -10 cm (12 h), -20 cm (18 h), and -50 cm (40 h). The volume of water exiting the core was collected and measured under each pressure potential. At the end of the experiment, soil cores were removed from the system and 10 g of soil was removed from the top and the bottom of the core, respectively, and dried separately at 105°C for 24 h; the average of the two samples was used to determine water content at equilibrium with -50 cm.

Following removal of the 10 g of soil, soil volume in each of the cores was determined in the following way: First, the core was weighed and then wrapped in cling wrap to adhere to the surface of the soil in the core. Warm paraffin was poured into the space left in the core by the soil removal mentioned above. The wax was allowed to dry, and superfluous paraffin sticking out from the core was removed using a heated knife; this procedure was repeated for the top and the bottom of the core. The core was then re-weighed to determine the weight of the paraffin. Paraffin weight was converted to volume using the known density of paraffin wax (0.91 g/cm^3). Soil volume in the core

was thus calculated as: V_c - V_p, where V_c is the volume of the core (i.e. 68.67 cm^3) and V_p is the volume of the paraffin. Water content at -50 cm was determined as average water content at the end of the experiment divided by the total volume of soil; water content at all other pressure potentials were back-calculated from this value using the volume of water exiting the core over each change in pressure potential.

For pressure potentials greater than -50 cm, water retention curves were determined using the pressure plate extractor system (Soilmoisture Equipment Corp., Santa Barbara, CA). Soil cores (5 cm in height, 8 cm in diameter) were collected from the 18 sites used in the hanging column analysis. Bulk density of soil in the large cores was determined in the following manner: each core was weighed prior to sub-sampling (described below); following sub-sampling, 10 g wet soil was scooped out of the top and bottom of the core, respectively. The 20 g was combined and dried at 105°C for 24 h, and used to calculate volumetric water content of the cores. Bulk densities calculated in this manner were comparable to bulk densities calculated using the paraffin method in the previous analysis (data not shown).

To prepare samples for the pressure plate extractor system, three subsamples were taken from the top and the bottom of each large core using metal rings (0.6 cm in height, 2.4 cm in diameter). The subsamples were then set on ceramic plates that were placed in chambers at one of three pressure potentials: -320 cm, -1000 cm, or -5000 cm. To increase contact between soil and the ceramic plates, plates were covered with a paste of diatomaceous earth and then layered with wet filter paper before setting down cores. The entire system (plate and soil samples) was left to saturate overnight in shallow water. Plates were placed into pressure chambers the following day, sealed, and left to

equilibrate. Soils were allowed to equilibrate for 17 d in the chambers at pressure potentials of -320 cm and -1000 cm, and for 27 d in the chambers at a pressure potential of -5000 cm.

To fit water retention curves for each site, water content values over the pressure potential sequence were fed into an online program (http://swrcfit.sourceforge.net) to calculate parameters for the van Genuchten model, i.e. water content at saturation (θ_s), the residual water content (θ_r), α, and n (van Genuchten 1980, Seki 2007). Water content at the inflection point of the water retention curve (θ_p) was calculated using the equation from Dexter (2004).

$$\theta_p = \theta_r + (\theta_s - \theta_r) * (1 + \left(\frac{n}{n-1}\right))^{\left(\frac{1}{n-1}\right)} \quad (2.1)$$

The program also calculates parameters for the lognormal model for water retention, i.e. θ_s, θ_r, h_m, and σ (Kousugi 1996). The latter model assumes a lognormal pore size distribution, where σ is a dimensionless parameter corresponding to the standard deviation of log-transformed soil pore radius, and h_m is the matric pressure head related to median pore radius.

Several parameters were calculated to characterize pore structure of the soil. Effective porosity was calculated as effective porosity = (θ_s - θ_p) using the parameters estimated from the van Genuchten model. Macroporosity, or the fraction of total pore space composed of the largest conducting pores, was calculated as macroporosity = (θ_s - θ_p) / θ_s using the parameters estimated from the van Genuchten model. Parameters related to pore structure from the lognormal equation (h_m, σ) were also used to characterize pore structure and water retention. Soil entropy (SH) is a variable that can be calculated using

parameters estimated by the lognormal model; it is a unified index of pore distribution. This variable was calculated using the equation from Yoon & Gimenez (*in review*):

$$SH = (\theta_s - \theta_r) * \ln\left(\frac{149}{h_m}\right) + 0.5 + 0.5 * \ln(2 * \pi * \sigma^2) - (\theta_s - \theta_r) * \ln(\theta_s - \theta_r) \quad (2.2)$$

Statistical Analysis

Nitrogen cycling measurements and pools (extractable NO_3^- and NH_4^+, potential denitrification, intact core denitrification) were highly variable, with little replication over time (since soils were collected on only two sample dates). Correlations between nitrogen variables and soil physical characteristics thus did not produce consistent or strong predictive relationships (data not shown). For this reason, cluster analysis (K-means) was used to uncover which soil physical and chemical characteristics tended to co-occur with high denitrification rates (SPSS Statistics 17.0). Four clusters were determined for each set of variables; four clusters was decided on in order to best capture the low, intermediate, and high ranges of denitrification rates measured in the study. Because cluster analysis cannot accommodate missing values and denitrification rate values were missing for a few samples collected in August 2009, 12 of the original 19 samples were used in the cluster analyses utilizing the August 2009 samples. Cluster center values of predictive variables (NO_3^-, soil physical characteristics) were then regressed against cluster center values of denitrification rates.

Spatial Analysis

Following cluster analysis to determine which soil characteristics co-occurred with high or low denitrification rates, maps were interpolated for these characteristics using the point data collected from Teaneck in 2007. At each of these points soil texture

fractions, elevation, and organic matter data were available. Because of the inaccessibility of the southern and eastern part of the site due to extreme flooding in 2007, data on texture fractions collected at a small number of points in this part of the site during 2005-06 was used to augment some interpolations (Figure 2.1). Collection and analysis of this latter data set is described in chapter 1 and Appendix A of chapter 4. Texture fractions were used to estimate soil structural variables, described in further detail in the discussion.

Soil characteristics at Teaneck are highly related spatially to human use (i.e., to where materials were dumped). To improve the spatial accuracy of the interpolated data, landuse in 1966 (following the heaviest dumping activity at the site, and immediately preceding site abandonment) was captured by digitizing aerial photography from 1966 of the site (Figure 2.2) (USGS-EROS 1966). The photograph was georeferenced in ArcMap (ArcGIS 10.0) using 2007 aerial photography (NJ-OIT, Office of Geographic Information Systems 2007), and then digitized into a polyline shapefile by visually assessing and delimiting areas of differing vegetation and areas with bare soil under different use (Figure 2.2). This layer was used to constrain an inverse weighted distance interpolation of macroporosity derived from the point data (maximum search radius 150 m), but was not used to constrain interpolations of soil organic matter, since the latter soil property was likely to be more related to vegetation and flooding than to previous land use.

Stormwater channels conveying water into and through the site were digitized as a polyline shapefile using 2007 aerial photography and converted to a raster layer (1.5 m cell size). A sampling analysis was used to determine the total area over which these flowpaths intersected with given soil physical characteristics and elevations of interest;

the layers sampled included the digital elevation model of the site, and the layers interpolated using inverted weighted distance analysis.

RESULTS AND DISCUSSION

Soil Physical Variables Regulate Nitrate Availability and Denitrification Rates

To address the original hypotheses, three cluster analyses were run: The first included all nitrogen cycling data, to address whether any general patterns emerged between inorganic nitrogen content of soil and intact core and potential denitrification rates (Table 2.1). The second examined the relationship between denitrification rate in intact cores, soil available NO_3^-, and soil physical characteristics potentially regulating NO_3^- production (SH, h_m, σ, effective porosity, macroporosity, elevation) (Table 2.2). The third cluster analysis used the same variables as in the second cluster analysis, but instead of intact core denitrification rates, the analysis used potential denitrification rate, or denitrification enzyme activity (DEA), instead of intact core denitrification rates (Table 2.3). All correlation analysis results presented here were obtained by regressing cluster center values against one another.

Cluster analysis of nitrogen cycling data over the entire study period indicated strong quadratic relationships between cluster center values of potential (DEA) and intact core denitrification rate and soil available NO_3^-, although the highest rates of denitrification were not consistently predicted by the same range of NO_3^- values (Table 2.1, Figure 2.3). In intact cores, slightly lower soil NO_3^- concentrations (600–2,600 μg NO_3^--N/kg soil) supported the highest denitrification rates as compared to the soil slurries used in the DEA analysis (2,000–6,000 μg NO_3^--N/kg soil). This discrepancy is likely due to the more anaerobic conditions and fewer limitations to NO_3^- diffusion in the DEA analysis

Table 2.1. Final cluster center values and number of cases in each cluster using all nitrogen cycling data collected in August and September 2009.

	Clusters			
Cluster ID	A	B	C	D
# of cases	1	1	2	8
Denitrification rate (8/09) (μg N_2O-N/kg soil/d)	-90.15	-47.79	-22.61	25.82
Denitrification rate (9/09) (μg N_2O-N/kg soil/d)	-695.7	-153.1	10.14	71.56
DEA (9/09) (μg N_2O-N/kg soil/d)	-3.93	-977.7	659.9	30.84
NO_3^- - 8/09 (μg N/kg soil)	8,850	655	6,961	757
NO_3^- - 9/09 (μg N/kg soil)	11,980	4,110	630	-70
NO_3^- - DEA (μg N/kg soil)	15,103	-0.025	5,727	3,277
NH_4^+ - 8/09 (μg N/kg soil)	926	15,610	2,382	2,440
NH_4^+ - 9/09 (μg N/kg soil)	1,799	49,639	2,807	1,604
NH_4^+ - DEA (μg N/kg soil)	3,179	13,637	17,186	2,650

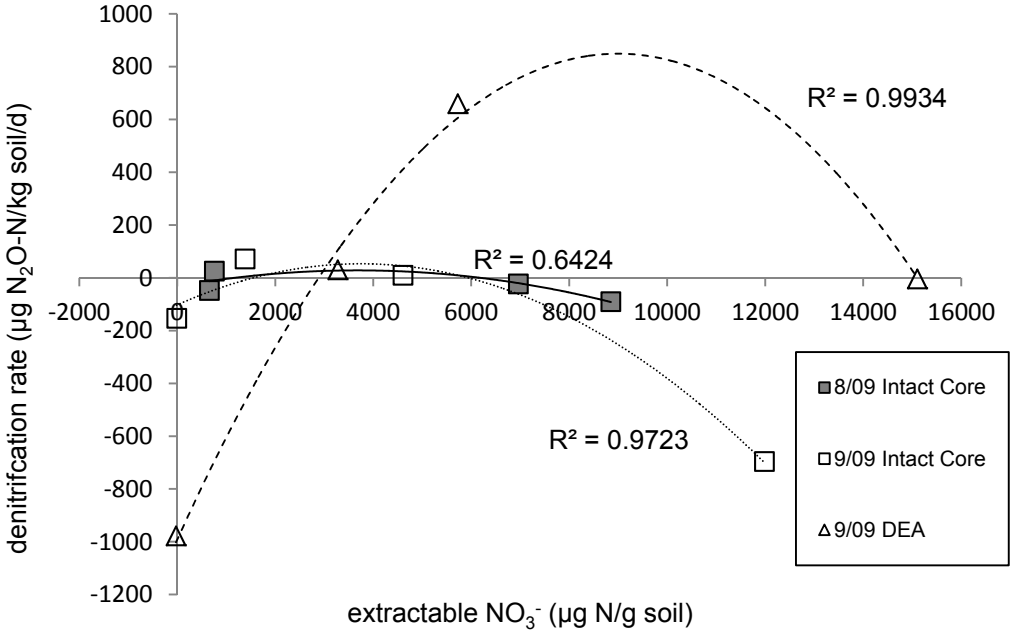

Figure 2.3. Relationship between potential (DEA) and intact core denitrification rates and soil extractable NO_3^-. Values for each variable in the graph are cluster center values as determined by the cluster analysis shown in Table 3.1.

(Myrold & Tiedje 1985). In intact cores, NO_3^- forms in aerated pores and diffuses slowly through the pore matrix to the anaerobic pores that support denitrifier activity. In soils with the higher soil NO_3^- content, denitrifier communities are likely inhibited in their activity due to the presence of oxygen and/or slow NO_3^- diffusion. Under the low oxygen conditions and low soil tortuosity of the slurry incubation experiment, however, oxygen does not inhibit denitrifier activity, and soils with high NO_3^- content can provide more substrate than soils with low NO_3^- content. In soils with the highest soil NO_3^- content, denitrifier communities are likely small and less active in general; in this situation, even potential denitrification is low.

The second cluster analysis further supported that dentrifier activity in Teaneck soils is strongly regulated coupled nitrification-denitrification as mediated by pore structure. NO_3^- was the strongest predictor (R^2=0.758) of intact core denitrification rate cluster center values (Table 2.2). The latter regression indicated a negative linear relationship between denitrification rate and NO_3^- rather than a quadratic relationship as found in the first cluster analysis (Figure 2.3). Cluster center values for intact core denitrification rate were slightly different between the first and second cluster analysis, however. This was likely due to the fact that soils analyzed for potential denitrification rate demonstrated different ranges and microbial community response (i.e., high vs. low activity) than when analyzed in intact cores. These inconsistencies in rate under the two types of analyses were expected and have been found in a number of other studies examining both potential and intact core denitrification rates (Smith & Parsons 1985, Groffman 1987, Groffman & Tiedje 1989, Simek et al. 2004).

Table 2.2. Final cluster center values and number of cases in each cluster using intact core denitrification rates and select soil variables from intact cores collected in August and September 2009. Cluster center values of denitrification rates for both dates were regressed against cluster center values of each variable below; resulting R^2 values are reported for these regressions in the last column (NO_3^- on both dates was pooled for the regression). Two variables (marked with asterisks) did not show consistent relationships with denitrification rate and were therefore not used in a regression analysis. Results of the cluster analysis (cluster center values, number of cases in each cluster) did not change when the analysis was re-run without these latter variables.

	Clusters				R^2
Cluster ID	A	B	C	D	
# of cases	1	5	7	1	
Denitrification rate (9/09) (μg N_2O-N/kg soil/d)	-695.7	-38.59	70.19	469.1	
Denitrification rate (8/09) (μg N_2O-N/kg soil/d)	-90.15	-16.40	31.87	171.1	
NO_3^- - 9/09 (μg N/kg soil)	11,980	4,110	630	-70	0.758
NO_3^- - 8/09 (μg N/kg soil)	8,850	4,940	930	130	
Elevation (m)	3.66	3.14	2.66	1.28	0.612
% effective porosity*	13	22	19	22	
% macropores	24	30	31	35	0.692
SH	3.29	3.13	2.18	2.14	0.486
σ	6.58	1.98	1.87	1.57	0.558
h_m*	52.62	12.27	26.69	30.51	

As hypothesized, percent macroporosity demonstrated a significant positive linear relationship with intact core denitrification rate in the second cluster analysis (R^2=0.692) (Table 2.2). This variable was the strongest predictor of denitrification rate cluster values following soil NO_3^-. Elevation and to a lesser extent σ (related to the standard deviation of the pore radius) and SH (a unified index of pore distribution) demonstrated negative relationships with intact core denitrification rates (Table 2.2). Effective porosity did not demonstrate a consistent relationship with denitrification rates, nor did h_m (Table 2.2). These results suggest, as hypothesized, that high elevation sites produce high NO_3^- but

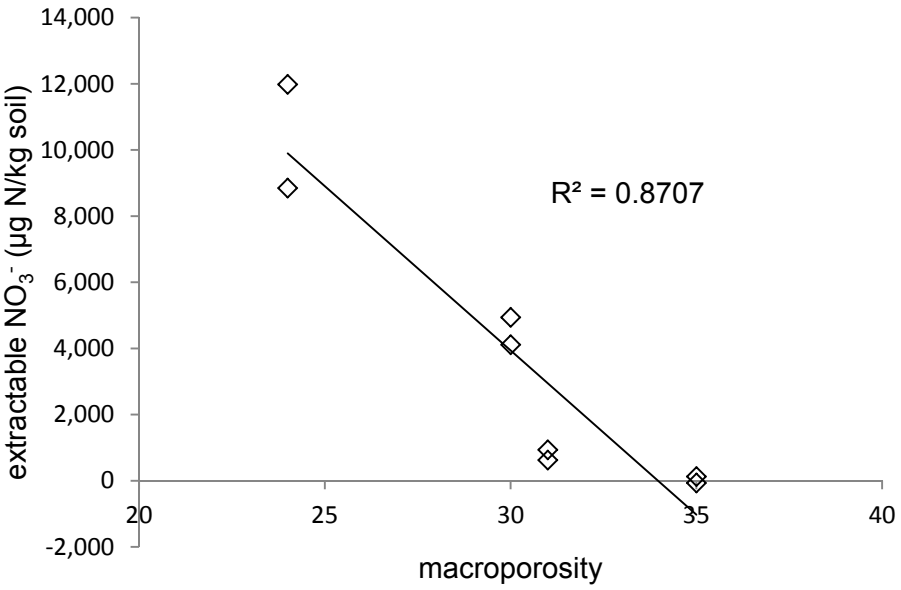

Figure 2.4. Macroporosity as a predictor of extractable NO_3^- in intact core soil samples collected in August and September 2009. Values for each variable in the graph are cluster center values as determined by the cluster analysis shown in Table 2.

are too aerobic to support high denitrification rates. It is surprising that denitrification rates did not drop at the lowest elevations as expected, but I did not sample semi-permanently flooded areas of the Teaneck site in this study, where previous work has found endogenous NO_3^- production and denitrification rate to be low under very wet conditions (chapter 1). The strong negative correlation found between macroporosity and soil extractable NO_3^- in the second correlation analysis (Figure 2.4) is likely the outcome of soils with high macroporosity supporting adequate aerobic pore space to produce NO_3^-. Soils with high macroporosity also appeared to occur at low enough elevations to support water-filled anaerobic pore space capable of fueling high NO_3^- consumption via denitrification (Table 2.2).

The results of the third cluster analysis (Table 2.3) show that potential denitrification rate demonstrated a strong positive correlation with elevation and with available NO_3^-. In the case of potential denitrification rate, available NO_3^- was measured prior to analysis,

Table 2.3. Final cluster center values and number of cases in each cluster using potential denitrification rates and select soil variables from cores collected in September 2009. Cluster center values of denitrification rates for both dates were regressed against cluster center values of each variable below; resulting R^2 values are reported for these regressions in the last column. Two variables (marked with asterisks) did not show consistent relationships with denitrification rate and were therefore not used in a regression analysis. Results of the cluster analysis (cluster center values, number of cases in each cluster) did not change when the analysis was re-run without these latter variables.

