THE EFFECTS OF URBAN HYDROLOGY AND ELEVATED ATMOSPHERIC DEPOSITION ON NITRATE RETENTION AND LOSS IN URBAN WETLANDS

By

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ABSTRACT OF THE DISSERTATION

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Wetlands are known for their ability to process nitrate inputs from uplands and groundwater and thus prevent nitrate discharge to sensitive waters. Wetlands in urban landscapes are subjected to numerous disturbances which may prevent them from serving as N sinks. The objective of this dissertation is to document N cycling in urban wetlands in the context of altered hydrology and elevated atmospheric N deposition, and to determine whether urban wetlands serve as sinks or sources of nitrate to receiving waters.

This study was conducted in palustrine, forested wetlands in northeastern New Jersey. *In situ* rates of net N mineralization, net nitrification, and denitrification were measured monthly for one year. Water table levels were monitored over five years, and soil and vegetation properties were characterized. Weekly nitrate inputs as throughfall and outputs as leachate were measured for one year and analyzed for stable isotopes of nitrogen and oxygen.

Due to altered hydrology, natural hydrogeomorphic setting was not an effective predictor of N cycling rates in urban wetlands. Many assumptions of functional assessment models used to make wetland management decisions were not met. Alternative models I developed using indicators of specific N functions successfully predicted nitrification rates, but they did not predict denitrification rates. Assessment of biogeochemical functions and reference standard site selection should be based on long-term monitoring of water table levels. Assessment models should be targeted to specific functions and may need to utilize intensive field or laboratory techniques. Local scale factors are better descriptors of N cycling rates than indicators of landscape scale urbanization.

Nitrate inputs were higher in more urban sites, but there was no urban effect in nitrate outputs. Urban wetlands generally retained nitrate, as demonstrated by higher nitrate inputs than outputs. However, two sites did demonstrate overall loss of nitrate. Two other sites exhibited direct leaching of atmospherically-derived nitrate, suggesting a lower capacity for N retention. Nitrate retention is not universal in urban wetlands.

Dedication

This dissertation is dedicated to my parents, Ross and Betty,

my sister, Gabrielle,

and my sweetheart, Casey.

Their love and support are behind every page.

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Introduction

Nitrogen is one of the most widespread and pervasive pollutants present in surface waters throughout the United States and much of the world (Vitousek, 1997, Lowrance et al. 1997, Caraco and Cole 1999, USGS 1999, Mitsch et al. 2001, Van Breeman et al. 2002, Van Drecht et al. 2005, Boyer et al. 2006). This problem is as widespread in urban or urbanizing watersheds as it is in agricultural areas receiving nitrogen inputs from fertilizer application (Nolan and Stoner 2000). The problem has been well-documented in the urban watersheds of New Jersey (Ayers et al. 2000). Excess nitrogen in surface waters can have drastic negative consequences for ecosystems. The zones of hypoxia in the Chesapeake Bay and the Gulf of Mexico are dramatic examples of the extent to which nitrogen excess can cause eutrophication in receiving water bodies (Lowrance et al. 1997, Mitsch et al. 2001). Also, because nitrate (NO_3^-) is a drinking water pollutant, elevated NO_3^- levels in surface waters pose a problem for human and wildlife health. These problems threaten to become more pervasive as more land is converted to urban land use. The twentieth century saw a ten-fold increase in the urban population and an increase from 14 to over 50% in the proportion of the human population living in urban areas (Platt 1994). These trends are continuing into the current century (UN 2006).

Wetlands are highly valued because they provide a number of ecosystem services that are beneficial to society. One of the most critical is the removal of excess NO_3^- from upland land uses before it reaches surface waters. NO_3^- is removed through the process of denitrification, the microbially-mediated transformation of NO_3^- to nitrogen gases which are released to the atmosphere. This process requires anaerobic conditions to go to completion, conditions which are commonly found in the saturated soils of wetlands.

The vast majority of studies which have evaluated the NO_3^- removal capacity of wetlands have concentrated on riparian buffers receiving groundwater NO_3^- inputs from agricultural land use (Lowrance et al. 1984, Cooper 1990, Lowrance 1992, Simmons et al. 1992, Haycock and Pinay 1993, Gilliam 1994, and Hill 1996). Little work has been done to verify that urban wetlands are indeed performing NO_3^- removal functions (but see Groffman et al. 2002, Groffman and Crawford 2003). Results of the US Geological Survey's National Water Quality Assessment program have shown elevated NO_3^- in streams and groundwater in urban areas (USGS 1999). Therefore, the function of wetlands in developed regions needs to be understood if these ecosystems are to be used to protect water quality.

It is not possible to extrapolate the results of agriculturally-oriented studies to urban wetlands due to the unique hydrological disturbances to which urban systems are subjected. While agricultural systems have been highly modified in terms of hydrology, this modification has come in the form of ditching and draining. In urban systems hydrological disturbance may be caused in part by ditches for mosquito management and from historical agricultural land uses, but disturbances are also the result of development and stormwater management practices at the watershed scale. Impervious surfaces associated with urban and suburban land use result in reduced infiltration of stormwater, which leads to reduced groundwater recharge and flow and thus reduced baseflow (Paul and Meyer 2001, Meyer et al. 2005, Walsh et al. 2005). Imperviousness also causes reduced surface water storage and thus increased surface runoff following rain events (Ehrenfeld 2000, Im et al. 2003). This runoff is quickly channeled from impervious surfaces directly to receiving water bodies (Klein 1979). The high volume of stormwater reaching receiving streams over a short period of time results in increased erosive force, which causes stream incision and downcutting (Hollis 1975, Booth 1990, Booth and Jackson 1997, Moscrip and Montgomery 1997). Streams in watersheds with old or stable urban land use may have particularly marked incision because there are few sources of sediment to replace material eroded during rain events (Booth 1990, Trimble 1997).

These large-scale hydrological alterations can cause hydrological alterations in wetland soils which in turn affect wetland function, including an increased loading of nutrients and a reduction in NO_3^- removal capacity (Paul and Meyer 2001, Im et al. 2003). Stream incision and downcutting caused by high peak flows can result in lowered water tables in adjacent wetlands (Groffman et al. 2002, Ehrenfeld et al. 2003). This means that the top 30 cm of the soil profile, which is the location of plant roots and the majority of soil biological activity, no longer experiences frequent saturation (Figure 1). As a consequence soils are dryer, which may facilitate nitrification, an aerobic microbial process, and inhibit denitrification, a microbial process which requires saturated, anoxic soils. The result may be leachate losses of NO_3^- to the shallow groundwater (Figure 1).