	Clusters				R^2
Cluster ID	A	B	C	D	
# of cases	1	2	9	3	
DEA (9/09) (μg N_2O-N/kg soil/d)	-977.6	15.12	279.8	659.9	
NO_3^- - DEA (μg N/kg soil)	-25	4,074	2,867	5,727	0.866
Elevation (m)	1.21	2.85	2.74	3.51	0.959
% effective porosity	23	19	21	16	0.757
% macropores	24	30	31	35	0.111
SH	3.29	3.13	2.18	2.14	0.245
σ*	6.58	1.98	1.87	1.57	
h_m*	52.62	12.27	26.69	30.51	

rather than after measuring denitrification rate (as in the case of the intact core analysis). These results from the third cluster analysis therefore further support the idea that at high elevations, anaerobic conditions are the most limiting factor for denitrification, and NO_3^- is in high supply. Other aspects of soil structure regulating NO_3^- production and availability that were important in regulating denitrification rates in intact cores were not generally strongly correlated with potential denitrification rates, as predicted (Table 2.3). Effective porosity was, however, strongly correlated with potential denitrification cluster center values (Table 2.3).

Scaling Up Denitrification Hotspots to the Landscape Level

A 2006 study at the same site examining denitrification rates at 14 points over three seasons found a lower range of denitrification rates (-0.08–0.49 mg $N/m^2/hr$) than those found in this study (-1.67–2.56 mg $N/m^2/hr$) (chapter 1). In the former study, a denitrification "hot spot" was defined as a denitrification rate that exceeded the 3rd quartile value of the data distribution (0.05 mg $N/m^2/hr$). Soils defined as "loamy fill" (i.e. loam soils characteristics of fill piles) exceeded 3rd quartile values more than any other soil type (clayey, organic-rich) in this study. Atmospheric loading rate of inorganic N to the site is approximately 0.04 mg $N/m^2/hr$ (0.02 mg NO_3^--N m^2/hr) (Ravit et al. 2006). Denitrification rates of all samples in clusters C and D of the second cluster analysis (Table 2.2) exceeded 0.05 mg $N/m^2/hr$ on one or both sample dates in all cases except one. Roughly 50% of the samples in these two clusters exceeded both 0.04 and 0.05 mg $N/m^2/hr$ on both dates. None of the denitrification rates in all samples in clusters A and B of the second cluster analysis (Table 2.2) exceeded 0.05 mg $N/m^2/hr$. Most of the samples in cluster B did exceed 0.04 on at least one of the two sampling dates, however. Based on these criteria, I defined the samples in clusters C and D as representing "hot spots" of denitrification.

Because macroporosity and elevation demonstrated strong predictive relationships with both extractable NO_3^- and intact core denitrification rates, these variables were used to identify potential denitrification hot spots at the watershed level. I did not analyze the 118 samples collected at the site for water retention or bulk density, and therefore needed a means of approximating macroporosity across the watershed. Macroporosity was estimated for the 118 points using an empirically-derived equation based on the 19

samples analyzed for water retention characteristics. To build the regression equation, I first calculated the geometric mean particle size (MPS, in mm) and parameters estimating particle size distribution (as variables that were likely to be related pore size distribution and macroporosity). To calculate SH_p (probability distribution of particle size), I used a modified version of equation 2.1:

$$SH_p = \ln(\text{MPS}) + 0.5 + 0.5 * \ln(2 * \pi * {\sigma_p}^2) \quad (2.3)$$

Where σ_p is the standard deviation of particle size. σ_p was calculated using the following equation from Shirazi & Boersma (1984):

$${\sigma_p}^2 = [\sum m_i x^2 - \ln(MPS)^2\ ]^{1/2} \quad (2.4)$$

Where m_i is the mass fraction of the textural fraction i and x is the log transformed particle size of the textural fraction i.

The 19 macroporosity values (M) calculated using the water retention curve parameters were then regressed against percent organic matter, percent sand, percent silt, SH_p, σ_p, and MPS, yielding the following equation ($R^2 = 0.657$, $p = 0.02$):

$$M = -0.128 + 0.291 * MPS - 0.041 * SH_p + 0.568 * OM + 0.373 * Sa\ +\ 0.477 * Si \quad (2.5)$$

Where OM is the soil organic matter fraction (g/g dry soil) Sa is the sand fraction (g/g dry soil), and Si is the silt fraction (g/g dry soil). Percent clay was not a significant predictor of macroporosity and was thus not included in the model. Mean pore size ($p = 0.12$) and SH ($p = 0.10$) were marginally significant predictors in the model; these were probably not more significant predictors due to the fact that they incorporated the clay fraction (a non-significant predictor) into their calculations. Organic matter, sand, and silt fractions of the soil were all significant predictors ($p \leq 0.01$) of macroporosity.

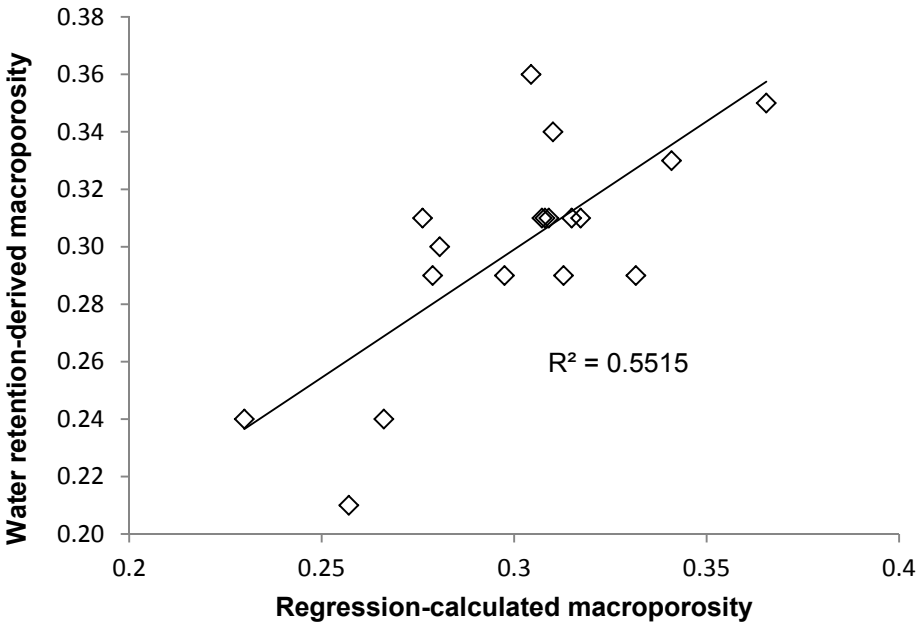

Figure 2.5. Relationship between macroporosity calculated using a measured and fitted water retention curve and macroporosity calculated using a water retention curve estimated by regression using sand and silt fractions, soil organic matter, and SH, mean pore size, and σ calculated using texture fractions in the same soil sample. Each point represents one of the 19 samples used for denitrification analyses and subsequent cluster analysis.

Macroporosity values predicted by this regression equation had a fairly good correlation with macroporosity values calculated using the water retention curve (Figure 2.5); this regression equation was therefore used to estimate macroporosity for the points for which texture fractions were analyzed. Estimated macroporosity was then interpolated for the entire site.

Organic-rich soils (percent organic matter > 15%) were found to support low rates of denitrification in the 2006 study (chapter 1) due to the fact that these soils were semi-permanently flooded with low endogenous NO_3^- production. I interpolated a layer for soil organic matter using inverse weighted distance (minimum number of points = 5) for use in assessing where high macroporosity was unlikely to sustain high levels of denitrification (Figure 2.6). Denitrification levels were assumed to be highest in areas

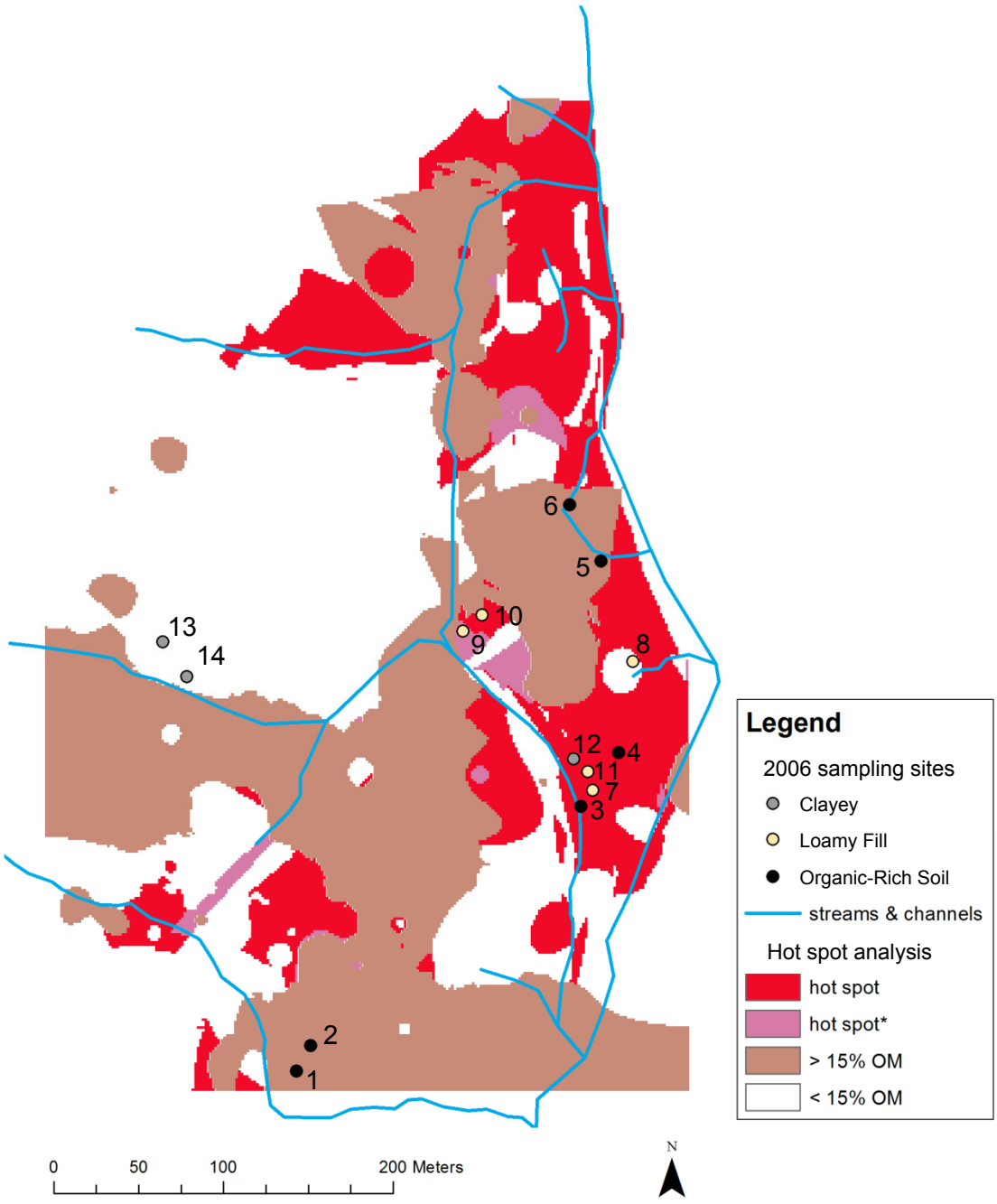

Figure 2.6. Percent organic matter (OM), predicted hot spots of denitrification activity in soils, and stormwater channels at Teaneck Creek Conservancy. Hot spots (red) are areas with macroporosity>0.30, organic matter<15%, and elevation<3.14 m. Hot spots* in purple are areas meeting these criteria, but with macroporosities exceeding 0.35 (the maximum macroporosity calculated using water retention variables). The long channel flowing along the far western boundary of the site is the Teaneck Creek main channel, and was not considered a stormwater channel in spatial analyses. Points represent locations of intensive sampling for denitrification rate in 2006 (chapter 1). In chapter 1, the soil types as these points were classified as organic, loamy fill, or clayey. See Table 2.4 for denitrification data at these sampling locations.

Table 2.4. Intact core denitrification rate summaries of soil samples collected during a 2006 study at Teaneck Creek Conservancy. Samples were collected for each site for 27 days over 3 seasons. Soil type was a descriptor assigned to each site based on texture data collected in 2006 (chapter 1). Minimum and maximum denitrification rates are in $mg/m^2/hr$. A denitrification rate of 0.05 mg N/m2/hr was the median denitrification rate for all samples collected during the 2006 study.

Site	Soil type (as defined in chapter 1)	Minimum	Maximum	% Rates exceeding 0.05 mg $N/m^2/hr$
1	Organic-Rich	-0.01	0.00	0
2	Organic-Rich	-0.00	0.07	4
3	Organic-Rich	-0.01	0.01	0
4	Organic-Rich	-0.01	0.00	0
5	Organic-Rich	-0.01	0.01	0
6	Organic-Rich	-0.01	0.05	0
7	Loamy Fill	-0.01	0.42	48
8	Loamy Fill	-0.01	0.49	70
9	Loamy Fill	0.00	0.35	63
10	Loamy Fill	-0.01	0.37	37
11	Loamy Fill	-0.07	0.43	59
12	Clayey	-0.02	0.28	35
13	Clayey	-0.00	0.25	27
14	Clayey	-0.01	0.11	7

with elevations < 2.66 m, but with < 15% soil organic matter and macroporosities exceeding 0.30 (Table 2.2).

The interpolated layer of organic matter predicted areas of organic-rich soils fairly well, based on field observations and actual measurements at points 1, 2, 5, and 6 (Figure 2.6). It did not capture some of the organic-rich soil areas near Teaneck Creek (Figure 2.6), possibly because these areas were flooded and therefore not well-sampled in the 2007 field sampling (Figure 2.1). Points 7–11 were considered hot spots according to the criteria in chapter 1. Points 7–9 and 11 in particular demonstrated denitrification rates exceeding the 3rd quartile value of the data distribution roughly 50% or more of the time (Table 2.4). The interpolated layer of hot spots accurately captured these hot spot areas and correctly identified sites 1, 2, 5, 6, 13 and 14 as cold spots. Sites 3, 4, and 12 were

incorrectly identified as potential areas of high denitrification, however, and site 8 was located at a borderline cold spot/hot spot area (Figure 2.6). These results may, however, be due to minor spatial accuracies of the map.

Stormwater channels intersected areas with conditions constituting hotspots roughly 31% of the time, indicating that NO_3^--laden surface flow may not be entirely bypassing areas capable of removing the NO_3^- via denitrification. This analysis did not, however, take into account residence time of the stormwater in a given area of soil. Measurements in the headwaters of Teaneck Creek have estimated a loading rate of 0.4–58.1 kg NO_3^- per day from surface water. The total channels areas digitized in this analysis total 4,240 m^2 in area; 3,154 m^2 of this area are the stormwater channels feeding Teaneck Creek. Using these numbers, loading through the stormwater channels is approximately 1.2–173.3 μg NO_3^--N/m^2/hr during water flow through the channels, making total loading to any given point along the stormwater channels (from atmospheric deposition and stormwater) approximately 27.9–200.0 μg NO_3^--N /m^2/hr. Points in cluster C of the 2nd cluster analysis did exceed denitrification rates of 27.9 μg N/m^2/hr during one or both sampling dates, but never equaled or exceeded 200.0 μg NO_3^--N /m^2/hr. The point in cluster D of the 2nd cluster analysis exceeded 200.0 μg NO_3^--N /m^2/hr on both sampling dates.

CONCLUSIONS

Soil properties related to the ability of a soil to simultaneously support nitrification and denitrification led to the highest rates of denitrification across a brownfield wetland site. Ostensibly for this reason, areas with high macroporosities and at low elevations appeared to support denitrification hotspots. These hotspots corresponded to the location

of stormwater channels at the site roughly one third of the time, indicating that soils may be reducing total NO_3^- loads to the creek flowing through the site. The denitrification rates occurring at these hotspots may not always be adequate to fully eliminate stormwater NO_3^- loads, however. Identifying soil structural properties in brownfield floodplain soils associated with high denitrification rates provided a useful way of estimating whole-site denitrification potential and could be used to design management plans by which NO_3^-–laden stormwater can be routed through areas with the ability to remove NO_3^-. Spatial analysis accurately predicted most locations of denitrification hot spots and cold spots, but the high level of heterogeneity in soils and topography at the site meant that smaller-scale variations (in organic matter, for example) were not always fully captured. This study demonstrates that even highly modified and unrestored sites in urban areas may be playing an important role in nitrogen cycling within these ecosystems, and that soil physical properties can be used for predicting the location of potential hot spots of denitrification at the landscape scale.

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CHAPTER 3

Denitrification and N_2O emissions in brownfield wetland soils

Figure 3.1. Liberty State Park interior wetlands and study sites. Red outline on 2006 photo (top) shows location of interior fenced-in study area. Close-up view (below) shows location of sample wetlands.

ABSTRACT

Brownfields are ubiquitous in urban areas, but rarely studied outside of identifying and remediating soil contaminants. In the northeastern United States, where atmospheric deposition of nitrate (NO_3^-) is high; denitrification, a common microbial process in wetlands, is a means of removing excess NO_3^- from soil and water. N_2 is the desired end product of denitrification, but incomplete denitrification can result in production of N_2O, a greenhouse gas. No studies have examined whether abandoned urban areas are capable of NO_3^- removal, and whether denitrification in these soils results in high or low N_2O:N_2. I examined N_2O production and limitations to denitrification in brownfield wetlands in New Jersey, USA. Soil C:N ratios were high and denitrification and N mineralization low for all sites, but soil NO_3^- increased during dry periods. NO_3^- additions to lab-incubated soils increased denitrification rates, while additions of labile carbon did not. Incubations indicated that the end product of denitrification was primarily N_2O and not N_2. These results indicate that brownfield wetlands can develop significant denitrification capacity; so much so that they are severely N-limited. They might be significant sinks for atmospheric NO_3^-, but may also become a significant source of N_2O if NO_3^- deposition were to increase.

INTRODUCTION

Nitrogen (N) removal is commonly cited as a rationale for wetland restoration projects, since wetlands have demonstrated the ability to prevent movement of excess N from upland areas into surface water (Mitsch et al. 2001). The ability of wetland areas to remove nutrients from surface water is of particular importance in the northeastern United States, where atmospheric N deposition is high, and dense human populations

generate high inorganic N levels in surface and ground waters (Driscoll et al. 2003, Gao et al. 2007). Nitrate (NO_3^-) is the most common drinking water pollutant in U.S. ground waters (Nolan & Stoner 2000)and is often transported to estuaries and coastal waters, causing eutrophication and biological perturbations such as dead zones (Mitsch et al. 2001). The conversion of NO_3^- to inert N_2 gas via the process of denitrification, which typically occurs at high rates under natural wetland conditions, is therefore a process of interest to water resource managers.

NO_3^- removal via denitrification is a microbial process performed by a diverse group of heterotrophic bacteria that are ubiquitous in the environment. It is mediated by three controlling factors: (1) the availability of organic carbon substrate (C); (2) the availability of NO_3^-; and (3) the presence of suboxic (< 0.2 mg O_2/L) conditions (Seitzinger et al. 2006). Under suboxic conditions, N_2 is the primary end product of denitrification, but denitrification can also result in release of nitrous oxide (N_2O), particularly if pH is low (which inhibits N_2O reductase), or some oxygen is present in the soil matrix (Hernandez & Mitsch 2006). The amount of N_2O produced relative to N_2 during denitrification is also higher if soil NO_3^- content is high, because NO_3^- is preferred over N_2O as an electron acceptor (Tiedje et al. 1984). Because N_2O is a potent greenhouse gas, with 310 times the heat trapping capability of CO_2 (EPA 2006), a low net N_2O:N_2 ratio produced from denitrification is desirable in a wetland ecosystem serving to reduce NO_3^- from the surrounding environment.

Brownfields, or areas previously developed and now derelict, vacant, or under-utilized (Lesage et al. 2007), are ubiquitous throughout urban areas, but rarely studied outside the context of identifying and remediating soil contaminants. A large body of

literature has examined the role of soil factors in removing metals and organic contaminants from brownfield soils (e.g., Wei & Yang 2010), but few studies have examined the relationship between nutrient cycling and brownfield soil biogeochemistry (but see Murray et al. 2000). Further, most studies examining brownfield soil function focus on remediated or replacement soils (but see Murray et al. 2000, Howard and Olszewska 2011). In these studies, the soil at the site of interest has been replaced with "natural" soils from another site (e.g., Baniulyte et al. 2009) or remediated using soil washing (e.g., Dermont et al. 2010), soil amendments (e.g., Beesley & Dickinson 2011), or added organisms such as plants and soil micro- or macrofauna (e.g., Aspray et al. 2007, Dickinson et al. 2009). No studies have examined whether abandoned urban areas are capable of NO_3^- removal, and whether NO_3^- removal via denitrification in these soils results in a high or low N_2O:N_2 ratio.

Brownfield soils have usually formed on non-soil materials, including construction fill, under hydrogeomorphic conditions unique to highly disturbed urban areas (e.g. low areas between fill piles trapping precipitation), and with an unusual assemblage of plant communities (e.g. combinations of urban invasive species and species planted over time by humans using the landscape). In addition to metal contamination, brownfield soils are often highly compacted, resulting in poor soil aeration (Puskas & Farsang 2009), and low in clay content and organic matter, resulting in highly variable soil water potentials. The urban environment imposes toxic, sub-lethal, or stress effects on soil decomposers (e.g., Pouyat et al. 1994) and primary producers (e.g., Gallagher et al. 2008), which can significantly affect soil biological processes (Pouyat et al. 2002). Additionally, depending on the source and content of the fill material, brownfield soils can demonstrate

unusually high (Puskas & Farsang 2009) or low (Gallagher et al. 2008) soil pH. The result of these soil properties is often compromised metabolic activity of microorganisms with specific microenvironment requirements (Murray et al. 2000).

The question of whether sites dominated by herbaceous or woody vegetation demonstrate greater rates of soil NO_3^- removal has generated many studies in the past decade, but results vary widely (Haycock & Pinay 1993, Schnabel et al. 1997, Addy et al. 1999, Groffman & Crawford 2003, Sabater et al. 2003). Belowground herbaceous and woody-dominated communities could demonstrate important structural differences, such as the mass of fine roots, size of root channels (woody > herbaceous), and root turnover (herbaceous > woody); the differences in soil C and O_2 availability that result may mediate denitrification rates. Additionally, litter-mediated differences in soil chemistry between herbaceous and forested communities may differ widely. Woody and herbaceous litter contain different C:N and N:lignin ratios, and differ in quantity of litter inputs; these characteristics can also vary widely between species within woody and herbaceous categories (Finzi et al. 1998, Ehrenfeld et al. 2005). Differences in these ratios are strongly linked to differences in N mineralization and soluble C inputs (Ehrenfeld et al. 2005). Soil NO_3^-, oxygen, and C availability differ widely between vegetation types (Addy et al. 1999, Verchot et al. 2001) and between environments, including rural vs. urban (Pouyat & Carreiro 2003). Whether a community dominated by a combination of both herbaceous and woody vegetation types induces different NO_3^- removal dynamics than a community dominated by only one vegetation type has not been examined.

The objectives of this study were to (1) examine denitrification and limitations to denitrification and (2) examine greenhouse gas emissions in restored and unrestored wetland areas on a former rail yard abandoned in 1967. I hypothesized that labile carbon in soils and development of the anaerobic conditions necessary for denitrification were likely to be the primary limiting factors to denitrification in unrestored wetlands at the site. I based this hypothesis on the relatively short time of soil development at the site (40 years) and the fact that the soils were unamended. NO_3^- inputs were expected to be high, and thus not a major limiting factor to denitrifiers, due to high NO_3^- deposition from the atmosphere in the region (Gao et al. 2007, Song & Gao 2009). I anticipated that the vegetation community dominating a particular wetland (grassy-herbaceous with no forest overstory or grassy-herbaceous with forest overstory) would affect labile C in soils, and thus determine which wetlands demonstrated the highest denitrification rates. N_2:N_2O ratio and CO_2 emissions were expected to be mediated both by soil organic matter and oxygen levels in wetland soils. I anticipated that wetland soils with more aerobic pore space (i.e. rocky soils) would have low soil organic matter, low N_2:N_2O production and low CO_2 production. I examined denitrification rates and limitations to denitrification using intact core field measurements of denitrification and laboratory incubation measurements of field soil denitrification and respiration. Soil potential for NO_3^- removal and greenhouse gas emissions was also examined using laboratory incubations.

MATERIALS AND METHODS

Site and Soils Description

The study was carried out in Liberty State Park (Jersey City, New Jersey), a 4.5 km^2 public park located on the west bank of Upper New York Bay, in the highly urbanized

lower section of the Hudson River watershed. A 1 km^2 undeveloped area inaccessible to the public within the park was used for this study. The site was originally an intertidal mud flat/salt marsh, and was filled between the years of 1860 and 1919 for use as a railroad yard by the Central Railroad of New Jersey. The fill materials consisted primarily of railway ties and beds (gravel, cinders, and coal ash), debris from construction projects, and refuse from New York City. After 1967, when the railroad discontinued operations, the site remained isolated and undisturbed. The site was transferred to the New Jersey Division of Parks and Forestry in 1970, at which time large areas of the park were fenced off and kept from public use. These fenced-off areas have since developed wetlands dominated by forest and marsh vegetation (Table 3.1). Wetlands range in size from 84–17,000 m^2. In this part of the park, the wetlands are rain-fed; flooding occurs when rain falls and pools on top of the compacted surface layers. Drainage is slow, and impeded further by an impervious clay layer beneath the fill. There are no surface inlets to the wetlands; water is therefore assumed to be lost through evapotranspiration and slow drainage to groundwater. Soil pH at the sites ranged from 5.0–5.2 (Gallagher et al. 2008).

A restored wetland was constructed at the site in 2007. Within a 0.6 km^2 parcel on the southeastern part of the site supporting a pond, 7,850 m^2 of soil was excavated in the spring of 2007 to remove soil contaminated with chromium. A cap of 15 cm of clean fill material under 15 cm of clean topsoil was added to the site following soil removal, and planting and flooding was started in fall of 2007. The soil is a sandy loam or loam, with 4.5–11% rocks. Soil pH ranged from 6.2–7.2, and percent organic matter ranged from 5.5–11.6%. The plant community at the collection site was dominated primarily by

Table 3.1. Vegetation and denitrification characteristics of Liberty wetlands. G1 and G2 are grassy/herbaceous wetlands, F1, F2, and F3 are forested wetlands. Different letters for each parameter represent significant ($p < 0.05$) differences between sites according to PROC mixed.

	G1	G2	F1	F2	F3
Vegetation overstory	NA	NA	***Acer rubrum*** ***Betula populifolia*** ***Fraxinus americana*** *Quercus palustris* *Rhododendron* sp.	***Acer rubrum*** ***Betula populifolia*** ***Fraxinus americana***	***Betula populifolia*** *Rhus copallinum*, *Salix* sp. *Rhododendron* sp.
Vegetation understory	***Eleochairus* sp.** *Cyperes* sp. ***Lythirum salicaria*** *Juncus effusus*, *Juncus* sp. **moss sp.** ***Panicum virgatum*** ***Phragmites australis*** *Ludwigia palustris* ***Scirpus cyperinus***	***Onoclea sensibilis*** ***Phragmites australis*** *Rosa rugosa* *Solanum carolinense* *Spiraea tomentosa* ***Thelypteris palustris*** ***Vitus labrusca***	*Agrostis capillaris* ***Lythirum salicaria*** ***Onoclea sensibilis*** ***Panicum virgatum*** ***Scirpus cyperinus*** ***Thelypteris palustris*** ***Toxicodendron radicans*** ***Vitus labusca***	***Eleocharis* sp.** ***Lythirum salicaria*** **moss sp.** ***Panicum virgatum*** ***Polygonum cuspidatum*** *Polygonum hydropiper* ***Scirpus cyperinus*** *Phalaris arundincea* *Rubus allegheniensis* ***Vitus labrusca***	***Panicum virgatum*** ***Phragmites australis*** ***Polygonum cuspidatum*** *Rubus histidus* ***Toxicodendron radicans***
Average *in situ* denitrification rate (May-June 2006) µg N_2O-N/kg dry soil/d	**2.54** ± 4.87	**11.6** ± 20.9	**2.17** ± 1.89	**4.39** ± 4.01	**-0.78** ± 0.36
Average *in situ* net mineralization rate (May-June 2006) mg N/kg dry soil/d	**0.53** ± 0.05 (0.52 ± 0.05) NH_4^+	**2.97** ± 1.1 (2.93 ± 1.1) NH_4^+	**0.11** ± 0.03 (0.10 ± 0.05) NH_4^+	**0.22** ± 0.96 (0.22 ± 0.95) NH_4^+	**0.19** ± 0.06 (0.20 ± 0.06) NH_4^+
% Rocks in soil (rocks > 2 mm) g rocks/g dry soil	**18.5** ± 1.8^A	**4.5** ± 0.4^B	**33.2** ± 1.9^C	**38.3** ± 2.2^C	**1.7** ± 0.4^B
% Moisture (May-August 2006) g water/g wet soil	**4 9.9** ± 1.8^A	**32.8** ± 1.1^B	**34.2** ± 1.0^B	**36.1** ± 1.0^B	**30.0** ± 0.9^B
% Organic Matter (May-August 2006)	**52.7** ± 2.3^A	**9.5** ± 1.4^B	**4.9** ± 1.0^C	**21.7** ± 1.2^C	**21.4** ± 1.0^B

Table 3.2. Sites used in various Liberty State Park studies

Study	Sample collection date	Sites used (# reps per site)
Intact core denitrification	May - August 2006	G1 (9), G2 (8), F1 (6), F2 (6), F3 (7)
C : N analysis	August 2009	G1 (9), F1 (6), F2 (6), F3 (7)
Incubation experiment	January - April 2011	G1 (2), F1 (2), F2 (2), F3 (2), Restored Wetland (3)

Elymus virginicus (Virginia wild rye), but included four *Carex* species and eight grass and reed species. Several saplings were also planted in the vicinity, including *Betula nigra*, *Quercus bicolor*, *Juniperus virginiana*, and *Amelancher canadensis*.

Above and Belowground Biomass Sampling

Above and belowground biomass and soil samples were collected from all sites used in the 2006 intact core denitrification study described below (except G2) in August of 2009, for determination of C:N ratio (Table 3.2). At each of the collection points used in the 2006 study, a 30 cm x 30 cm quadrat was laid on the ground; all aboveground biomass was clipped off at the soil surface, all litter on the soil surface was removed and a soil core (5 cm deep, 4.8 cm across) was taken in each corner of the quadrat. The clipped biomass was later oven dried at 75°C for one week, and the plants from each collection point were sorted into broad categories (grasses, herbaceous, woody, and moss) to determine composition (by weight) of each category. Three representative (by weight) subsamples of the plant community at each sampling point were then ground and integrated in a Wiley mill. Litter from each quadrat was air dried for one week in the lab, then thoroughly integrated in a large paper bag through stirring, and 3 large handfuls were pulled at random from the bag to grind in the Wiley mill. This subsampling was

repeated 3 times for each litter sample. 2 of the soil cores taken in each quadrat were carefully rinsed over a 600 μm sieve to pick out all visible root material. Roots were oven dried at 75°C for one week before being ground in a Wiley mill. Because of the low root biomass at most sampling points, subsampling was usually not necessary, with the exception of areas supporting *Phragmites australis* (12 sampling points). The other 2 soil cores taken in each quadrat were air dried in the lab for 2 weeks, then ground with a mortar and pestle to break all large soil aggregates. Soils were then passed through a 2 mm sieve to remove rocks.

Intact Core Denitrification Measurements

To quantify *in situ* rates of denitrification and N mineralization in both forested and herbaceous wetlands, I carried out static core, acetylene-based measurements of denitrification (Groffman et al. 1999) and buried-core measurements of net N mineralization (Robertson et al. 1999) once a month during May-August 2006 in five wetland sites (Table 3.2). Intact cores 6–18 cm long and 2.5 cm in diameter were collected using an auger; in instances where sites were flooded to depths of more than 5 cm, augering was not possible and a trowel was used to fill cores.

Static core analysis for denitrification rate was performed immediately upon returning to the lab (less than 8 h) using procedures outlined in Groffman et al. (1999). Gas samples were taken at 2 and 6 h, stored in evacuated glass tubes, and analyzed for N_2O by electron capture gas chromatography.

Samples were stored at 4°C between sampling and analysis for extractable NO_3^- and NH_4^+, gravimetric moisture content, and soil organic matter (less than 24 h) using procedures modified from Robertson et al. (1999). Soil samples were hand sorted to

remove large pieces of vegetation and rock, mixed, and held at field moisture for extraction of NO_3^- and NH_4^+. Soil moisture content was determined by drying at 105°C for 48 h. Soil organic matter content was determined by loss on ignition at 450 °C for 4 h. Available soil NO_3^- and NH_4^+ contents were determined by extraction of 10 g of soil with 2M KCl followed by colorimetric analysis with an Omnion Lachat Quickchem 8000 (Lachat Instruments, Loveland, CO). KCl extracts were frozen and stored at -20°C until they could be analyzed.

Substrate Limitations and Greenhouse Gas Emissions

Denitrification enzyme activity (DEA) and soil respiration rates were measured in samples taken from 4 of the original 5 sites used in the 2006 study in a soil incubation experiment carried out in April 2011. In the 4 year period since the original field experiment, one of the sites (G2) had shifted to an upland assemblage of plants and drier soils and was therefore excluded from analysis. This shift was likely due to changes in the water table of that particular area resulting from water diversions toward the restored wetland in the park (F. Gallagher, *pers. comm.*). As a result, soil samples were instead taken from the new restored wetland area (IC) and incubated with the original 4 sites for comparison (Table 3.2). Soil samples were collected in December 2010 and stored at 4°C between sampling and analysis (95 d). Soils were taken out 14 d prior to the incubation analysis and stored in the dark at 20°C. 20 g of each soil sample was placed in one of 4 flasks; a solution containing 100 ppm N-NO_3 (as KNO_3) was added to 2 of the flasks and a solution containing 100 ppm N-NO_3 and 40 ppm dextrose was added to the other 2 flasks. All flasks were evacuated and flushed with N_2 gas 3 times, then brought to atmospheric pressure using ambient air. 10 cc of either acetylene (C_2H_2) or N_2 was

added to the flasks, yielding the following 4 treatments for each sample: (1) NO_3^- + N_2; (2) NO_3^- + C_2H_2; (3) dextrose + NO_3^- + N_2; (4) dextrose + NO_3^- + C_2H_2.

Data Analysis

To identify significant differences in denitrification rate, mineralization rate, % moisture, and % organic matter between sites during the 2006 study, a repeated measures mixed model with site subsamples as the random effect (PROC mixed) and a general linear model using site as a predictor (PROC glm; Tukey's test) were used (SAS Institute 2008). PROC mixed was also used to assess which variables best predicted percent soil organic matter; models were compared using the Akaike Information Criterion with a modification for finite sample sizes (AICC), where lower AICC means better goodness-of-fit. The NO_3^- and NH_4^+ data distributions were highly skewed to the left, due to (1) the low soil NO_3^- values in May-July and the high values in August; and (2) the high soil NH_4^+ in site G1 relative to the other sites. New binomial variables were therefore developed for these two variables based on whether individual NO_3^- or NH_4^+ measurements exceeded the (1) median value or (2) 3rd quartile value (0 = below, 1 = above). A logistic regression (PROC genmod) was then used to assess significant differences between sites and months for NO_3^- or NH_4^+ measurements, and assess which soil variables best predicted soil NO_3^- and NH_4^+. For the incubation experiment, respiration and denitrification rates were compared between treatments (NO_3^- + N_2; NO_3^- + C_2H_2; dextrose + NO_3^- + N_2; dextrose + NO_3^- + C_2H_2) and sites using a general linear model (PROC glm; Tukey's test).