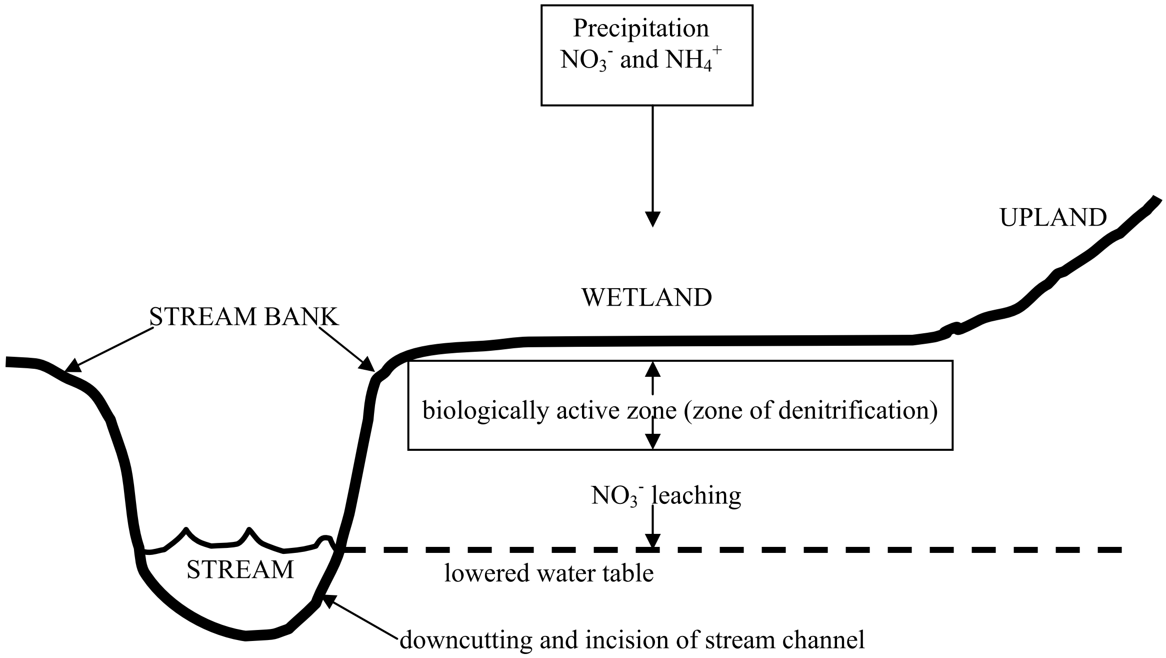

Figure 1. Urban hydrology leads to stream downcutting and lowered water tables in the adjacent wetland. Drier conditions result in the biologically active zone of the wetland. Complete denitrification to nitrogen gas is inhibited and nitrate leaching facilitated following a rainstorm.

Several studies have looked at nitrogen dynamics in wetlands receiving NO_3^- from upland residential land use (Hanson et al. 1994, Gold et al. 2001, Groffman et al. 2002, Groffman and Crawford 2003), but the literature from urban systems is still limited. These studies also did not look for direct loss of NO_3^- to the groundwater but rather measured rates of internal nitrogen cycling processes. Other studies have demonstrated elevated levels of nitrogen mineralization and nitrification in non-urban wetland mineral soils during periods of lowered water tables (Updegraff et al. 1995, Bechtold et al. 2003). The stimulation of nitrification following wetland drainage has been well-documented in peatlands (Regina et al. 1999, Olde Venterink et al. 2002). The effects of wet-dry cycles on denitrification rates have been studied in wetland systems which have been restored following drainage for agriculture (Davidsson et al. 2002, Olde Venterink et al. 2002) and also in less disturbed wetlands which were artificially flooded in an attempt to increase nutrient removal (Davidsson and Leonardson 1996). These studies indicated that denitrification was stimulated in dry soils following rewetting, but they did not evaluate NO_3^- loss during the initial flush. It remains to be seen if hydrological disturbance associated with urbanization affects the ability of these wetlands to remove NO_3^- through denitrification and thus prevent NO_3^- losses through leaching.

Under Section 404 of the Clean Water Act, the federal regulatory community is charged with protecting and maintaining wetland functions, in part to minimize NO_3^- levels in streams and rivers which feed larger estuary systems (Hauer and Smith 1998, Carletti et al. 2004). As a result regulatory agencies are focusing on identifying wetlands which may be capable of removing NO_3^- from upland sources before it reaches streams. Agencies are also under increasing pressure to quantify the amount of NO_3^- removal performed by wetlands. Due to financial and logistic constraints, this is accomplished through modeling rather than direct measurement. A number of existing functional assessment methods attempt to model wetland N cycling functions, but the Hydrogeomorphic (HGM) functional assessment method developed by the Army Corps of Engineers is currently the preferred method in the United States (Brinson 1993, Brinson et al. 1995, Smith et al. 1995, Hauer and Smith 1998). The concept of HGM setting integrates hydrological information such as source of water input, within-site movement of water, and geological and topographical processes which impact water movement. Because NO_3^- removal processes are clearly driven in part by hydrological dynamics, in theory HGM could be useful for predicting levels of NO_3^- removal in different types of wetlands (Cole and Brooks 2000). Nitrogen cycling data collected in reference wetlands representing the range of HGM classes for a particular region would be used to develop and calibrate models for predicting nitrogen cycling functions in more human-impacted wetlands in the same region based on a rapid assessment of structural features (Smith et al. 1995, Brinson and Rheinhardt 1996, Rheinhardt et al. 1997). However, the altered hydrological regimes in urban wetlands described above may limit the ability of models developed in less impacted wetlands to model N cycling functions in urban-impacted wetlands. Also, the difficulty of finding relatively unaltered reference standard sites in urban regions may hamper the ability of regulatory agencies to conduct HGM functional assessment protocols.

Another issue which emphasizes the need to study NO_3^- removal in urban wetlands is the significant input of nitrogen into the system through atmospheric deposition. Rates of atmospheric N deposition have increased as much as 90% in the northeastern United States over historical levels as a result of human activities, particularly fossil fuel combustion (Vitousek et al. 1997). Atmospheric N deposition represented 31% of N inputs and was the largest single N source to the combined area of 16 watersheds in the northeastern US (Boyer et al. 2002). Jaworski et al. (1997) explicitly linked atmospheric nitrogen N with eutrophication of coastal waters in the Northeast. NADP estimates from Washington Crossing State Park in Mercer County, New Jersey, show 13.93 kg/ha of NO_3^- deposition and 2.62 kg/ha of ammonium deposition in 2003 (http://nadp.sws.uiuc.edu/ads/2003/NJ99.pdf). This is a relatively rural part of New Jersey. The density of urban development and amount of vehicular traffic in close proximity to many urban wetlands, particularly in the northeastern part of the state, suggests that N deposition rates at the local scale may be significantly elevated, perhaps above regional averages, as Lovett et al. (2000) documented along an urban-rural gradient from New York City to outlying northern suburbs. Aside from this study, there have been few attempts to document rates of atmospheric N deposition in urban areas.

I propose a conceptual model in which fluctuating water table levels and elevated rates of atmospheric N deposition can result in NO_3^- loss from urban wetlands (Figure 2).