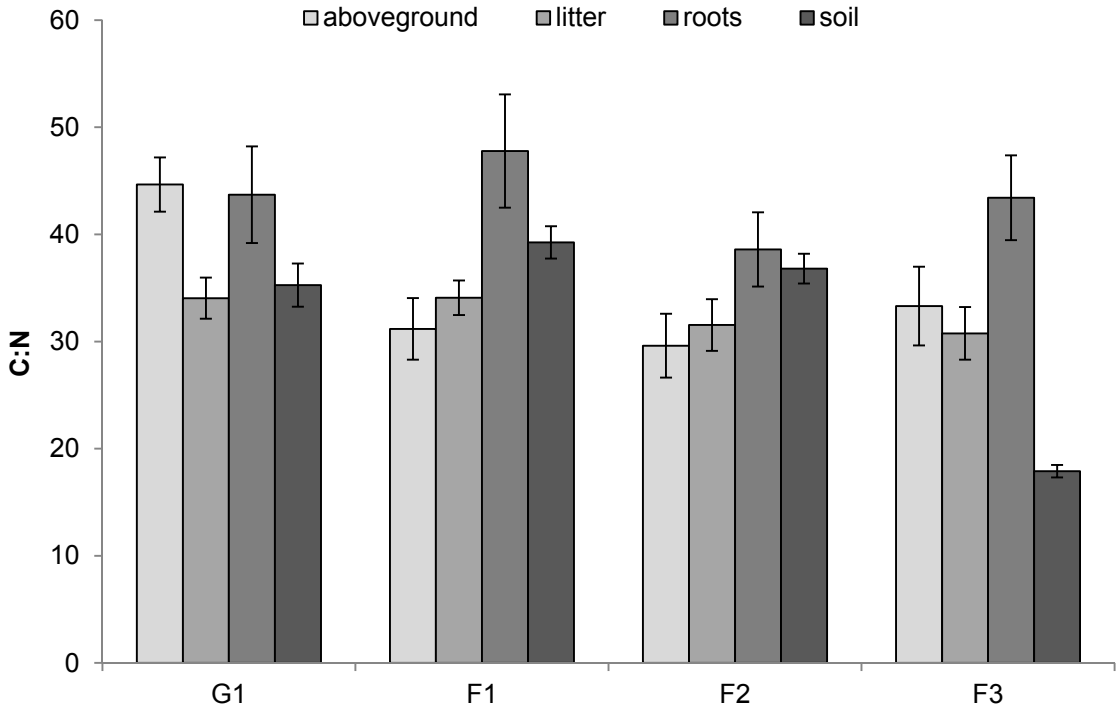

Figure 3.2. C:N ratios of plant aboveground biomass, plant roots, litter, and soil at each of 4 Liberty wetlands. G1 is a grassy/herbaceous wetland, F1, F2, and F3 are forested wetlands. Error bars represent one standard error of the mean.

RESULTS AND DISCUSSION

Nitrogen Limitations to Soil Microbes

Contrary to the expectation that denitrifiers would be carbon limited, soil microbes in the study wetlands appear to be highly nitrogen limited and mineralization of organic nitrogen from litter and roots and atmospheric deposition are not adequate to compensate for this limitation. C:N ratios in the above and belowground biomass of vegetation, litter, and soil of all Liberty State Park sites was fairly high, with the exception of soil C:N ratios in one of the forested sites (Figure 3.2). In a review of 42 studies spanning forested and grassland areas at latitudes 2–70, Cleveland and Liptzin (2007) found soil C:N ratios averaging 14.3, and ranging in value from 2-30. With the exception of F3, the C:N ratios of all Liberty State Park sites had soil C:N ratios substantially higher than this. Average

soil C:N at sites G1, F1, and F2 ranged from 35.3–39.3, and subsamples within these sites ranged from 20–72 (Figure 3.2). At site F3, soil C:N averaged 17.9 and subsamples within the site ranged from 15–20 (Figure 3.2). Soils at F3 were sandy with low rock content and a large soil organic fraction (Table 3.1). These properties may explain the lower C:N ratio at this site, since soils with low rock content are more likely to have organic matter complexed in soil aggregates, which would stabilize soil nitrogen. G1 also had a large soil organic fraction, but soils at this site consisted of a mixture of partially decomposed plant material and coal rocks.

Microbial biomass C:N ratios usually vary between 8:1 and 12:1 on a mass basis (Cleveland & Liptzin 2007). In their review, Cleveland and Liptzin (2007) found a mean C:N ratio of 8.6 ± 0.3 for microbial biomass and that this ratio did not vary significantly with changing soil C:N ratios. Assuming 50% growth efficiency (Demoling et al. 2007) and a bacterial C:N ratio of 8.6, we might assume a switch from carbon to nitrogen limitation at a soil C:N ratio of roughly 16–18. Chapin et al. (2002) assume a C:N ratio for microbial biomass of 10 and a 40% growth efficiency, citing 25 as the critical substrate C:N ratio for microbes to meet their growth requirements (Chapin et al. 2002). With the exception of F3, the C:N ratios of all Liberty State Park sites had soil C:N ratios above the 16–18 or 25 C:N threshold for microbial nitrogen limitation (Figure 3.2).

I expected vegetation community (grassy-herbaceous with no forest overstory or grassy-herbaceous with forest overstory) to be the primary mediator of available carbon through differences in litter and root quality and turnover. However, carbon was uniformly high relative to nitrogen at all sites, and percent organic matter in the soil was better predicted by standing water levels (AIC=830.8) than by plant community type

(AIC=1183.1). Litter and root C:N ratios exceeded 25 at all sites, with the exception of two litter samples (22.2 (F3), 24.6 (F2)) and one root sample (20.5 (G1)). These three exceptions still exceeded a C:N value of 20, however.

Intact core measurements of denitrification were low at all sites throughout the summer of 2006, as was net mineralization rate and soil NO_3^- and NH_4^+ content (Table 3.1, Figure 3.3). Soil NO_3^- was low throughout the 2006 field study (Figure 3.3). Average NO_3^- levels did increase in August to detectable levels (Figure 3.3), but still ranged from undetectable–24.5 μg NO_3^--N/g dry soil in any given sample. Studies of urban riparian and wetland soils in Baltimore (Groffman et al. 2002) and New Jersey (Stander & Ehrenfeld 2009) found soil extractable NO_3^- levels several orders of magnitude higher than those found in this study.

Mineralization rates were low at most sites, with site G2 demonstrating the highest average rate (2.97 mg N/kg/d) and the rest of the sites averaging 0.11–0.53 mg N/kg/d (Table 3.1). Mineralization measured at all sites was due almost exclusively to NH_4^+ production (Table 1), likely because soils were anaerobic for most of the summer (Reddy & DeLaune 2008). Net N mineralization rates demonstrate a wide range of values depending on the system in which they are measured (Robertson 1982, Reddy & DeLaune 2008). Mineralization rates in forested upland soils in the northeastern United States ranged from 0.2–32.1 mg N/kg/d; with nitrification accounting for from 0–100% of mineralization in these studies (number of studies=10; Robertson 1982). Recorded mineralization rates in forested wetland sites in New Jersey are on the lower end of the range reported by Robertson (1982); Zhu & Ehrenfeld (1999) measured mineralization

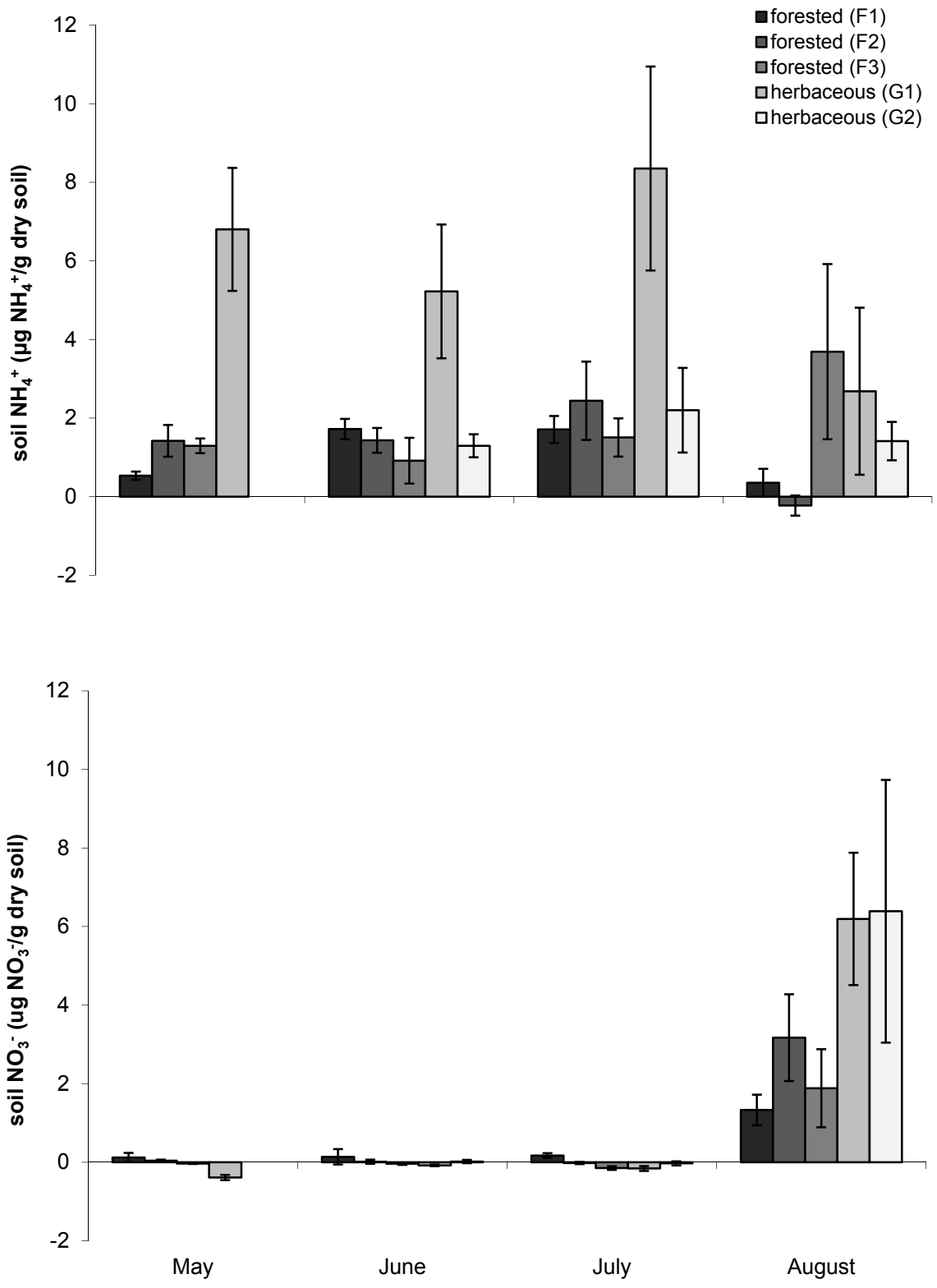

Figure 3.3. Ammonia and nitrate content of soils in five urban wetland sites sampled monthly from May–August 2006. Error bars represent one standard error of the mean.

rates ranging from 3.6–4.9 mg N/kg/d in white cedar-dominated wetlands in suburban and undeveloped areas (4 sites). A study of red maple-dominated wetlands in urbanized (31–93% urban land cover) landscapes in New Jersey found even lower mineralization rates, comparable to those found in this study, ranging from -0.01–0.81 mg N/kg/d in (14 sites, Stander & Ehrenfeld 2009). However, nitrification constituted about 50% of net mineralization in the latter sites (Stander & Ehrenfeld 2009).

Intact core measurements of denitrification at all sites except G2 were 2–47 times lower than rates measured in the urbanized wetland forest sites studied by Stander & Ehrenfeld (2009) (range: -0.6–60.96 μg N_2O-N/kg/d) in New Jersey; G2 had a denitrification range comparable to the range found in the latter study). Intact core measurements at all Liberty sites, including G2, had rates as much as five to several hundred times lower (range: -43.2–364.8 μg N_2O-N/kg/d; chapter 1) than measurements made during the same time frame in a grass-dominated fill soil at a New Jersey brownfield site 19.5 km north of Liberty (chapter 1).

Denitrification rates did increase severalfold in response to experimental NO_3^- additions, indicating that an active denitrifier community does exist in Liberty soils and supporting the idea that NO_3^- is the key factor limiting denitrification at these sites. There were no significant differences in denitrification or respiration rate between NO_3^- and dextrose + NO_3^- treatments in sites G1, F1, F2, and F3 in the incubation study, further supporting the idea that the soil microbial community at these sites was not carbon-limited (Figure 3.4). Potential denitrification rates with C_2H_2 + NO_3^- and C_2H_2 + NO_3^- + dextrose additions were, on average, 4 times higher in G1, 20 times higher in F1, 10 times higher in F2, and more than 100 times higher in F3 than field measurements

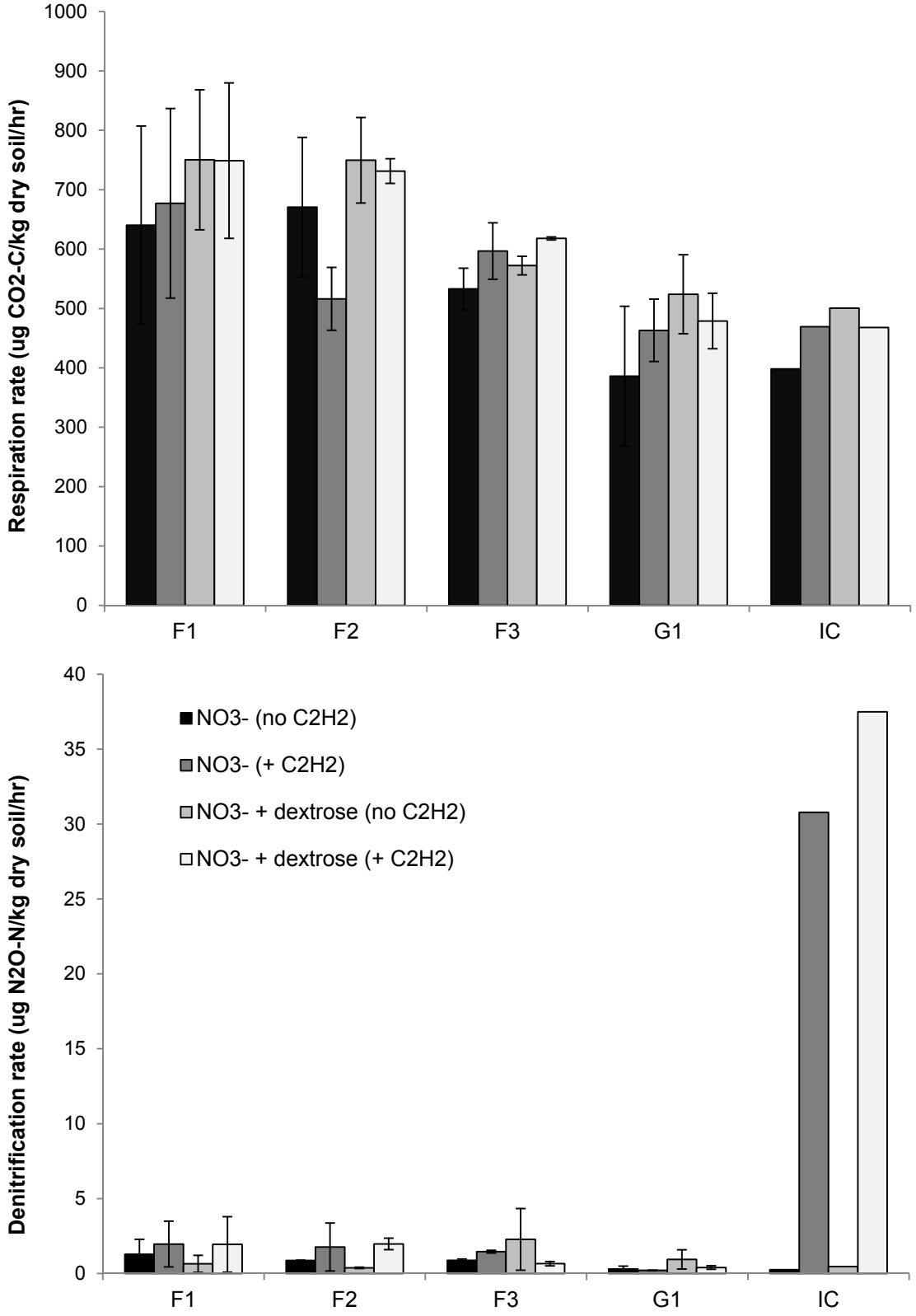

Figure 3.4. Soil respiration (A) and denitrification enzyme activity (B) in soils from forested (F1, F2, F3), herbaceous (G1) and constructed (IC) wetland sites. Error bars represent one standard error of the mean

made in 2006. These findings support the idea that NO_3^- availability is the major limitation to denitrification in Liberty State Park. The lack of increase in rates of CO_2 production in response to dextrose and NO_3^- addition in soils from all sites may be indicative of a limited ability of the general heterotrophic community to degrade dextrose, or of the fact that these communities are not carbon limited in these sites. Site was a significant ($p = 0.001$) predictor of respiration rate (PROC glm) and site IC had a significantly ($p < 0.05$) lower respiration rate than all other sites according to Tukey's test.

Soil Drainage Characteristics and Denitrification Mediate Nitrate Availability

Low soil NO_3^- and high C:N ratios in soils and vegetation was surprising, given the documented high levels of NO_3^- deposition in the immediate vicinity of Liberty State Park. Song & Gao (2009) found NO_3^- concentrations in rainwater ranging from 72–955 μg/L NO_3^--N over the year 2006–07 at a site ~10.5 km west of Liberty State Park, with an average of 339 μg/L NO_3^--N in the summer. NH_4^+ ranged from 16–1,346 μg/L NH_4^+-N over the year, with an average of 560 μg/L NH_4^+-N in summer (Song & Gao 2009). Dry deposition is also substantial in the region, averaging 0.2 mg NO_3^--N/m^2/d at a coastal site ~26 km south of Liberty State Park (Gao et al. 2007). Together, this wet and dry atmospheric deposition contributes roughly 140 μg NO_3^--N/m^2/h to the study wetlands at the site. The low denitrification rates; low ambient total N and NO_3^- in field soils; high C:N ratios in soils and vegetation; and the positive response of denitrification rates to NO_3^- additions in the incubation experiment could in part be due to the fact that the site is geologically young, and thus has not developed adequate soil structure to retain soil N. Even under conditions more ideal for organic matter and N accumulation than ours

(warmer climate, vegetation plantings, high allochthonous inputs of nutrients in surface water), created marshes take decades to centuries to develop the levels of N and organic C found in natural marshes (Craft et al. 2002).