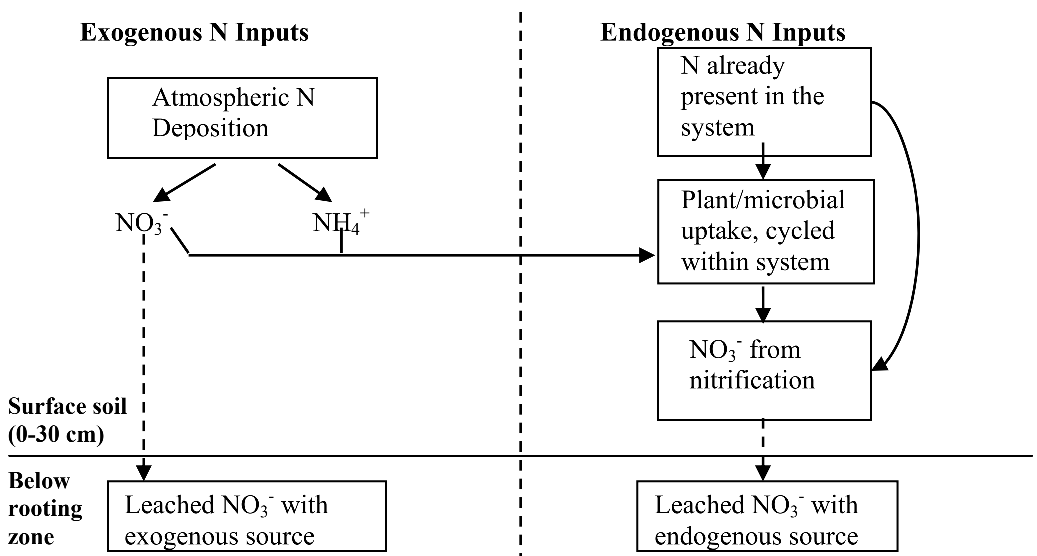

Figure 2. Conceptualization of the sources and fates of exogenous versus endogenous N inputs. Boxes represent N pools, solid arrows represent movement of N between pools, and dotted arrows represent leaching of NO_3^- below the rooting zone.

NO_3^- produced endogenously during dry periods may leach during the initial flush following a rain event. NO_3^- from exogenous inputs may leach directly without being biologically processed in the soil or it may be taken up by plants or microbes and cycled within the soil. Exogenous inputs may also stimulate endogenous NO_3^- production

(Figure 2). Studies in upland terrestrial forests have shown that N deposition can stimulate N mineralization and nitrification (Aber et al. 1989, Aber et al. 1995, McNulty et al. 1996, Peterjohn et al. 1996, Magill et al. 2000).

The fact that urban wetlands may be experiencing high levels of both endogenous and exogenous NO_3^- begs the question: if these wetlands are leaking N, is atmospheric deposition or internal NO_3^- production making a larger contribution to NO_3^- loss? Typically stable isotope analysis is conducted to determine the sources and fates of nitrogen compounds in ecosystems. In this case, N isotope ratios alone cannot be used to distinguish between atmospheric deposition and soil nitrification as sources of NO_3^- to soil leachate, because the natural abundance $\partial^{15}N$ values of these two sources are too wide and overlapping. Fortunately oxygen isotope ratios can be used for this purpose. $\partial^{18}O$ values of NO_3^- in atmospheric deposition range from +25 to +90‰ (Kendall et al. 1998, Ohte et al. 2004), while NO_3^- derived from microbial soil nitrification has $\partial^{18}O$ values ranging from -5 to +15‰ (Durka et al. 1994, Mayer et al. 2001). $\partial^{18}O$ values from nitrification-derived NO_3^- are so different because up to two of the oxygen atoms are derived from soil water while the remaining atom or atoms is derived from atmospheric oxygen. The exact ratio varies depending on the pathway of nitrification (heterotrophic versus autotrophic) (Mayer et al. 2001). In addition, the dual isotope approach is useful because the $\partial^{15}N$ values can be used to detect isotopic enrichment caused by denitrification (Spoelstra et al. 2001). This is because denitrifiers discriminate against the heavier ^{15}N isotope during the denitrification process, therefore enriching the remaining NO_3^- pool in ^{15}N.

The dual isotope method for determining sources of NO_3^- exported to surface and ground waters is fairly new. Early methods were developed and utilized in Europe (Amberger and Schmidt 1987, Durka et al. 1994, Revesz et al. 1997) and were not employed in the US until Kendall and colleagues popularized the technique in early studies of snowmelt and drainage waters in northern temperate forests (McGlynn et al. 1999, Shanley et al. 2002) and alpine watersheds in the Sierra Nevada region (Sueker et al. 2000, Unnikrishna et al. 2002, Campbell et al. 2002, Sickman et al. 2003). Since then other research groups have recognized the power of this technique and have employed it to study N sources and transformations in the Mississippi River and its basin (Battaglin et al. 2001, Chang et al. 2002), precipitation and drainage waters in Ontario (Spoelstra et al. 2001, Spoelstra et al. 2004), leachate from agricultural soils (Mengis et al. 2001), streams draining Appalachian forests (Williard et al. 2001), runoff from watersheds in the Catskill Mountains (Burns and Kendall 2002), and multiple watersheds across the northeastern region of the US (Mayer et al. 2002).

The bulk of these studies used methods modified from the original European efforts (Chang et al. 1999, Silva et al. 2000). These new methods quickly became the standard in dual isotope studies because they enabled the analysis of $\partial^{18}O$ in freshwater samples with low NO_3^- concentrations (0.7-10 μM, compared to a lower detection limit of 40 μM in prior methods). This was accomplished by preconcentrating NO_3^- in the samples using anion exchange columns. NO_3^- is then converted to N_2 and CO_2 using a high-temperature combustion process. $\partial^{15}N$ and $\partial^{18}O$ can be determined from these products using continuous flow isotope ratio mass spectrometry.

Although these new methods represented a significant advance in dual isotope technology, the drawbacks are prohibitive for many potential applications. Even the lower detection limit requires high volumes of sample (on the order of liters) which is not easy to obtain with certain types of analyses (e.g., soil leachate) or in remote areas. The multiple and complex NO_3^- purification steps make the analysis time and labor intensive and also costly (in some cases $300 per sample) (Sigman et al. 2001). Beyond the logistical problems, there are also important analytical issues. Oxygen from dissolved organic matter in the samples can exchange with oxygen in NO_3^- during the combustion process, resulting in $\partial^{18}O$-NO_3^- values which shift according to the variable concentration of dissolved organic matter in individual samples (Silva et al. 2000).

Sigman and colleagues developed a new method, commonly referred to as the "denitrifier method," for the analysis of natural abundance N and oxygen isotope ratios in seawater and freshwater (Sigman et al. 2001, Casciotti et al. 2002). According to this method, sample NO_3^- is reduced to nitrous oxide (N_2O) by denitrifying bacteria. Dentrification is a stepwise reduction of NO_3^- to nitrite, nitric oxide, N_2O, and finally nitrogen gas (N_2). Each reduction step is catalyzed by a different enzyme which is encoded by a distinct gene. Many natural bacterial strains lack specific components of the denitrification pathway. The denitrifier method makes use of bacteria, specifically *Pseudomonas aureofaciens* and *Pseudomonas chlororaphis*, which naturally lack N_2O reductase and so are unable to reduce N_2O to N_2 (Sigman et al. 2001). The isotopic composition of the end product N_2O is then analyzed. Because atmospheric concentrations of N_2O are much lower than those of N_2, N_2O analysis is easier and more accurate. In comparison with the combustion method, the denitrifier method has the advantages of a 100-fold reduction in sample size requirement, a reduction in sample analysis time, a detection limit equal to or lower than the combustion method, and the ability to analyze the oxygen isotope composition of seawater (Casciotti et al. 2002).