The N cycling characteristics of Liberty soils also suggest, however, that high denitrification rates are responsible for keeping wetlands at Liberty State Park nitrogen-poor. Intact core denitrification rates ranged from -36–131 μg N_2O-N/m^2/h in the herbaceous sites and from -36–69 μg N_2O-N/m^2/h in the forested sites. The primary source of N to these wetlands is the atmosphere: overland flow inputs are negligible, and groundwater levels are typically 0.39–1.65 m below the soil surface (USACE 2004). Measured removal rates of NO_3^- via denitrification were low in the study; however, measured rates did occasionally approach NO_3^- loading rates from the atmosphere (i.e., 140 μg NO_3^--N/m^2/h) in the unflooded herbaceous site (G2). There is a general expectation that when soils are anaerobic, NH_4^+ accumulates from decomposition activity and NO_3^- is consumed by denitrifiers (Reddy and Delaune 2008). When soils dry out, denitrifiers are inactivated by aerobic conditions and NO_3^- begins to accumulate. This pattern was observed in study sites in August 2006, when all sites dried substantially and NO_3^- levels increased (Figure 3.3). Prior to August, sites G1, F1, F2, and F3 all had standing water above or within 8 cm of the soil surface in all areas sampled. G2 generally had better drained soils, with water levels 0–17 cm below the soil surface in most sampled areas. In August, none of the soils sampled had any water above or below the soil surface, and soil NO_3^- was an order of magnitude higher in this month than in any other month during the 2006 study (Figure 3.3). Soil NH_4^+ was higher than soil NO_3^- throughout the 2006 study, and generally did not vary significantly from month to month

within each site (Figure 3.3), indicating low NH_4^+ consumption and generally low oxygen conditions in the soil. Site-to-site differences varied depending on month (Figure 3.3). The only NH_4^+ values in G1 that were below the median value of the data were those taken in August, and one sample taken in June. G1 also had significantly more NH_4^+ measurements exceeding the 3rd quartile value throughout the study than any other site (PROC genmod); G1 also had significantly higher soil moisture on average than any other site (Table 3.1). F1 had no NH_4^+ values exceeding the median value in May, and F2 had no NH_4^+ values exceeding the median value in August. Percent moisture was a significant ($p < 0.0001$) positive predictor of soil NH_4^+ content, and of whether soil NH_4^+ content exceeded both the median and 3rd quartile value (PROC genmod). Percent moisture was a significant negative predictor of whether soil NO_3^- exceeded the 3rd quartile value ($p = 0.01$) (PROC genmod).

Soil rockiness appeared to be the primary mediator of soil aeration and dominant inorganic N species. Percent rocks in the soil was highest in F2 and F3 and lowest in F3 and G2 (PROC mixed) (Table 3.1). Percent rocks was a significant positive predictor in the 2006 study of whether NO_3^- fell above the 3rd quartile value, and a significant negative predictor of whether NH_4^+ fell above the 3rd quartile value (PROC genmod). Gravel particles and small rocks in soil typically decrease the amount of soil matrix in which water can be stored or conducted (Saxton & Rawls 2006). Higher rock content of a soil may, therefore, have increased the amount of aerated spaces in that soil. In their study of the activity of soil biota in three abandoned railway yards, Murray et al. (2000) found that nitrification was most influenced by organic matter and total N, but that sandy soils and low precipitation were also likely a limitation to nitrification (Murray et al.

2000). In my study, where organic matter was relatively high and sites had high soil moisture and/or flooding all summer, higher rock content appeared to augment NO_3^- production, and reduce NH_4^+ concentrations. Net N mineralization rate was not significantly different between sites in May-June 2006, but ammonification rate was significantly higher during this period in site G2 (PROC mixed) (Table 3.1). This site was also the only site without standing water during this period, so the aerated pores provided by high rock content appears to have been more important in promoting nitrification than the presence of standing water.

Greenhouse Gas Emissions

Comparison of results from the Liberty State Park wetlands with other studies of brownfield soils suggest that my study sites are not a major potential source of N_2O and CO_2The soil incubation study yielded potential CO_2 production from 268–879 μg CO_2-C kg^{-1} h^{-1}. Murray et al. (2000) found potential respiration rates many orders of magnitude higher in their study of soils from abandoned railway sites in Canada, ranging from 3,800–14,700 μg CO_2-C kg^{-1} h^{-1} (Murray et al. 2000). However, these soils were well-drained upland soils, and many of them had very high nitrification potential (Murray et al. 2000). Chodak and Niklinska (2010) found respiration rates ranging from 708–1,192 μg CO_2-C kg^{-1} h^{-1} in their study of reclaimed mine soils in Poland (Chodak & Niklinska 2010). Again, however, soils in their study were upland soils, and treated in the field with an NPK fertilizer as part of the reclamation process; C:N ratios were therefore relatively low, ranging from 18-19 (Chodak & Niklinska 2010).

Contrary to expectation, differences in soil texture, percent organic matter, and vegetation community did not lead to significant differences in CO_2 production in

unrestored Liberty soils. Even more surprising was the fact that respiration rate was significantly lower at the restored and amended IC site than in the unrestored sites. These differences may have been due to higher porosity and clay content in the soil: more anaerobic pore space may have meant that CH_4 production in IC soils was high relative to CO_2 production. It is important to note that I did not measure CH_4, and although CO_2 production was not very high in the Liberty soils in response to labile C additions, CH_4 production was not measured and might have been high, particularly given the anaerobic conditions created for the incubation.

There were no significant differences in N_2O production between acetylene and non-acetylene treatments at each site except site IC, suggesting that the end product of nearly all denitrification activity in the soils from sites G1, F1, F2, and F3 was N_2O (Figure 3.4). A caveat to this interpretation is, however, that comparison of C_2H_2 and non-C_2H_2 treated cores is not a perfect method for assessing N_2O:N_2 ratios. C_2H_2 treatment eliminates nitrification, which can be a source of N_2O and can also directly drive denitrification when NO_3^- levels are low. My results therefore need to be verified with field measurements of N_2O flux and/or detailed studies of N_2O:N_2 with more accurate methods (Beaulieu et al. 2011).

Site IC had N_2O production in the acetylene treatments that was orders of magnitude higher than the non-acetylene treatments and all treatments for all other sites (Figure 3). This site appears, therefore, to not only support higher potential denitrification rates than all other sites, but to have the majority of denitrification activity result in N_2 rather than N_2O production. Higher O_2 availability during denitrification usually results in a decrease in N_2:N_2O (e.g., Davidson 1991). Since site IC had a higher clay content and

higher soil porosity, it is likely that soils at the site support more microbially-habitable pore space and can better sustain anaerobic conditions within pores.

Although denitrification in site IC resulted in a higher N_2:N_2O ratio than the unrestored sites, none of the unrestored sites were very significant sources of N_2O relative to natural wetlands or wetlands constructed for wastewater treatment. In their study of constructed and natural wetlands in Florida, for example, Gale et al. (1993) measured N_2:N_2O ratios ranging from 5–7.7, and N_2O emission rates ranging from 0–2,134 μg N_2O-N/kg soil/d under additions of 2–20 ppm NO_3^--N. In my study, N_2:N_2O ratios averaged 0–2.0 in the unrestored sites and 79.9–119 in the restored site, and N_2O emission rates ranged from 2–103 μg N_2O-N/kg soil/d.

CONCLUSIONS

Despite the large number of modifications to soils and hydrology at Liberty State Park, wetlands at the site have developed active plant and soil nutrient cycling after 40 years of abandonment, even without mitigation measures. The wetlands have developed a significant capacity for denitrification, to the extent where the wetlands are kept in a very N limited state and are highly effective sinks for exogenous NO_3^- inputs from the atmosphere. Due to the high gravel and rock content and visible bits of trash remaining in soils at the site, it would appear that the soils have not yet developed textural and structural (e.g., porosity, % clay, and aggregate formation) properties comparable to natural soils, and likely support less microbially habitable and anaerobic pore space than a native soil would under the same hydrology and vegetation community composition. These properties mean that denitrification is lower overall in these soils than in native

soils, but also means that N_2:N_2O is low, i.e. these sites are not yet a major source of N_2O, but could become so if exogenous NO_3^- inputs increased.

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CHAPTER 4

Use of nitrogen budgets and N_2 flux measurements to estimate the role of denitrification in brownfield stormwater wetlands

ABSTRACT

Wetlands are constructed or restored in urban and agricultural areas to reduce inorganic nitrogen contamination of surface water runoff. Few studies, however, have examined the performance of unrestored but highly impacted wetlands within an urban context. These wetlands tend to be the primary recipient of nitrate (NO_3^-)-enriched storm and rainwater due to their ubiquity in low-lying portions of the urban landscape. Wetland studies anticipate high rates of NO_3^- removal via the microbial process of denitrification when labile carbon (C), and NO_3^- are high and O_2 is low. The ability to quantify and predict the role of denitrification within particular systems is limited, however, and denitrification estimates are compromised by our inability to accurately measure N_2 flux. In this study, I calculated loading rates of inorganic N and used measurements of N_2/Ar, O_2/Ar, and NO_3^- flux in sediments to generate inorganic N budgets for brownfield stormwater wetland sites. Loading of inorganic nitrogen via rain and stormwater ranged from 4–533 mg N/m^2/d, and large amounts of NH_4^+ were additionally created from mineralization of decomposing organic matter, leading to high fluxes of NH_4^+ out of sediment into water (2–117 mg N/m^2/d). Hydrology was a strong driving force of N_2 flux; lowering of the water table allowed surface sediments to oxidize, leading to production of NO_3^-, which fueled N_2 production lower in the sediment profile. Overall, the wetlands are denitrifying NO_3^- at a rate of around 620–2,580 μg N/m^2/day. Flux of NO_3^- out of sediments was higher in some cases (630–1,900 μg N/m^2/day), likely due to plant uptake. These

wetlands appeared to be serving as a sink for NO_3^-, but were net sources of NH_4^+; periodic drainage of the wetlands to promote oxidation of NH_4^+ may be a strategy for promoting higher inorganic nitrogen removal from these sites.

INTRODUCTION

Wetlands are constructed or restored in urban and agricultural areas to reduce inorganic nitrogen contamination of surface water runoff. Nitrogen enrichment of surface water leads to eutrophication and hypoxia in recipient estuaries; this phenomenon is a problem worldwide (Freeman et al. 2007). Wetland areas within a watershed can intercept and remove large quantities of inorganic nitrogen through microbial processes in the sediments. Wetland creation and restoration has perhaps been most visibly proposed as a means of mitigating hypoxia in the Gulf of Mexico (Mitsch et al. 2001), but is a mitigation strategy cited by studies of estuaries on every continent (Dodds et al. 2009, Li et al. 2009, Petrone 2010, Voss et al. 2011).

Although many studies have examined the efficacy of natural, constructed, or restored wetlands in removing inorganic nitrogen (Kadlec & Knight 1996), few have examined the performance of unrestored, highly impacted wetlands within an urban context. This type of wetland system is pervasive throughout urbanized areas worldwide and is usually the primary recipient of nitrogen-enriched stormwater from upland areas due to their low-lying position in the landscape (Ehrenfeld 2000). Cities cover almost 0.5% of the planet's land area, and this coverage is projected by some estimates to increase fourfold over the next 50 years (Angel et al. 2011). Further, urban areas generate large amounts of inorganic nitrogen in surface water, due to fossil fuel

combustion, fertilizer use and leaky sanitary sewer infrastructure (Groffman et al. 2004). Despite the fact that they potentially play a key role in nitrogen cycling, unrestored urban wetlands are generally little studied and understood. This study examines inorganic nitrogen removal in two unrestored urban wetland environments located on former brownfields in New Jersey, USA.

Nitrogen retention of urban wetlands is often low due to high loading rates of inorganic nitrogen and altered conditions that compromise denitrification (Groffman et al. 2004, Grimm et al. 2005, Stander & Ehrenfeld 2009). Denitrification is a microbial process occurring in wetland sediments that converts reactive nitrogen in the form of nitrate (NO_3^-) to inert N_2 gas. NO_3^- removal via denitrification is a process mediated by three controlling factors: (1) the availability of organic carbon substrate (C); (2) the availability of NO_3^-; and (3) the presence of suboxic (<0.2 mg O_2/L) conditions (Seitzinger et al. 2006). Denitrification studies anticipate, therefore, that high rates of NO_3^- removal are created by the co-occurrence of these conditions (Boyer et al. 2006). In a wetland context, a number of "primary variables," namely plant, hydrology, and soil characteristics, regulate NO_3^-, C, and O_2 availability in time and space (McClain et al. 2003). Despite a broad understanding of the multiple environmental factors that control rates of denitrification, however, we still have limited ability to estimate and validate denitrification rates on landscape scales (Boyer et al. 2006). Due to the high sampling effort required, the full scope of conditions experienced by denitrifying bacteria throughout the year and even within seasons (most importantly, changes in temperature and moisture) is likely not captured by denitrification studies. Further, many field studies

of denitrification do not measure denitrification directly, but rather denitrification potential, removal of labeled NO_3^-, or gas production under lab incubations.

Because denitrification is the only permanent retention mechanism of NO_3^-, NO_3^- will either accumulate in a system, leach to groundwater, or be exported via surface flow to rivers and estuaries if denitrification rates fail to match loading rates of NO_3^-. Recent papers have identified the need for field studies that can be used to assess the distribution, magnitude, and overall importance of denitrification, particularly in aquatic systems (Boyer et al. 2006). In this study, I quantified inorganic N inputs and acquired empirical measurements of water and sediment chemistry to generate a mass balance of inorganic N for small urban wetlands and quantify the role of denitrification in removing this inorganic N from the wetlands. The objectives of this study were (1) to utilize in situ measurements of N_2 gas production and NO_3^- loss in the sediment profile to calculate denitrification rates; (2) to characterize inorganic nitrogen loading and denitrification rates and drivers in urban wetlands receiving nitrogen-enriched overland runoff from paved upland areas and rainwater; and (3) to examine the role of denitrification in nitrogen cycling in these wetlands. Previous studies in the same wetland systems (chapter 1, unpublished data) suggested that: (1) denitrification rates in the sediments were low; (2) NO_3^- was a limiting factor while suboxic conditions and labile carbon were non-limiting in most areas/times. I therefore hypothesized that: (1) Water table dynamics in the sediment column of the wetlands were the primary control on oxygen conditions within the sediment column; (2) Oxygen conditions were the primary determinant of whether NO_3^- is produced in the sediment; (3) NO_3^- production was the primary limitation of N_2 production in wetland sediments.

MATERIALS AND METHODS

Study Sites

The study took place in two highly urbanized (95% urban land use) settings in northeastern New Jersey (NJ): the Teaneck Creek Conservancy watershed, a small (0.2 km^2) freshwater floodplain ecosystem that is part of the larger Hackensack River watershed; and Liberty State Park, a freshwater wetland system (4.5 km^2) adjacent to Newark Bay. Both sites were originally marshes (the Teaneck site was a freshwater marsh, the Liberty site was a salt marsh), but in the early 1900's were covered with fill composed primarily composed of gravel and sandy/silty loam to raise site elevation for construction of trainyards and dumping grounds. After abandonment around mid-century, wetlands began to form in low-lying areas of the sites. These wetlands are roughly 10,000–11,000 m^2 in size, and are dominated by monotypic stands of the common reed *Phragmites australis* (Fig. 4.1). They are fed by precipitation and stormwater runoff from nearby upland areas, and are typically flooded or saturated for the majority of the year. Soil profiles consist of a highly organic (13–37% organic matter, on average) surface layer ranging in depth from 11–36 cm in the deepest parts of the wetland to only a few cm at the margins, with an underlying layer of silty or sandy fill. At Teaneck, augering has confirmed that the underlying fill is at least 40 cm deep, while at Liberty, the underlying fill layer has been confirmed to be at least 4–6 m deep (American Geotech, Inc. 2003). In this study, two of these wetlands (subwatersheds of the larger Teaneck and Liberty wetland systems), were characterized and modeled for inorganic N inputs and N removal via denitrification. The wetland at Teaneck (subwatershed area= 0.06 km^2) is fed primarily by precipitation, and partially by overland flow through a small

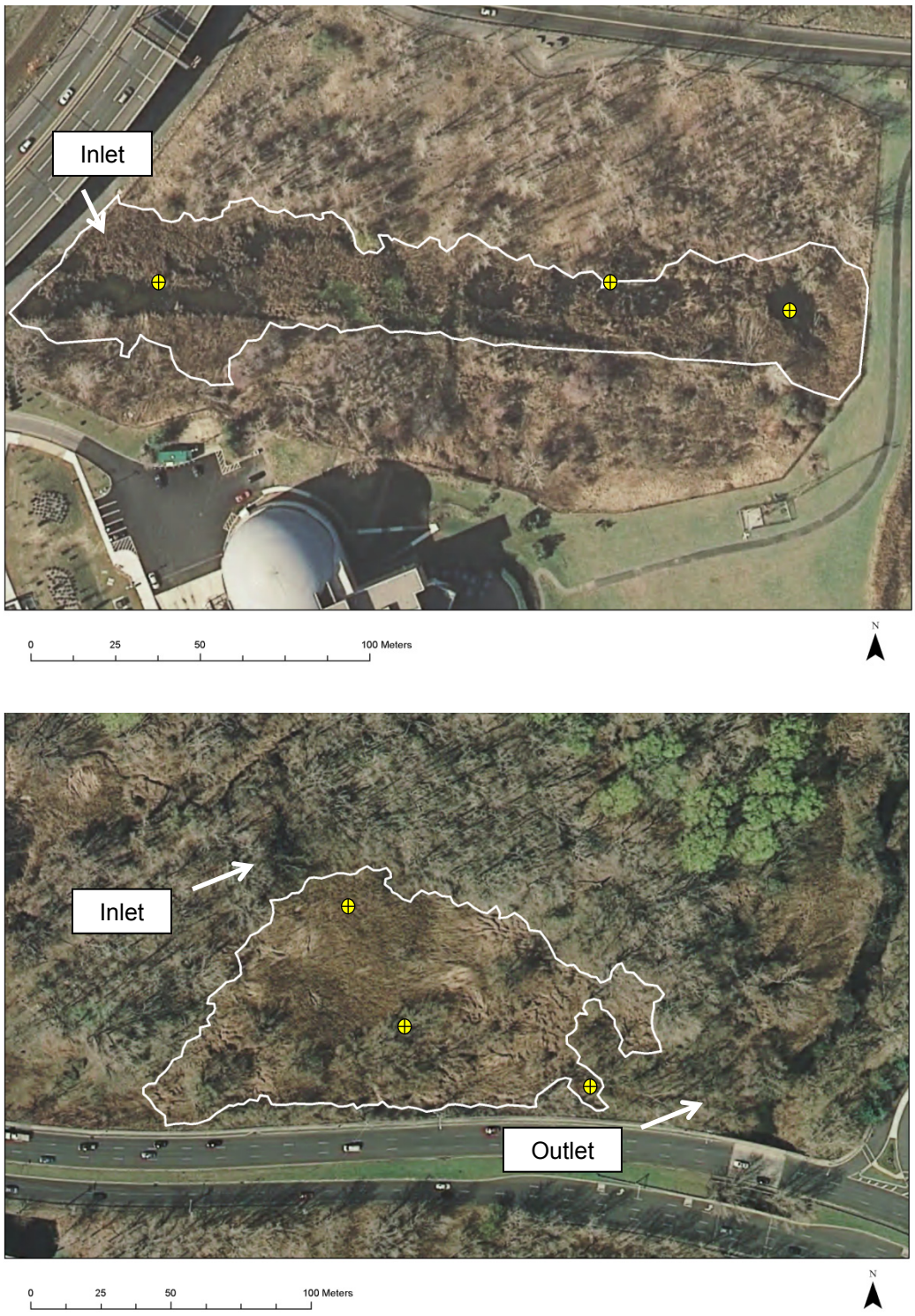

Fig. 4.1. Liberty State Park (top) and Teaneck Creek Conservancy (bottom) wetlands. White outline delineates where the low-lying semi-permanently flooded area lies. Flow in both diagrams moves west to east—surface water enters the wetland at the far left west side of the photograph. Teaneck Creek is at the far eastern side of the lower photograph.

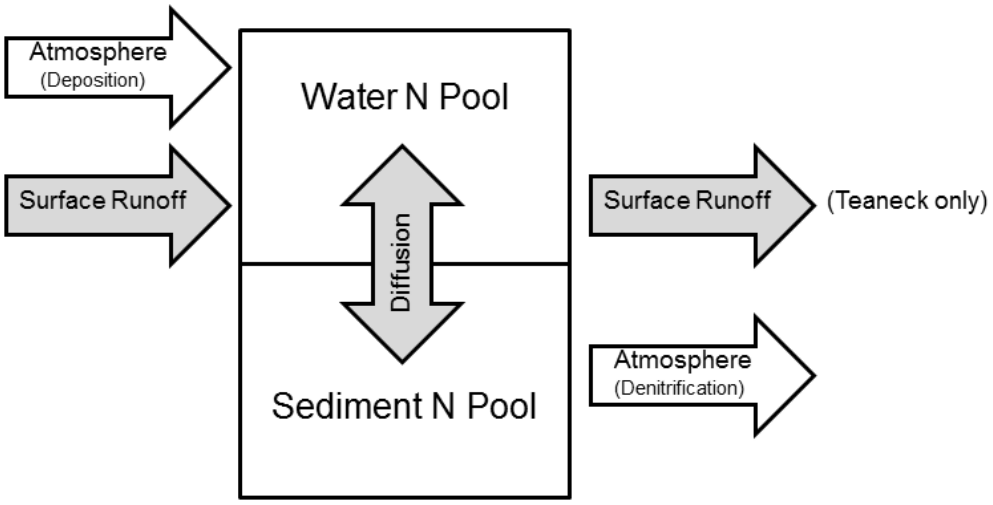

Fig. 4.2. Schematic diagram showing the pools and fluxes of inorganic N included in the budgets of the study wetlands at Teaneck Creek Conservancy and Liberty State Park under wet and dry conditions. Arrows indicate the major fluxes into, between, or out of pools. Gray arrows indicate hydrologic fluxes, white arrows indicate fluxes into or out of the atmosphere. Atmospheric fluxes into the water and soil N pools include both wet and dry deposition. Change in storage was calculated as the difference between all inputs and outputs to a pool.

channel entering the wetland. Surface water exits the wetland via a small channel that feeds into Teaneck Creek (Fig. 4.1 and 4.2). The wetland at Liberty (subwatershed area=0.07 km^2) is fed primarily by stormwater, and partially by precipitation (Fig. 4.1 and 4.2). Surface water exits the wetland by slow drainage to groundwater.

Stormwater Sampling

Sampling of rainwater and surface runoff was used to estimate loading rates of nitrogen to the study wetlands to develop N budgets (Fig. 4.2) for the two wetlands. Loading of organic carbon was also estimated from these measurements. Stormwater sampling was undertaken at Liberty on four dates, in September and October 2008. An ISCO sampler was deployed at the inlet of the wetland and programmed to initiate sampling when water levels at the inlet increased by 2 cm, and then to sample every half hour thereafter. 24 samples total (total sampling time=12 h) were collected during each

storm event. Water samples were retrieved from the ISCO, filtered with combusted GF/F filters, and frozen within 24 hours of sampling. Samples were analyzed for NO_3^-+NO_2^- and NH_4^+ on an Omnion LACHAT, and for total organic carbon (TOC) and nitrogen (TON) on a Shimadzu TOC/TON analyzer (TOCAN).

To estimate the total volume of water entering the Liberty wetland through the inlet during a rain event, I used a US Environmental Protection Agency Storm Water Management Model (SWMM). SWMM is a comprehensive deterministic model for urban stormwater runoff, designed to simulate real-time storm events based on rainfall, topography, impervious cover, storm drainage attributes such as slope and geometry, Manning's n, and infiltration rates. Based on these parameters, SWMM will model infiltration and storage and divert the remaining runoff as sheet flow (Burian et al. 2001). The primary source of stormwater to the Liberty wetland is an adjacent New Jersey Transit parking lot (total area=45,041 m^2, 100% impervious); stormwater running off the lot is diverted into a pipe and then an open channel that feeds into the wetland (USACE 2004). Ground and surface water monitored hourly during August 2008–September 2009 using autowells in three locations and/or a pressure transducer at the inlet of the wetland were used for calibration of the SWMM model (see Appendix A). Precipitation data from NOAA Station at Newark Airport were used to simulate the model during peeper deployments (2009 and 2010).

At Teaneck, wet deposition was collected during 19 rain events between April 2005 and February 2006 and analyzed for NO_3^-+NO_2^-, NH_4^+, TON, and TOC (Ravit et al. 2006). Surface water was sampled in various tributaries to Teaneck Creek and at several points in Teaneck Creek itself for NO_3^-+NO_2^- and NH_4^+ at on five dates ranging from

October 2005–February 2007 (Ravit et al. 2006). To estimate the total volume of water entering the Teaneck wetland through the inlet during a rain event, I used a rating curve developed for the inlet by Mak (2007) using a SWMM model. Water levels were measured using a pressure transducer in the inlet during the summer of 2010; these values were converted to water volume using the rating curve.

To estimate the total volume of water exiting the Teaneck wetland through the outlet, the hydrology of the entire Teaneck subwatershed was simulated using the Mike SHE/Mike 11 software system from the Danish Hydraulic Institute (see Appendix B for a full description of the model and its parameterization and calibration for the Teaneck wetland site). Water levels in the outlet were measured using a pressure transducer during the summer of 2010; these values were used to calibrate the Mike SHE/Mike 11 model for outlet hydrology. Volume of water exiting the wetland through the outlet during summer 2010 was then simulated using Mike SHE/Mike 11.

Loading Rate Calculations

Inorganic N loading from the atmosphere and from stormwater was calculated for time periods coinciding with peeper deployments in 2009 and 2010 to construct an inorganic N budget for both the Teaneck and Liberty wetlands (Table 4.1, Table 4.2). These calculations were made for peeper deployments occurring during wet and dry time periods to examine whether N budgets differed under these conditions. At the Teaneck site, peeper deployments during June and during August 2010 were categorized as wet and dry, respectively. At the Liberty site, peeper deployments during July 2009 and during September 2010 were categorized as wet and dry, respectively.

To calculate atmospheric loading rate of inorganic N to the Teaneck site, total precipitation volume falling over the time period during which a given peeper was deployed was calculated on a m^2 basis, and multiplied by the average N (in μg/L) of rainwater measured during 2005-06 by Ravit et al. (2006) (Table 4.1). Dry deposition was calculated using measurements made during 2005-06 by Ravit et al. (2006). To calculate atmospheric loading rate of inorganic N to the Liberty site, total precipitation volume falling over the time period during which a given peeper was deployed was calculated on a m^2 basis, and multiplied by the average N (in μg/L) of rainwater measured during 2006-07 by Song and Gao (2009) at a site ~10.5 km west of the Liberty wetland (Table 4.2). Dry deposition was calculated using measurements made during 1998-1999 by Gao et al. (2007) at a site ~26 km south of the Liberty wetland.

Loading rate from surface water was calculated for the Teaneck site by multiplying total volume flowing through the inlet during the peeper deployment period by the maximum and minimum NO_3^- and NH_4^+ concentrations in Teaneck Creek tributaries sampled in 2005–2006 (http://cues.rutgers.edu/teaneckcreek/data). It was assumed that water from the inlet distributed itself evenly over the low-lying wetland area (Fig 4.1) and divided inlet water volume by the wetland area (10,000 m^2) to calculate loading on a m^2 basis. Loading rate from surface water was calculated for the Liberty site by multiplying total volume flowing through the inlet during the peeper deployment period by the maximum and minimum NO_3^- and NH_4^+ concentrations measured during 2008 (Fig 4.3).

To calculate the amount of inorganic nitrogen exiting the Teaneck wetland site, total volume flowing through the outlet during the peeper deployment period was multiplied

by the maximum and minimum NO_3^- and NH_4^+ concentrations measured in Teaneck Creek at the confluence of Teaneck Creek and the wetland outlet in 2005–2006 (http://cues.rutgers.edu/teaneckcreek/data).

Porewater Collection

Sediment porewater samples were collected for two summers (2009-2010) from Liberty and for one summer (2010) from Teaneck to calculate denitrification rates (Fig. 1). Sediment porewater profiles of dissolved constituents (NO_3^-+NO_2^-, NH_4^+, N_2, O_2, Ar, N_2/Ar, O_2/Ar) were obtained using porewater diffusion equilibration samplers ("peepers"). Peepers were constructed of heavyweight PVC, with eight 19 mL wells (2 cm wide, spaced 0.5 cm apart). Prior to deployment, wells were filled with deionized water and covered with a 0.22 micron Polysulfone membrane. Assembled peepers were then submerged in a bucket of deionized water and allowed to equilibrate for 48 hours. Peepers were kept and transported underwater in the bucket until inserted vertically into sediment at three locations within each of the two wetland areas; once deployed, peepers were left to equilibrate in the sediment for 2–2.5 weeks.

To measure temperature at each peeper collection depth, iButton® temperature loggers were affixed to a narrow vinyl post at intervals corresponding to the middle of each peeper well. A post was pushed into the sediment a few inches away from each deployed peeper. Temperature was monitored at three depths in August 2010 and at all eight depths in September 2010.

During collection, peepers were pulled from the sediment and processed within 15 minutes to minimize gas exchange out of or into water samples. To extract water from peepers, a 20 mL glass syringe with a 12G needle was inserted through the membrane

over each well. Water was slowly drawn into the syringe and the needle was replaced with a narrow piece of tubing. Air bubbles were eliminated by tapping and expelling water while pointing the syringe upward. The tubing was then fed into the bottom of a 9 mL glass screwtop exetainer. Exetainers were filled from the bottom up, and allowed to overflow 2–3 times before being poisoned with 200 µL of a saturated zinc chloride solution and capped. Care was taken throughout this process to remove any large bubbles or headspace from the water samples, and replication of the extraction method in the lab using deionized water confirmed that it did not significantly alter dissolved gas concentrations in the samples. Samples were stored underwater at 2°C to minimize diffusion of gas out of the samples.

To measure dissolved gas content (N_2, O_2, Ar, N_2/Ar, O_2/Ar) of each peeper sample, samples were run on a quadrupole membrane inlet mass spectrometer (MIMS) dissolved gas analyzer (Balzers, Prisma^{TM}) with an electron multiplier detector (Kana et al. 1994). Samples and standards were kept at a constant temperature (19.7°C for 2009 LSP samples, 23°C for all other samples) during MIMS analysis using a water bath. Following analysis on the MIMS, the remaining sample in each vial was filtered using a combusted GF/F filter and frozen until they could be analyzed for NO_3^-+NO_2^- and NH_4^+ on an Omnion LACHAT.

Dissolved Gas Corrections and Calculations

N_2/Ar ratios were calculated by correcting the quadrupole instrument signal and standardized using an air-equilibrated nanopure water standard (salinity=0). To estimate denitrification rates (i.e., increases in N_2 concentration with increases in depth through the profile), the saturation normalized N_2/Ar ratio, $(N_2/Ar)_{sat}$ was calculated for all

measurements using the following equation: $(N_2/Ar)_{sat}=(N2/Ar)_{molar\ ratio}/(N_2/Ar)_{saturation\ equilibrium\ ratio}$ (Emerson et al. 1991). The saturation equilibrium ratio (hereafter referred to as $(N_2/Ar)_{sat}$) was determined by calculating the solubility of N_2 and Ar (Weiss 1970) at field-measured temperature and at a salinity of zero. $(N_2/Ar)_{sat}$ is a measure of the relative excursion from solubility equilibrium with the atmosphere; values greater than 1.0 represent supersaturation, or N_2 production (Hartnett & Seitzinger 2003). To calculate N_2 concentrations, I used the equation $(N_2/Ar)_{sat}*(Ar)_{sat}$, where $(Ar)_{sat}$ is the saturation equilibrium concentration of Ar at field measured temperature (Weiss 1970). To ensure that N_2/Ar ratios were not changing due to changes in Ar concentration due to factors other than temperature change (e.g., methane gas ebullition), any sample demonstrating a >10% difference in Ar concentration from the nanopure standard was not used in analysis.

Flux Calculations

Diffusive N_2, NO_3^- and NH_4^+ fluxes in sediments were calculated at the point of maximum slope of all dissolved constituents in the profile and where $(N_2/Ar)_{sat}$ exceeded 1.0 (Fig. 4.5 and 4.6). NO_3^- and NH_4^+ fluxes were calculated using equations in James et al. (2008): $J = -\varphi * D * \theta^{-2} * (\delta C / \delta z)$, where φ=sediment porosity, D=areal sediment diffusion coefficient (NO_3^-=1.9x10^{-5} cm^{2}s^{-1}; NH_4^+=1.98x10^{-5} cm^{2}s^{-1}), θ^2=sediment tortuosity, C=maximum change in profile N. Measured porosity was used in these equations; tortuosity was calculated using the equation given in Tremblay et al. (2008). In cases where standing water was present over the sediment, the maximum slope occurred at the sediment-water interface at the top of the profile (Fig. 4.5 and 4.6). In this case average concentrations of N in stormwater (Liberty) or precipitation (Teaneck)

were used to calculate fluxes. Stormwater contributed greater volumes of water to the Liberty wetland than overland flow (Table 4.2) and precipitation contributed greater volumes of water to the Teaneck wetland than overland flow (Table 4.3); average N concentrations from these sources were therefore used as an estimate of surface water N concentrations in situations with standing water over sediment. The average values measured in stormwater at Liberty in 2008 were 16.6 μM NO_3^- and 9.9 μM NH_4^+. The average values measured in rainwater at Teaneck in 2005-06 were 37.0 μM NO_3^- and 26.5 μM NH_4^+ (Ravit et al. 2006).

N_2 flux (denitrification rate) was estimated using Fick's first law: N_2 flux = -D * (δC / δz), where D=sediment diffusion coefficient (5.4 x10^{-6} cm^2s^{-1}). δC was calculated using the concentration of N_2 in uM at depth (dashed line) minus the saturation equilibrium concentration of N_2.

RESULTS

N Loading to Wetlands

Concentrations of NO_3^- in surface water at Liberty State Park (71–1161 μg/L NO_3^--N, average 233 μg/L NO_3^--N) were within the same range as precipitation NO_3^- concentrations measured within a few miles of the site (Fig. 4.3). Song & Gao (2009) found NO_3^- concentrations in rainwater ranging from 72–955 μg/L NO_3^--N over the year during 2006–07, with an average of 339 μg/L NO_3^--N in the summer. NH_4^+ ranged from 16–1,346 μg/L NH_4^+-N over the year, with an average of 560 μg/L NH_4^+-N in summer (Song & Gao 2009). NH_4^+ in stormwater at Liberty was lower than this range, 29–493 μg/L NH_4^+-N, with an average of 138 μg/L NH_4^+-N. DOC concentrations in Liberty stormwater were generally higher than in precipitation sampled at Teaneck (Fig. 4.3 and

4.4). Volumes of overland flow entering the Liberty wetland were much higher than volumes entering the Teaneck wetland, resulting in greater inorganic N loading overall during both wet and dry conditions (Table 4.2).

Concentrations of NO_3^--N and NH_4^+-N measured in surface water at Teaneck were much lower than those measured at Liberty, ranging from 5–55 and 0.4–17 μg/L, respectively. Concentrations in precipitation were higher than in surface water at Teaneck, however, and within the same range as at Liberty (Fig. 4.3 and 4.4), although average NH_4^+ concentration was higher (316 μg/L NH_4^+-N). Annual wet deposition rates of inorganic nitrogen measured at Teaneck (Fig. 4.4) were within the range of rates reported for 30 watersheds along the East and Gulf coasts of the U.S. (Meyers et al. 2001), but slightly lower than the rates reported by the national atmospheric deposition program (NADP) for the Hudson/Raritan watershed, of which Teaneck Creek is a tributary (Meyers et al. 2001, Ravit et al. 2006).