So far few investigators have attempted to use dual isotope techniques to study sources of NO_3^- in urban or wetland areas, and none have utilized the denitrifier method. There is a growing literature on sources of NO_3^- contamination of groundwater (see review paper by Choi et al. 2003) including one study of an urban aquifer (Fukada et al. 2004). Several studies have used the technique to investigate NO_3^- removal in riparian zones (Mengis et al. 1999, Cey et al. 1999, Sidle et al. 2000, Fukada et al. 2003), but these studies were focused mainly on NO_3^- from agricultural sources. However, because of the unique hydrological disturbances and their associated effects on N fluxes in urban wetlands, there is a clear opportunity to utilize dual isotope methodology to answer questions about sources and fates of N in this system.

Hypotheses and Methodological Approaches

This dissertation focuses on the effects of urbanization on N cycling dynamics in urban wetlands. The components of urbanization I have chosen to study are altered hydrology and elevated atmospheric N deposition. The main hypotheses of my dissertation are as follows:

1a. HGM classification is not an effective predictor of N cycling rates in urban wetlands.

1b. *A priori* designation of reference standard sites according to a qualitative assessment of alteration does not identify sites with low nitrification and high denitrification rates.

1c. *A posteriori* classification of reference standard sites according to quantitative analysis of hydrological regimes is more effective than *a priori* designation.

Due to altered hydrological regimes in urban wetlands, I hypothesized that the main assumptions of the HGM method would be invalid in this system. The first assumption is that HGM classes in a particular region have unique and predictable rates of N cycling functions. The HGM method also assumes that reference standard sites, which represent sites with the best or most characteristic rates of N cycling processes, are identifiable as those sites with the least amount of apparent alteration according to a qualitative assessment. To determine whether there was a relationship between HGM class and rates of N functions, I measured *in situ* rates of net N mineralization, net nitrification, and denitrification monthly over the course of one year in three HGM classes common to urban wetlands in northeastern New Jersey. I also designated two reference standard sites in each HGM class prior to the study (*a priori* classification). After analysis of long-term hydrology data, I reclassified study sites as reference or non-reference according to the presence or absence of altered hydrological regimes (*a posteriori* classification). I then compared N cycling rates between sites according to both *a priori* and *a posteriori* classification.

2a. Existing HGM functional assessment models do not predict N cycling rates in urban wetlands.

2b. Models based on functional indicators and targeted to specific functions more effectively describe N cycling rates in urban wetlands.

2c. Models based on non-rapid indicators are more effective than models based on rapid indicators.

I conducted rapid assessments of 14 palustrine, forested wetlands in northeastern New Jersey according to published HGM guidebooks. Using these data, I calculated functional scores using existing models developed for similar HGM classes. Calculated scores were then compared with actual measures of N cycling rates to test the effectiveness of existing models. I developed additional models targeted specifically to nitrification and denitrification, and designed them using functional indicators of known controlling factors on these processes. Some models used only rapidly measured indicators, while other models utilized "non-rapid" indicators which require either long-term data from field studies or data from simple laboratory analyses of soil properties. Then, as above, I calculated functional scores using my own models, and compared the scores to actual N cycling rates to test the effectiveness of my rapid and non-rapid models.

3a. Hydrology, which may be affected by both landscape scale urbanization and by local scale soil properties, is a predictor of N cycling rates in urban wetlands.

3b. Landscape indicators of watershed urbanization are both direct and indirect (as mediated through hydrology) predictors of N cycling rates, but its indirect effects are stronger.

3c. Local scale soil properties are both direct and indirect (as mediated through hydrology) predictors of N cycling rates, but their effects are not as strong as landscape indicators.

3d. Local scale vegetation properties are direct predictors of N cycling rates, but their effects are not as strong as landscape indicators.

In this study I evaluated the possible controlling factors of N cycling on both the landscape and the local scale. I hypothesized that both landscape and local scale factors would be important predictors of N cycling rates in urban wetlands. However, I predicted that landscape scale effects would be the strongest, because I hypothesized that landscape effects on hydrology would be the primary drivers of N cycling rates. I used GIS-based spatial analyses to quantify commonly used indicators of watershed urbanization (i.e., percent impervious cover, population density, percent urban land cover, etc.), and field measurements of water table levels, *in situ* N cycling rates, soil properties, and vegetation properties in 14 urban wetlands to test these hypotheses.

4a. Concentrations and fluxes of NO_3^- in throughfall are higher in wetlands located in more urban watersheds than those in less urban watersheds.

4b. Concentrations and fluxes of NO_3^- in soil water and leachate are higher in wetlands located in more urban watersheds than those in less urban watersheds, thus N retention is greater in wetlands in less urban watersheds.

4c. Endogenous NO_3^- production by nitrification is a more important contributor to NO_3^- export in leachate than atmospheric N deposition.

To test these hypotheses, I measured throughfall and soil water by tension lysimetry on a weekly basis at least once per month in nine sites over the course of one year. These nine sites were located along a gradient of urban conditions ranging from very urban to less urban. Samples were analyzed for NO_3^- concentrations and for natural abundance isotope values of $\partial^{15}N$ and $\partial^{18}O$.

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CHAPTER 1

Rapid assessment of urban wetlands:

Do hydrogeomorphic classification and reference criteria work?

Introduction

The evaluation of wetland functions is a primary goal of wetland assessment methodologies (Hauer and Smith 1998, Carletti et al. 2004). Of the numerous assessment protocols that have been developed, the hydrogeomorphic (HGM) method is conceptually appealing, because it relates ecological function to the determinants of water flow, a fundamental feature of wetlands (Mitsch and Gosselink 2000). The HGM method is based on the assumption that ecological functions are determined by the sources and hydrodynamics of the water that create a given wetland (Brinson 1993, Brinson et al. 1995, Smith et al. 1995). By first classifying wetlands according to their hydrological characteristics, and by quantifying functional processes within sites deemed to be representative of the least-disturbed condition of a given HGM type, functions in other wetland sites can be evaluated in comparison to these representative “reference standard” sites. In urban areas, however, the HGM approach to wetland functional assessment may not be effective. The pervasive hydrological alteration of wetlands in developed regions (Paul and Meyer 2001, Groffman et al. 2002, Ehrenfeld 2000, Ehrenfeld et al. 2003, Faulkner 2004, Meyer et al. 2005, Walsh et al. 2005) may compromise both the accuracy of HGM classification and the designation of “least disturbed” reference standard sites. I have tested the applicability of HGM classification and criteria for reference site identification by evaluating a prominent wetland function, removal of nitrogen through denitrification, in wetlands within a heavily-developed region.