Sediment Fluxes

Profile data revealed highly reduced conditions in both wetlands, and the Liberty site had more reduced sediments overall than the Teaneck site (Fig. 4.5 and 4.6). In several cases at both sites, methanogenesis was likely a dominant process in the sediment, as ebullition of dissolved gases by methane was apparent from examining Ar content in the profiles. In these cases N_2/Ar and O_2/Ar profiles were meaningless, and were excluded from analysis. The sharp decrease in oxygen in each sediment profile corresponded with where the water table began (Fig. 4.5 and 4.6). At Liberty, oxygen concentrations were at <40% saturation at the top of the profile, and around 0% at the bottom of the profile in

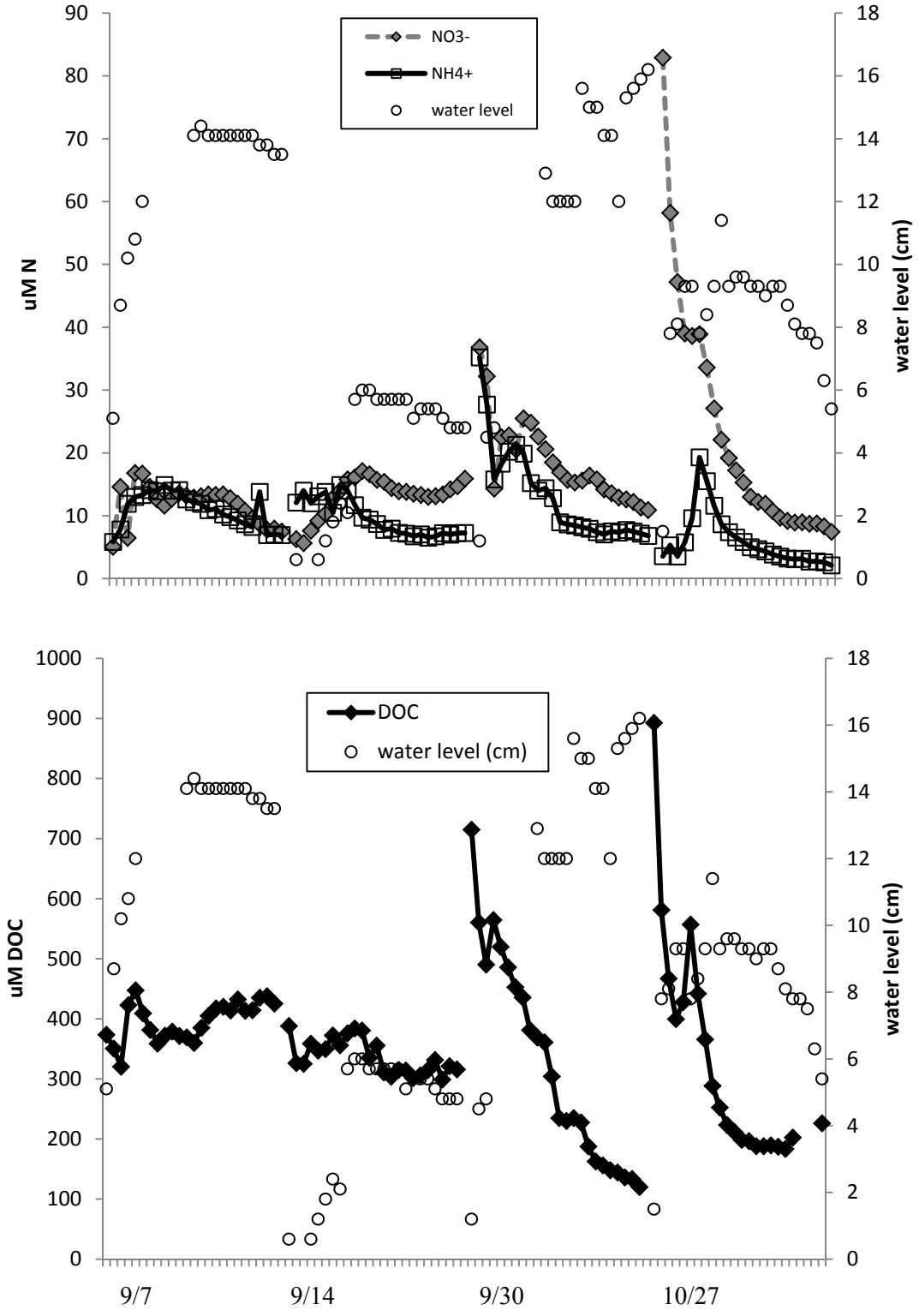

Fig. 4.3. Organic carbon and inorganic nitrogen concentrations in surface water entering the Liberty wetland during 2008. Water levels were measured using a pressure transducer during each rain event

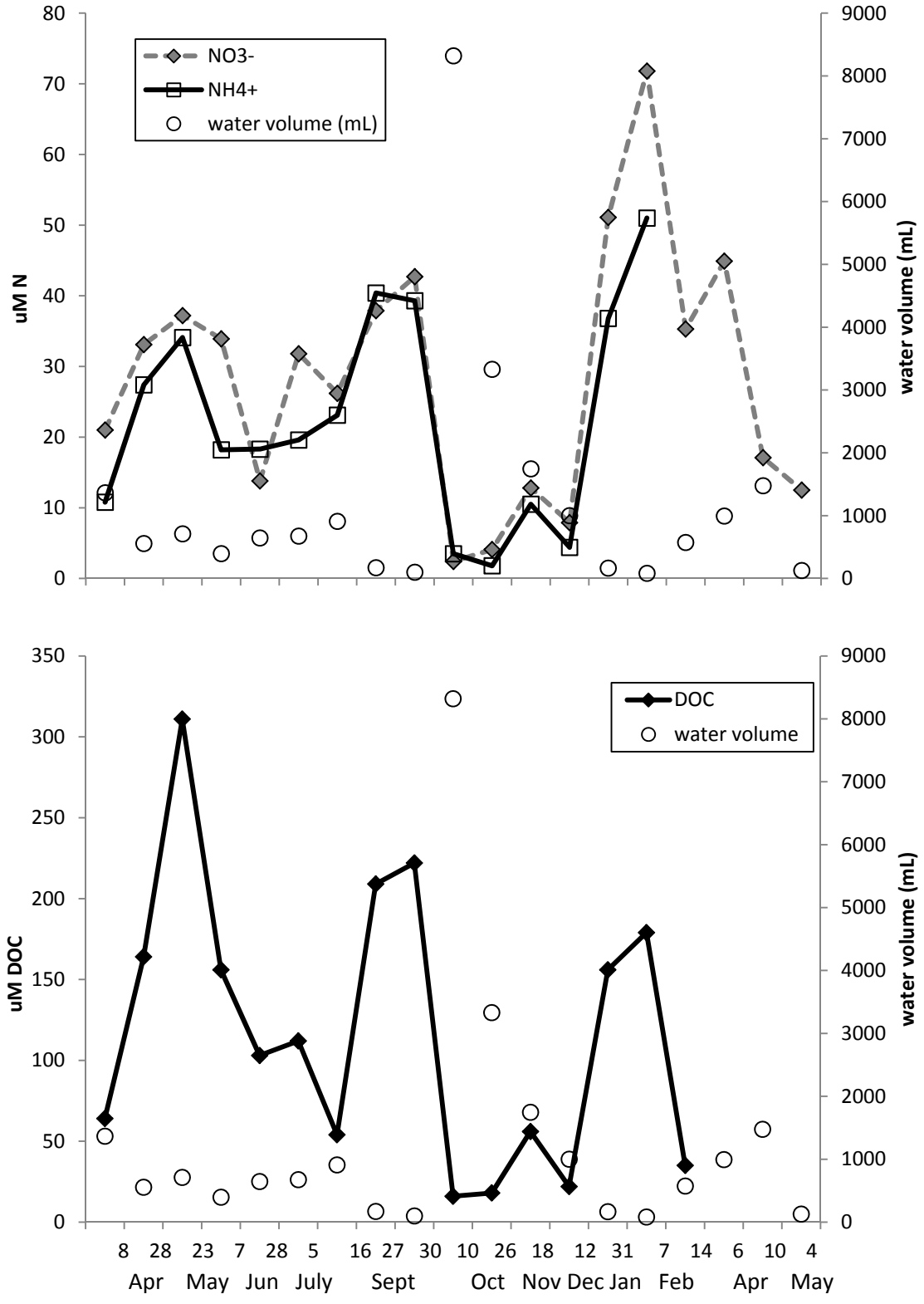

Fig. 4.4. Organic carbon and inorganic nitrogen concentrations in wet deposition at Teaneck 2005–06 (Ravit et al. 2006). Water volumes represent volume of precipitation collected during each rain event.

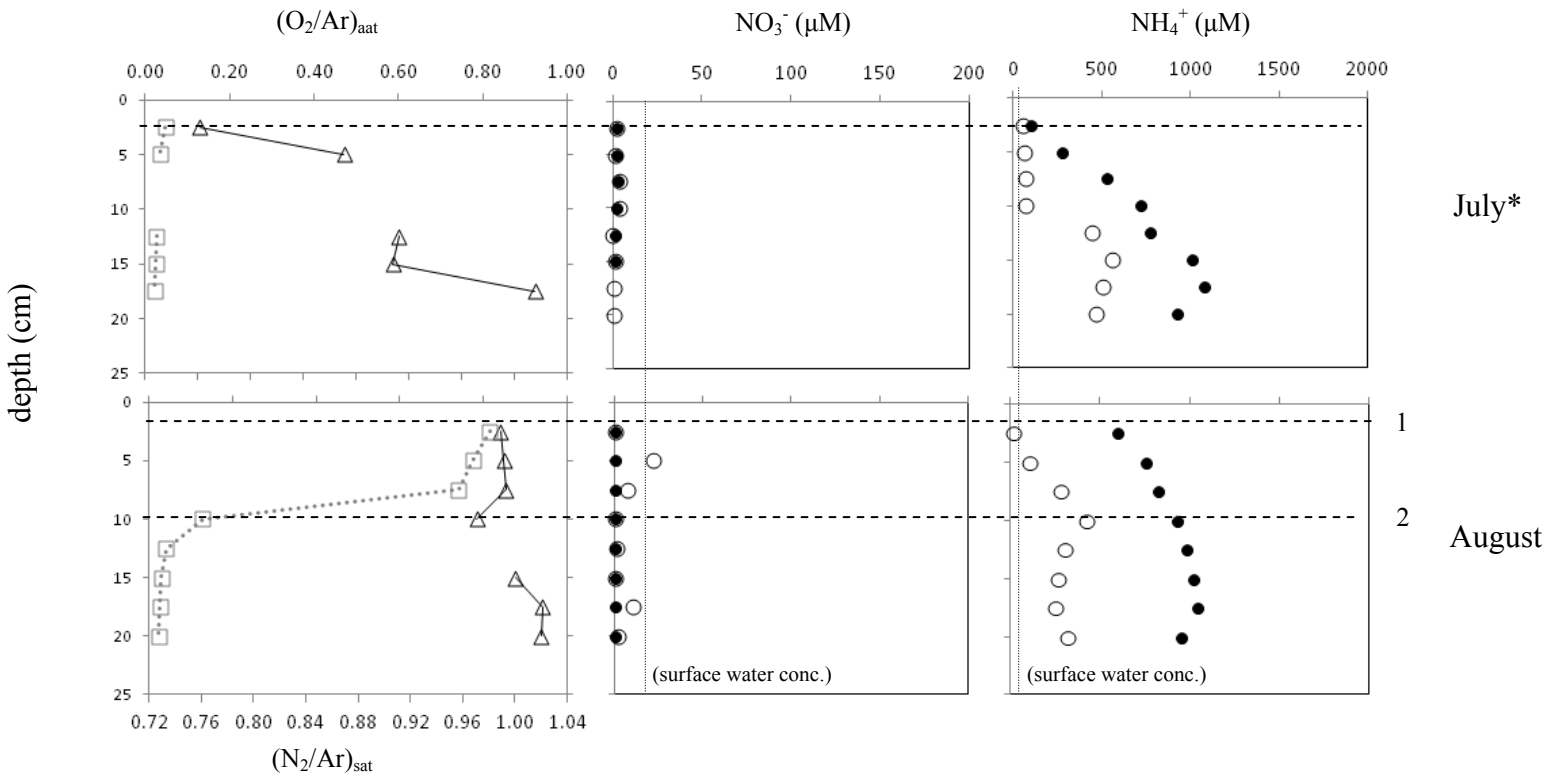

Fig. 4.5A. Pore water data from Liberty during 2009. Columns from left to right are saturation-corrected N_2/Ar and O_2/Ar ratios, dissolved NO_3^-, and dissolved NH_4^+. Square symbols=$(O_2/Ar)_{sat}$; triangles=$(N_2/Ar)_{sat}$; circles=dissolved NO_3^- and NH_4^+. Filled symbols=mid-pond; open=pond edge. Dashed lines represent the depth of the water table. In the case of the bottom row of graphs, where there are two dashed lines, 1 = water level in the mid-pond site, and 2 = water level at the pond edge. Asterisk indicates profile used for Liberty budget for wet conditions. Surface water concentrations are indicated on graphs where they were used to calculate rates of flux between sediment and water pools.

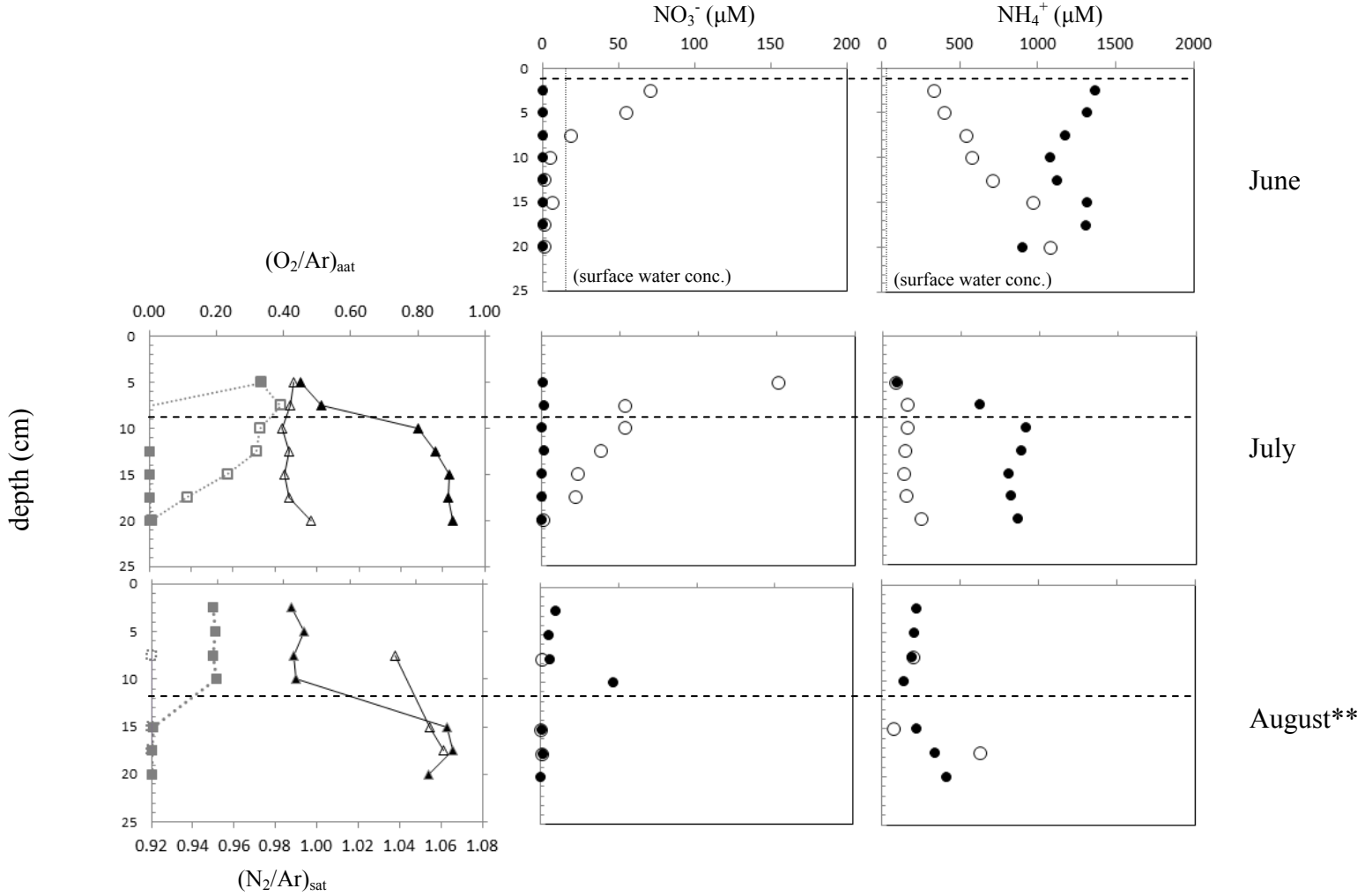

Fig. 4.5B. Pore water data from Liberty during 2010. Columns from left to right are saturation-corrected N_2/Ar and O_2/Ar ratios, dissolved NO_3^-, and dissolved NH_4^+. Square symbols=$(O_2/Ar)_{sat}$; triangles=$(N_2/Ar)_{sat}$; circles=dissolved NO_3^- and NH_4^+. Filled symbols=mid-pond; open=pond edge. Dashed lines represent depth of the water table. Double asterisks indicate sample date used for Liberty budget for dry conditions.