In an attempt to comply with federal regulations mandating the protection of wetland functions (NRC 1995, Hauer and Smith 1998), including N cycling functions, federal regulatory agencies have in the last fifteen to twenty years developed numerous methods for classifying wetlands and assessing wetland functions (Brinson 1993, Smith et al. 1995, Brinson et al. 1995, Rheinhardt et al. 1997, see also http://www.epa.gov/owow/wetlands/monitor/). The underlying concept is that under a policy of no net loss of wetland function, any wetland function that is lost due to permitted draining or filling of wetlands must be replaced through wetland mitigation (Conservation Foundation 1988, Rheinhardt et al. 1999). Functional assessment procedures have thus been developed and advanced to improve the rigorousness of permitting and mitigation decisions (Carletti et al. 2004). However, due to logistical constraints related to funding, personnel, and perhaps most importantly, time, regulatory agencies are under pressure to complete functional assessments quickly and cheaply (Brinson 1995, Rheinhardt et al. 1997, Hauer and Smith 1998, Carletti et al. 2004, Cole 2006).

The HGM functional assessment procedure, currently the federal government's stated preferred method (Hauer and Smith 1998, Hruby 1999), is designed to determine functional capacity of wetlands in particular HGM classes in a specified region. Simple, semi-quantitative models are created which allow for the calculation of functional capacity scores based on indicators of vegetation, soil, and hydrological structure which can be measured in a half-day field visit. Wetlands which show little or no signs of alteration, either human or natural, are assumed to have characteristic levels of function for that HGM class in that region, and functional capacity scores of more altered wetlands in the same HGM class and region are indexed relative to the unaltered sites (see Brinson 1993, Brinson et al. 1995, Smith et al. 1995, Brinson and Rheinhardt 1996, and Rheinhardt et al. 1997 for a more detailed description of this methodology). The methodology is predicated on a hypothesized relationship between HGM class and function; because HGM classification is based on geomorphic setting, hydrological input, and within-site hydrodynamics, theoretically wetlands in one HGM class in a specific region should express different levels of a particular function than wetlands in other HGM classes in that same region (Bedford 1996, Rheinhardt et al. 1997, Gwin et al. 1999, Cole et al. 1997, Cole and Brooks 2000). This should be true in particular for nitrogen cycling functions whose rates are so dependent on hydrological conditions.

Accordingly, several studies have found relationships between HGM classes and various measures of wetland structure and function. Cole et al. (1997) found differences in median depth to water table among riparian depression, slope, mainstem floodplain, and headwater floodplain HGM classes in central Pennsylvania, and Shaffer et al. (1999) found differences in water level and extent and duration of inundation among three naturally occurring HGM classes (slope, riverine, and depression) in the Portland, Oregon, region. Findlay et al. (2002) found significant differences among enclosed, sheltered and fringe tidal marshes in 10 of 12 functions measured; these functions included nutrient retention via assimilation into plant biomass and nitrogen removal as measured by potential denitrification (these particular functions were measured directly using standard research techniques, not rapid assessment protocols).

Wetlands in urban landscapes, however, are subjected to a variety of hydrologic alterations which may affect rates of N cycling processes. Numerous studies have documented the various forms of hydrologic alterations of streams (Paul and Meyer 2001, Meyer et al. 2005, Walsh et al. 2005) and their resulting impacts on wetland hydrology (Groffman et al. 2002, Ehrenfeld et al. 2003, Faulkner 2004). These alterations include incised streambanks (Hollis 1975, Booth 1990, Booth and Jackson 1997, Moscrip and Montgomery 1997) which can result in lowered water tables in adjacent wetlands (Stromberg et al. 1996, Groffman et al. 2002, Ehrenfeld et al. 2003), reduced surface water storage and decreased groundwater recharge in the surrounding watershed (Im et al. 2003) resulting in reduced surface and groundwater inputs to wetlands (Owen 1995), and increased river discharge during storm events resulting in increased flooding frequencies in wetlands (Moscrip and Montgomery 1997). Ditches, berms, and other physical modifications of the wetland itself are also common in urban landscapes (Ehrenfeld 2004). Taken together, these alterations cause many forested urban wetlands in northeastern New Jersey to be drier and flashier (rapid fluctuations between dry and wet conditions) than they have been historically (Golet et al. 1993, Ehrenfeld et al. 2003). In theory these kinds of hydrological changes should have dramatic consequences for N cycling processes, but this has only been documented in a few studies in Rhode Island and Maryland which found higher rates of N mineralization and nitrification and high levels of denitrification potential associated with urban land uses (Hanson et al. 1994, Groffman et al. 2002, Groffman et al. 2003). There has not yet been a real test of the relationship between HGM class and N cycling functions, in urban landscapes like those found in northeastern New Jersey, or anywhere else. In this study I will address the ability of the HGM classification to infer wetland N cycling functions in an urban/suburban landscape.

A critical element of the HGM assessment method is the use of reference standard sites. Reference standard sites are those wetlands which are unaltered and are thus assumed to perform functions at a sustainable level which is characteristic of their HGM class and region (Brinson 1993, Brinson et al. 1995, Smith et al. 1995, Brinson and Rheinhardt 1996, Rheinhardt et al. 1997, Rheinhardt et al. 1999). These sites are then used to develop and calibrate the models used for rapid functional assessment. Functional capacity index scores are set to a value of 1 in the reference standard sites. Scores at non-reference sites (sites with evidence of disturbance, both human and natural) are indexed relative to the reference standard sites. Reference standard sites are chosen based on a qualitative assessment of degree of alteration. There are no published guidelines for determining degree of alteration. In practice, alteration assessments are conducted visually in a field visit by a trained wetland expert and through a review of the relevant scientific literature (Brinson and Rheinhardt 1996, Hruby 2001). The method thus relies heavily on best professional judgment (Brinson and Rheinhardt 1996). Designation of reference standard sites is typically conducted before quantitative data have been collected; I refer to this methodology as an "*a priori*", meaning before data collection, designation of reference standard sites.

The effectiveness of *a priori* designation of unaltered sites as reference standard sites has not been tested in an urban landscape, and there are several reasons to believe there may be inherent difficulties. First, and perhaps most obviously, it is difficult or impossible to locate wetland sites in the urban landscape which are unaltered (Ehrenfeld 2000, 2005). Brinson and Rheinhardt (1996) warn against using degraded sites as reference standards in urban areas, stating that "this would be counterproductive to goals of restoring and creating wetlands that will function at high levels." However, they also recognize that landscape/watershed level characteristics may prevent wetlands in highly urbanized landscapes from functioning at characteristic levels for their HGM class and region, particularly for functions such as maintaining characteristic hydrologic regime, which then affects other critical functions, such as N cycling functions. Another closely related issue is that a qualitative, visual assessment of commonly used hydrologic indicators, such as drift lines, buttressed trunks, sediment deposits, and redoximorphic features in soils, may not correspond well with actual, current hydrologic patterns, particularly in sites which have experienced hydrologic alteration (Ehrenfeld et al. 2003). Thus, the bases for choosing reference standard sites for the assessment of functions in wetlands in urban regions, including both the primary division of wetlands into HGM classes with separate reference standard sites for each class, and the designation of "least disturbed" as the criterion for designation within a HGM class, need to be critically examined.