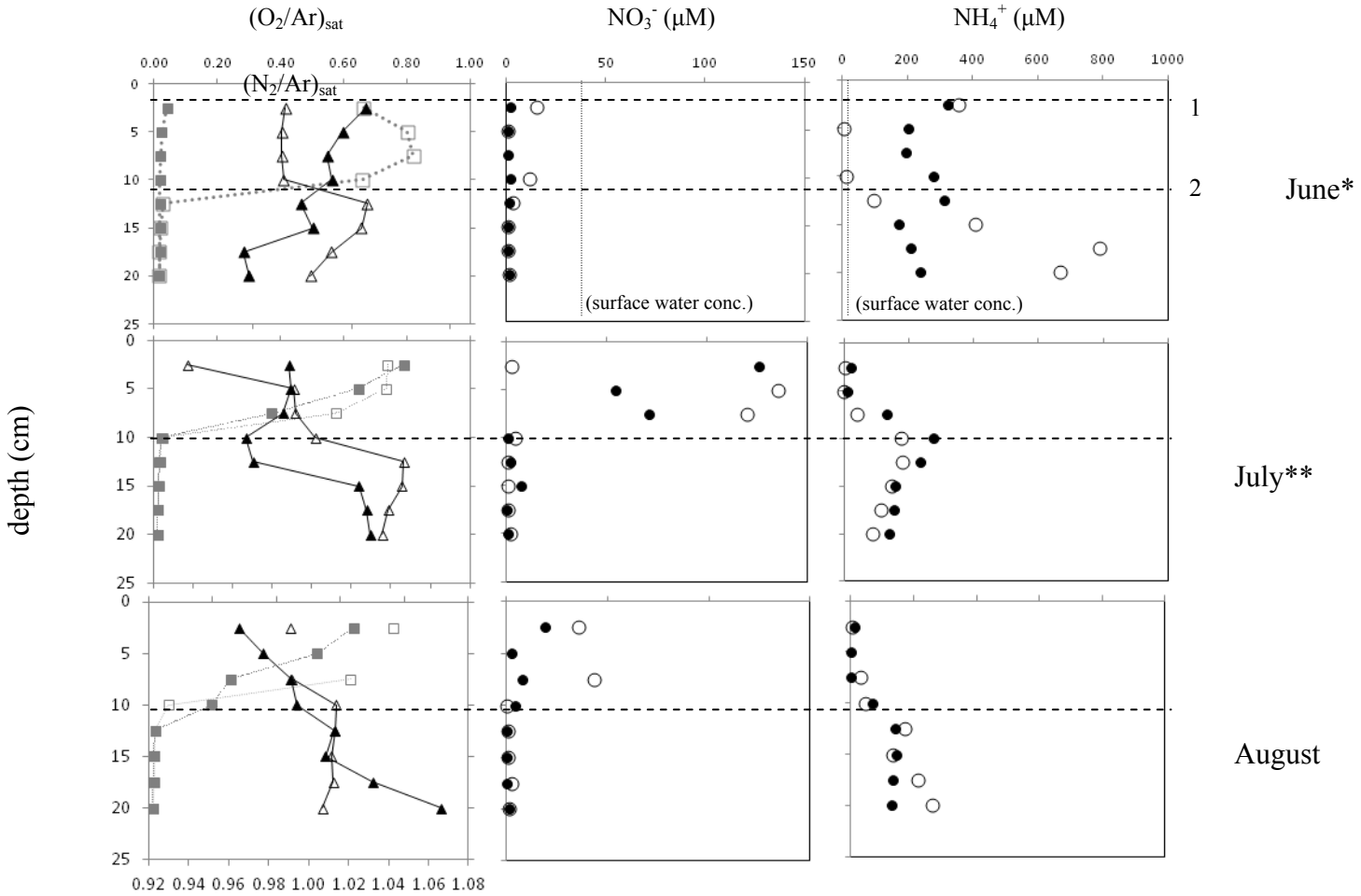

Fig. 4.6. Pore water data from Teaneck during 2010. Columns from left to right are saturation-corrected N_2/Ar and O_2/Ar ratios, dissolved NO_3^-, and dissolved NH_4^+. Square symbols=$(O_2/Ar)_{sat}$; triangles=$(N_2/Ar)_{sat}$; circles=dissolved NO_3^- and NH_4^+. Filled symbols=outlet site; open=inlet site. Dashed lines represent depth of the water table. In the case of the top row of graphs, where there are two dashed lines, 1 = water level at the outlet site, and 2 = water level at the inlet site. * = date used for Teaneck budget for wet conditions, ** = date used for dry conditions.

2010 (Fig. 4.5B). In 2009, a wetter year than 2010 when water tables were often above the sediment surface, oxygen concentrations were around 0% saturation through the entire profile (Fig. 4.5A). Apparent methanogenesis precluded use of most profiles for N_2 flux estimation during 2009. At Teaneck, oxygen concentrations were at 70–80% saturation at the top of the profile, and at around 0% saturation at the bottom of the profile (Fig. 4.6). At both Liberty and Teaneck, one sample site of the three (at Liberty, the wetland inlet; at Teaneck, in the mid-wetland) had very reduced conditions and/or methanogenesis for the majority of the study. These sites were therefore not used for sediment flux calculations.

Of the samples where apparent methanogenesis did not occur, N_2/Ar, O_2/Ar, dissolved NO_3^-, and dissolved NH_4^+ profiles tracked each other closely, and were related to water table level. $(N_2/Ar)_{sat}$ increased when $(O_2/Ar)_{sat}$ dropped to <0.06; this coincided with a sharp reduction in NO_3^- concentrations (Fig. 4.5 and 4.6). NH_4^+ concentrations in general were very high in sediments at both sites, much higher than concentrations of NH_4^+ in rain or stormwater (Fig. 4.5 and 4.6). Concentrations increased sharply as O_2/Ar ratio dropped to around zero (Fig. 4.5 and 4.6). NO_3^- concentrations were also generally much higher in the top of the profile than concentrations of NO_3^- measured in precipitation and stormwater.

Estimated N fluxes out of sediments were relatively high at both Teaneck and Liberty, and the magnitude of fluxes varied according to ambient moisture conditions (Table 4.1 and 4.2). Differences between wet and dry conditions were more pronounced at Liberty, possibly because wet/dry comparisons were made between two dates over a year apart at Liberty and between two dates one month apart at Teaneck when

Table 4.1. Inorganic N budget for the Teaneck wetland site. Rates of flux between sediment and water were calculated based on sediment profiles collected at two points on two dates in July (dry) and June (wet) of 2010. All rates are in $\mu g/m^2/day$. Volumes are reported on a per m^2 basis and are calculated as totals over the period of peeper deployment (2 weeks). Area of the wetland was estimated to be 10,000 m^2

	Dry Conditions	Wet Conditions
Surface Water N Fluxes (IN)		
Dry Deposition		
$N\text{-}NO_3^-$	68.6	68.6
$N\text{-}NH_4^+$	29.4	29.4
Wet Deposition	[Vol: 47.3 L]	[Vol: 41.8 L]
$N\text{-}NO_3^-$	1,590–47,560	1,410–42,040
$N\text{-}NH_4^+$	2,320–33,780	2,050–29,860
Overland flow	[Vol: 9.03 L]	Not measured
$N\text{-}NO_3^-$	1.33–5.37	
$N\text{-}NH_4^+$	0.19–6.17	
Fluxes Between Water and Sediment		
$N\text{-}NO_3^-$ (OUT water pool, IN sediment pool)	1,020–1,390	330–1,440
Denitrification $N\text{-}N_2$ (IN atmosphere, OUT sediment pool)	640–1,320	780–800
$N\text{-}NH_4^+$ (IN water, OUT sediment)	1,820–1,920	12,670–34,450
Surface Water N Fluxes (OUT)		
Overland flow	[Vol: 36 L]	Not measured
$N\text{-}NO_3^-$	1.21–8.97	
$N\text{-}NH_4^+$	0.10–4.20	
Total N fluxes into water pool	**5,830–83,270**	**16,258–106,498**
Total N fluxes into sediment pool	**1,020–1,390**	**330–1,440**
Total N fluxes out of wetland via water	**1–13**	**Not measured**
Total N fluxes out of wetland via atm	**640–1,320**	**780–800**
Change in Storage (Water Pool)†	**+ 4,809–81,871**	**+ 16,158–105,058**
Change in Storage (Sediment Pool)‡	**- 960–1,310**	**- 12,340–33,320**

† Calculated as total fluxes into water pool minus fluxes out via water and into sediment pool
‡ Calculated as total fluxes into pool minus fluxes out to water and atmosphere pools

Table 4.2. Inorganic N budget for the Liberty wetland site. Rates of flux between sediment and water were calculated based on sediment profiles collected on two dates: one in August 2010 (dry, profiles collected at two points) and the other in July 2009 (wet, profiles collected at two points; denitrification could only be calculated at one point). All rates are in $\mu g/m^2/day$. Volumes are reported on a per m^2 basis and are calculated as totals over the period of peeper deployment (2 weeks). Area of the wetland was estimated to be 11,000 m^2

	Dry Conditions	Wet Conditions
Surface Water N Fluxes (IN)		
Dry Deposition		
$N\text{-}NO_3^-$	3,090	3,090
$N\text{-}NH_4^+$	4,511	4,511
Wet Deposition	[Vol: 36.0 L]	[Vol: 57.3 L]
$N\text{-}NO_3^-$	2,592–34,380	4,125–54,722
$N\text{-}NH_4^+$	576–48,456	917–77,125
Overland flow	[Vol: 35.2 L]	[Vol: 237.9 L]
$N\text{-}NO_3^-$	2,498–40,853	16,886–276,107
$N\text{-}NH_4^+$	1,045–17,347	7,061–117,237
Fluxes Between Water and Sediment		
$N\text{-}NO_3^-$ (OUT water pool, IN sediment pool)	640–1,900	590–630
Denitrification $N\text{-}N_2$ (IN atmosphere, OUT sediment pool)	1,000–2,580	620
$N\text{-}NH_4^+$ (IN water, OUT sediment)	3,740–8,160	3,050–6,530
Total N fluxes into water pool	**18,252–156,797**	**39,640–539,322**
Total N fluxes into sediment pool	**640–1,900**	**10–630**
Total N fluxes out of wetland via water	**none**	**none**
Total N fluxes out of wetland via atm	**1,000–2,580**	**620**
Change in storage (Water Pool)†	**+ 16,231–154,344**	**+ 39,630–538,692**
Change in storage (Sediment Pool)‡	**- 3,300–6,780**	**- 3,120–48,150**

† Calculated as total fluxes water into pool minus fluxes from water into sediment pool
‡ Calculated as total fluxes into pool minus fluxes out to water and atmosphere pools

evapotranspiration differed but total precipitation volumes did not differ by much (leading to more flooding in June than in July). Under all conditions, NO_3^- demonstrated net fluxes out of the water pool into the sediment pool, and NH_4^+ demonstrated large net fluxes out of the sediment pool into the water pool (Table 4.1 and 4.2). The latter was higher under wet conditions, and the former was higher under dry conditions (Table 4.1 and 4.2). Denitrification rates were also higher under dry conditions at both sites (Table 4.1 and 4.2).

DISCUSSION

Inorganic Nitrogen Loading to Water Exceeds Losses

Semi-permanently flooded wetlands on brownfield sites in New Jersey are recipients of large quantities of inorganic N from stormwater and precipitation. Although some of this N appears to be permanently removed from the system to the atmosphere via denitrification, substantial amounts of inorganic N also enter the water column from sediments, which are a net source of inorganic N in the form of NH_4^+. NH_4^+ is produced through the breakdown of organic matter, which typically decreases under oxygen-poor conditions. Because of low requirements of anaerobic microorganisms for NH_4^+ and low oxidation rates of NH_4^+ under low-oxygen conditions, however, wetland soils typically accumulate high levels of NH_4^+ (Reddy & DeLaune 2008). If the NH_4^+ produced in these sediments is transported out of the wetland via subsurface flow, it will likely oxidize to NO_3^-, in areas of groundwater upwelling near the stream (Teaneck) or estuary (Liberty), making the wetlands a net source of inorganic N to nearby water bodies.

Denitrification is Driven by Nitrate Availability

Denitrification rates ranged from 0.02–0.09 mmoles N_2 /m^2/day, with the highest rates occurring when conditions were drier and O_2 and NO_3^- concentrations in surface sediments were high. These denitrification rates are considerably lower than those measured by Hopfensperger et al. (2009) in an urban tidal freshwater marsh in Virginia (1.2–5.4 mmoles N/ m^2/day) and those measured by Hartnett & Seitzinger (2003) in the Raritan Bay, an estuary downstream of both the Hackensack River (to which Teaneck Creek belongs) and Hudson River (to which Liberty Park belongs) watersheds (1.9–3.7 mmoles N/ m^2/day). The former was a measure of potential denitrification rates in the system, however, and tidal areas are the recipients of large pulses of nutrients on a daily basis. As predicted, much of the N_2 produced in the wetlands examined in this study appears to be the result of coupled nitrification-denitrification rather than as a result of high exogenous N loading. N_2 did not increase over saturation concentration ($(N_2/Ar)_{sat}$ > 1.0) unless O_2 concentrations were close to zero, however, indicating that the ideal conditions for denitrification likely occurred when NO_3^- had built up in the profile and then the water table rose to create anoxic conditions. This is illustrated by the lower denitrification rates under wet vs. dry conditions: under wet conditions, both wetlands had lower fluxes of NO_3^- out of the water pool into the sediment, and lower rates of NO_3^- removal via denitrification (Table 4.1 and 4.2). Under dry conditions, NO_3^- concentrations in the sediment above the water table were up to 3–9 times higher in both wetlands than the average surface water NO_3^- concentrations recorded in that wetland, implying nitrification was occurring under these conditions.

The Role of Plant Uptake and Litter Decomposition

NO_3^- flux out of the water pool into the sediment pool generally (though not always) exceeded NO_3^- removal from sediments via denitrification (Tables 4.1 and 4.2). This was likely due to plant uptake; both wetlands supported dense stands of *Phragmites australis* up to 3 m tall, suggesting high plant productivity and inorganic N uptake. Plant uptake of NO_3^- is not a permanent removal mechanism from the wetland system, however. In fact, the apparent high plant N uptake appears to lead to the large production of NH_4^+ in the wetland sediments as plant material breaks down under low oxygen conditions. *Phragmites* has a number of potentially beneficial effects on sediments in wetlands constructed for nutrient removal and reduction, namely in the provisions of root surface area for bacterial growth and labile carbon for denitrification (Vymazal 2011). Plant roots also exude oxygen, which potentially oxidizes NH_4^+ and fuels denitrification. However, if wetlands are not harvested, most of the nutrients from the plant biomass are returned to the water during the decomposition process (Vymazal 2011). *Phragmites* has high ammonia and total nitrogen removal capability; these high levels of removal also mean that *Phragmites* has high litter N content (Windham & Ehrenfeld 2003). While plant N uptake was estimated to be 41,918 μg N/m^2/day in *Phragmites*-dominated brackish marshes in southern New Jersey, N mineralization from litter in the same system was estimated to be 55,890 μg N/m^2/day (Windham & Ehrenfeld 2003).

Use of Peepers in Estimating Denitrification Rates

Peeper data appear to be an effective way of estimating denitrification rates in wetland sediments, but the method is limited by the fact that sediments need to be relatively saturated (in order to not dry out the peeper wells), but not so reduced that

gases are stripped out (ostensibly by methane bubbles). This study is the first to my knowledge to utilize peepers to measure N_2 fluxes, and one of the few studies to utilize MIMS for measuring N_2 flux in non-tidal freshwater sediments. Despite the drawback of not being able to use this technique when sediments are very highly reduced (and methane is produced), it offers several advantages over other methods measuring denitrification in sediments: (1) it can be undertaken without the need to transport intact sediment cores back to the lab (e.g., as in Hartnett & Seitzinger 2003, Hartnett et al. 2008, Hopfensperger et al. 2009); and (2) it appears to provide more accurate and reliable data on *in situ* denitrification rates than acetylene-based techniques (both intact core and denitrification enzyme analysis methods) in these types of sediments (Seitzinger et al. 1993). Since water level was closely related to O_2 levels, N_2 production, and NO_3^- loss in sediments at both Teaneck and Liberty, a combination of peeper measurements and development of spatially explicit hydrologic models to simulate water fluctuations over time may be key to more accurately predicting annual N_2 flux.

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Appendix A. Locations of hydrologic monitoring equipment at the Teaneck Creek and Liberty sites. Blue stars = pressure transducers, orange circles = autowells.

Appendix B. Description of Mike SHE/Mike 11 model and calibration for the Teaneck wetland site.

Mike SHE/Mike 11 is a fully integrated modeling framework capable of simulating all components of the land-phase of the hydrologic cycle (Refsgaard 1997). It consists of several individual models, which are integrated by the model framework. These are: (1) a saturated zone groundwater model, which calculates three-dimensional flows using the non-linear Boussinesq equation; (2) an unsaturated zone model, which calculates vertical flow via the Richard's equation; (3) an overland flow model, which calculates two dimensional flow using the St. Venant's equations; and (4) a channel flow model, which incorporates channel cross sections to calculate one dimensional river flow by the St. Venant's equations (Christiaens & Feyen 2011). Each of the models and the connections between them are built into the Mike SHE framework. Variable time steps are built into each of the models to optimize performance. For the wetland at Teaneck, the entire sub-watershed surrounding the low-lying wetland area (0.06 km^2) was modeled in the simulation.

Hydrologic inputs needed to run the Mike SHE/Mike 11 submodels are precipitation, temperature (to simulate evaporation), evapotranspiration (PET), and a boundary condition regulating surface water drainage. Precipitation and temperature data were acquired from the Teterboro Airport Climate Station (NOAA). Solar radiation data for calculation of PET was acquired from a weather station at Rutgers Gardens. The boundary condition at TCC is water levels in Teaneck Creek. Surface water level was monitored every hour from July–October 2010 using pressure transducers deployed at the inlet, outlet, and in Teaneck Creek (see Appendix A).

The unsaturated zone model in Mike SHE/Mike 11 is driven largely by soil water retention properties. Soil layers for each site were created by combining data sets from several different sampling periods in 2006–2008 (chapter 2). At TCC, soil texture data from 59 points sampled in 2006–2007 were used to characterize the texture and water retention properties of the top 3 m of the soil profile across the site. Separate raster layers for percent sand, percent silt, and percent clay were created through an inverted weighted distance interpolation of the original 59 sample points. These three layers were then reclassed to create a unique range of values for percent sand (0–10% = 1, 10–20% = 2, etc.), percent silt (0–10% = 10, 10–20% = 20, etc.), and clay (0–10% = 100, 10–20% = 200, etc.). The three reclassed layers were added together, so that each cell had a single value for sand, silt and clay (e.g., if the cell value was 255, texture fractions = 40–50% sand, 40–50% silt, 10–20% clay). The latter raster layer was then converted to polygon features using the "simplify polygons" option in ArcMap. These numbers assigned to each resulting polygon feature were compared against a soil texture pyramid (USDA) to determine the textural class for each polygon. Polygons were then assigned parameters for the van Genuchten water retention curve (van Genuchten 1980) based on empirically-derived (chapters 1 & 2) van Genuchten parameter values for point(s) falling within each polygon.

The impact of vegetation (i.e., on PET and on the speed of overland flow) in the Mike SHE/Mike 11 modeling system is determined via the leaf area index (LAI) and rooting depth. Vegetation layers were created by digitizing 2007 aerial photographs. Vegetation was categorized as forested (deciduous), tall grass (*Phragmites australis*), short grass

(lawn), bare soil, or open water. These categories were used to estimate leaf area index and Manning's n roughness coefficients for each vegetation polygon.

Once a calibrated model was produced, Mike 11 was used to simulate water table dynamics and discharge through the outlet over most of the period during which pore water data (dissolved N_2, O_2, NO_3^-, NH_4^+) were collected (July-September 2010).

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