Wetlands have become high-profile ecosystems as a result of the many functions they perform which have both ecological and societal importance. One of these functions is the removal of N, typically in the highly mobile form of nitrate, from upland land uses before it is released to surface waters, where it contributes to eutrophication and drinking water pollution (Lowrance et al. 1997, Mitsch et al. 2001). Wetlands are increasingly used by managers to combat the problem of excess NO_3^- based on the documented ability of wetlands to remove NO_3^- from sewage effluent (Boustany et al. 1997) and upland agricultural land use (Lowrance et al. 1984, Cooper 1990, Lowrance 1992, Simmons et al. 1992, Haycock and Pinay 1993, Gilliam 1994, and Hill 1996). NO_3^- is removed through the process of denitrification, the microbially-mediated transformation of NO_3^- to N_2 gas which is released to the atmosphere. This process requires anaerobic conditions which are typically found in the saturated soils of wetlands.

Wetlands have special significance in urban/suburban landscapes like northeastern New Jersey because in these heavily developed areas, the wetland function of nitrogen retention has become a highly-valued ecosystem service (Ehrenfeld 2004, Groffman et al. 2004). Findings of the US Geological Survey's National Water Quality Assessment program show that elevated NO_3^- is as common in urban streams and groundwater as in agricultural areas (USGS 1999**.** The problem has been well documented in the urban watersheds of New Jersey (Ayers et al. 2000). These problems threaten to become more pervasive as more land is converted to urban land use.

My purposes in this paper are to: 1) to test the validity of HGM classification in predicting N removal functions and related N cycling processes in urban wetlands, 2) to test the validity of commonly-used criteria for *a priori* identifying reference standard wetland sites in urban areas, and 3) to compare the effectiveness of *a priori* designation with one based on long-term hydrological observations (*a posteriori* designation). To achieve these objectives, I used a long-term record of water table levels and *in situ* measurements of net N mineralization, net nitrification, and denitrification rates taken over the course of one year in a set of urban wetlands in northeastern New Jersey. I thus examine these questions using direct measurements of functions rather than structural indicators with poorly-tested relationships to actual functional values.

Methods

Study Sites

Fifteen palustrine, forested wetland sites were selected in northeastern New Jersey. All sites are located within the Piedmont physiographic province. This places the sites in the most urbanized region of the state and within the third largest urban agglomeration in the world with a population of 18.7 million (UN 2005) (Figure 1.1). Population densities range from 177 to 3,585 persons km^{-2} and road densities range from 4.6 to 33.1 km km^{-2} in the watersheds containing the 15 sites.

Study sites were chosen from the population of palustrine, forested wetlands (Cowardin et al. 1979) in the region, as identified by the New Jersey Freshwater Wetlands Inventory maps (http://www.state.nj.us/dep/gis/). Many of these wetlands are naturally-occurring fragments remaining from larger wetland complexes created by the deposition of dense clays in two large glacial lakes, glacial lake Passaic and glacial lake Hackensack, which covered much of northeastern New Jersey following the retreat of the Wisconsin glaciation (Wolfe 1977). These wetland fragments persist despite close to 400 years of human land use and development in the region (Ehrenfeld 2004); most of these fragments are currently protected at the federal, state, county, or municipal levels as open space, wildlife refuges, and/or natural floodwater retention basins.

All sites had a closed-canopy deciduous forest dominated by red maple (*Acer rubrum* L.) and plant communities as described by Ehrenfeld (2005). Sites were selected to represent three of the most prevalent HGM classes in the region: riverine, mineral flat, and mineral flat-riverine (hereafter, flat-riverine). Sites were placed into HGM classes according to methods outlined in detail by Ehrenfeld et al. (2003); briefly, assessment of topographic maps, presence of natural stream channels, and field assessment of sources and dynamics of water as described by Smith et al. (1995). Riverine wetlands receive their primary

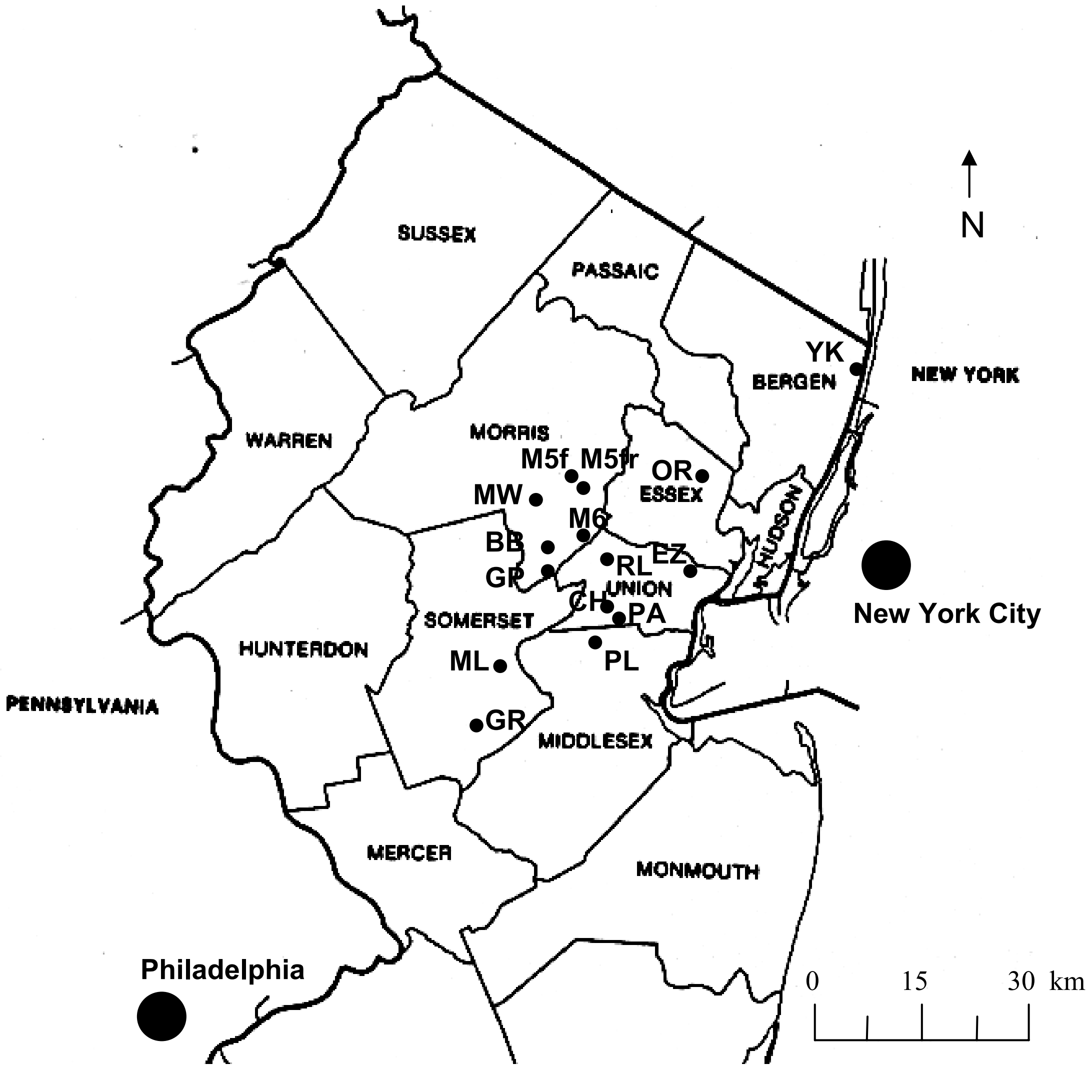


Figure 1.1. Fifteen palustrine, forested wetlands were chosen for this study. All sites are located in the Piedmont physiographic province in the northeastern, most urbanized portion of New Jersey.

hydrological input from overbank flooding of streams. Hydrological input to mineral flat wetlands is primarily in the form of precipitation and groundwater; these wetlands occur on the poorly drained mineral soils of the two major glacial lake sediments (Ehrenfeld 2005). Overbank flooding and precipitation/groundwater input are both important hydrological inputs to flat-riverine wetlands. Five sites were chosen in each of the three HGM classes.

A Priori Designation of Reference Standard Sites

Reference standard sites were designated prior to field measurements according to methods described in technical reports and guidebooks authored by Brinson and colleagues (Brinson 1993, Brinson et al. 1995, Brinson and Rheinhardt 1996). Reference standard sites are those sites in a particular HGM class in a particular region which are qualitatively assessed to have the least alteration and are thus thought to have the highest or most characteristic level of performance of a given function for a wetland of that type in that place. Relative degree of alteration is assessed by best professional judgment of a wetland scientist with experience within the chosen region. All wetland fragments remaining in northeastern New Jersey have been altered directly or indirectly in some way due to the urban context in which they are currently situated (Ehrenfeld 2000), as well as the cumulative effects of land use and disturbance in the region’s 400-year history of dense settlement (Wacker and Clemens 1995).

I designated as “reference standard” sites those wetlands within each of the three HGM classes that were less disturbed than the others, according to the following criteria:

1. Size. Larger sites are likely to have less disturbed interiors. Sites located in wetland complexes that were at least 100 ha in size were considered large enough to be reference standard sites.

2. Surrounding human population density. Sites located in watersheds with lower population densities are likely to be subject to less alteration from direct and indirect human impacts. Sites with surrounding human population densities less than 500 people/km^2 were considered low enough for a reference standard rating.

3. Management. Sites with a history of protection are likely to be less disturbed. Sites which were protected at the federal or state level or by non-profit organizations were chosen to be reference sites rather than sites protected at the municipality level.

4. Visual assessment. No obvious large disturbances evident within or along the perimeter of the site.

If sites met all four of these criteria, they could be designated as reference standard sites. The designation of reference standard sites using best professional judgment of these criteria is referred to as the "*a priori*" designation. Two reference standard sites were selected in each of the three HGM classes using the *a priori* designation (Table 1.1). One reference standard site in the flat-riverine class had to be eliminated during the course of the study because it became clear after the study was initiated that the site was located in an active management area; floodwaters were channeled towards the stream and away from the floodplain during rain events to manage for water bird populations (the site is located in a National Wildlife Refuge). Therefore the site no longer fit the criteria of the

Table 1.1. Sites were *a posteriori* reclassified according to a long-term record of water table readings. Altered sites were either dry, flashy, or both. Dry sites had at least 50% of daily mean water table observations less than 30 cm deep and 20% of daily mean water table observations at detection level (100 cm deep). In flashy sites at least 5% of the hydrological record crossed the 30 cm depth mark. Sites in bold were designated as reference sites by *a priori* criteria. N/A indicates that data were not available for these variables.

Site	***HGM Class***	***A Priori Designation***	***% < -30 cm***	***% at -100 cm***	***% crossings at -30 cm***	***A Posteriori Designation***
ML	**Riverine**	**Reference**	**88.5**	**6.02**	**8.28**	**Altered**
GR	**Riverine**	**Reference**	**60.7**	**9.95**	**4.13**	**Normal**
EZ	Riverine	Non-reference	98.6	26.2	0.492	Altered
OR	Riverine	Non-reference	100	94.1	0.00	Altered
MW	Riverine	Non-reference	27.4	7.45	4.61	Normal
M5f	**Mineral Flat**	**Reference**	**97.9**	**12.2**	**2.12**	**Altered**
BB	**Mineral Flat**	**Reference**	**38.2**	**2.36**	**5.46**	**Altered**
M6	Mineral Flat	Non-reference	61.1	19.3	5.68	Altered
PL	Mineral Flat	Non-reference	64.4	0	9.26	Altered
YK	Mineral Flat	Non-reference	N/A	N/A	N/A	N/A
M5fr	**Flat-Riv**	**Reference**	**N/A**	**N/A**	**N/A**	**N/A**
CH	Flat-Riv	Non-reference	29.6	1.05	4.19	Normal

PA	Flat-Riv	Non-reference	2.24	0	0.748	Normal
RL	Flat-Riv	Non-reference	8.26	0	1.65	Normal

HGM flat-riverine classification or the criteria of the *a priori* designation (too much alteration as qualitatively assessed by best professional judgment).

Hydrology

Water table dynamics were measured in 12 of the 14 sites to determine whether sites had normal or altered hydrology. These 12 sites were equipped with an automatically recording well (hereafter, autowell) (either a WL-40 or an Ecotone model, Remote Data Systems, Inc., Whiteville, NC). Specific locations for each autowell were chosen based on the presence of typical wetland soils (i.e., redoximorphic features, peat accumulation) and forested conditions on both sides of the stream. Autowells were installed to a depth of 100 cm at a distance of 25 m from the stream bank. Autowells were programmed to collect water table measurements four times daily. The autowells' data loggers were downloaded bimonthly. Measurements of hydrology were taken between October 2002 and May 2006, with sporadic gaps at different times from site to site when wells stopped collecting data due to dead batteries or repairs. Due to problems with vandalism, wells had to be removed from two of the sites (YK and M5fr). Thus, there is a long-term hydrological record for only 12 of the 14 sites used in this study.

In Situ Soil Nitrogen Cycling Rates

Rates of net N mineralization, net nitrification, and denitrification were measured in all 14 sites to determine N cycling function of wetlands in different HGM classes and in reference standard versus non-reference sites as determined by both *a priori* and *a posteriori* designations. Soil sampling was conducted monthly at five points along a transect perpendicular to the stream. The first sampling point was located 9 m from the stream bank; subsequent sampling points were positioned 7.5 m apart. Soil cores were taken monthly between October 2002 and November 2003, except during the winter months of December through March, during which cores taken in November were incubated in the ground until harvested in April.

The intact static core technique developed by Robertson et al. (1999) was used to measure *in situ* rates of net N mineralization and net nitrification. The acetylene block technique was used to measure denitrification rates on the same cores (Tiedje et al. 1989). Each month five replicate, 2.5 cm diameter cores were taken at the five sampling points to a depth of 20 cm and were returned to the lab immediately for processing. Another five replicate cores were taken and returned to their holes to incubate in the ground for a month. After a month the cores were harvested and returned to the lab for processing.

Upon arrival at the lab, the denitrification incubation was carried out; rubber septa were placed on each end of the cores, and five ml acetylene gas were added to the headspace of each core to block denitrification from progressing from N_2O to N_2. N_2O samples were taken after 2 hours and 6 hours and analyzed using a Shimadzu GC-14A gas chromatograph equipped with an electron capture detector. Denitrification rates were calculated as the amount of N_2O produced between the two hour and six hour sampling events. After the six hour denitrification incubation, soil samples were stored at 4ºC until further processing.

Within the next two days measurements were taken for bulk density and moisture content. Soil from the top 10 cm was then homogenized and extracted for inorganic nitrogen using a 2 M KCl solution at a 4:1 KCl to soil ratio. KCl extracts were frozen until analyzed colorimetrically on a QuikChem® Flow Injection Analyzer+ 8000 Series (Lachat Instruments, Loveland, CO) for nitrate and ammonium concentrations. Rates of net N mineralization were calculated as the amount of ammonium and nitrate accumulated over the course of the month-long incubation; net nitrification rates were the amount of nitrate accumulated over the month.

Data Analyses

A posteriori designation of reference standard sites I used the continuous water level records to develop a classification of the sites that was independent of the *a priori* classification. This new classification is referred to as the "*a posteriori*" classification, and represents an alternative to the *a priori* criteria for determining sites which might serve as reference standard sites. Previous studies (Golet et al. 1993) have shown that the natural hydrology of red maple swamps in the northeastern United States is characterized by water table depths within 30 cm of the soil surface for much of the year with a drawdown during the summer, and water tables that are generally stable with few large fluctuations. I used this description as the criterion for designating sites as having "normal" hydrology. I defined sites that had hydrologic patterns that were dry or flashy or both as "altered." Dry sites were arbitrarily defined as sites with at least 50% of the water table observations below 30 cm and 20% of the observations at 100 cm (detection level). Dryness at 30 cm depth is significant because this is the extent of the rooting zone and is where rates of N cycling should be optimized. It is also the depth of saturation recommended for wetland delineation protocols (National Research Council 1995) and has been used as a definition of wetland dryness in other studies (Cole and Brooks 2000, Ehrenfeld et al. 2003). A drawdown of the water table is typical during the growing season (Golet et al. 1993), so sites were still considered normal with water tables below 30 cm deep up to 50% of the time. Dryness at 100 cm is the detection limit of my autowells and was used as an arbitrary level to represent conditions which are uncharacteristic of red maple swamps in the northeast (Golet et al. 1993). I identified flashy sites as those in which more than 5% of the hydrological record represents consecutive daily mean water table readings that crossed the 30 cm depth mark. This represents a high occurrence of water table fluctuation in the portion of the soil profile in which wet conditions are most critical in controlling rates of nitrification and denitrification (Golet et al. 1993). *A posteriori* designation of normal versus altered hydrology and all data analyses using hydrological variables were performed only on the 12 sites instrumented with autowells.

Mean monthly rates of net N mineralization, net nitrification, and denitrification were analyzed using mixed model repeat measures analysis of variance (ANOVA) (SAS Statistical Systems ver. 9.1). To test the ability of HGM to describe N cycling function, HGM class was the fixed factor, site was the random factor, and time was the between subjects factor. To test the ability of quantitative hydrologic classification to predict N cycling function, normal versus altered categorization across the 12 sites with hydrology data was substituted as the fixed factor, and site and time remained as the random and between subjects factors, respectively. The unstructured covariance structure was the best fit model for these comparisons based on the results of Akaike Information Criterion (AIC) tests. Degrees of freedom calculations for all ANOVAs were conducted using the Kenward-Roger method. SAS's lsmeans statement was used to carry out pairwise comparisons between HGM classes, and the "adjust=simulate" command was used to control for error due to multiple comparisons.

The effectiveness of the *a priori* designation of reference standard sites was also tested using mixed model repeat measures ANOVA. Reference standard and non-reference sites (*a priori* designation) were compared within each HGM class separately. Riverine sites with normal versus altered hydrology (*a posteriori* designation) were also compared; mineral flat and flat-riverine sites did not have a mix of normal and altered sites (the five mineral flat sites were all altered and the four flat-riverine sites were all normal; see Table 1.1). The compound symmetry covariance structure was the best fit for the ANOVAs testing the *a priori* designation, but the unstructured covariance structure was used to test the *a posteriori* designation. Matrix structure was selected based on the results of AIC tests.

As an alternative method for comparing the effectiveness of the *a priori* versus *a posteriori* designations of reference standards, I ranked the sites in order of the quantitative values of their functions, and then tested mean ranks among wetland classes. Sites were ranked separately according to rates of net N mineralization, net nitrification, and denitrification. In the cases of net N mineralization and denitrification, the site with the highest rate of the function in question was given the #1 rank, as net N mineralization and denitrification are considered valuable functions (N mineralization converts organic N to inorganic forms which are then available to plants microbes; denitrification removes NO_3^- to the atmosphere before it leaches to the groundwater) in which higher rates reflect "better" functional capacity. In the case of net nitrification, the site with the lowest rate was given the #1 rank, as nitrification is considered to have negative value, as nitrate can leach to surface waters and contribute to eutrophication. Ranks for all three functions were averaged for each site over all observations (9 months for net N mineralization and net nitrification and 10 months for denitrification, 5 observations per site per month). Average site rankings were compared between reference standard and non-reference sites using both *a priori* and *a posteriori* designations using Wilcoxon-Mann-Whitney tests (SAS Statistical Systems, ver. 9.1). Results are reported from two-sided, exact tests. By definition, reference standard sites should have higher rankings than non-reference sites. A significant difference between rankings in reference standard versus non-reference sites would indicate that the sites identified as reference standards are indeed functioning at a higher, or better, level than the non-reference sites that would be evaluated against the standards in an assessment methodology.

Results

HGM Classification as a Descriptor of N Cycling Functions

Rates of net N mineralization were not significantly different among HGM classes, but rates of net nitrification and denitrification were (Table 1.2, Figures 1.2a-c). This effect was driven entirely by the flat-riverine class, which had significantly lower rates of nitrification and higher rates of denitrification than the riverine and mineral flat classes (Table 1.2, Figures 1.2a-c). The mineral flat and riverine classes were not significantly different from each other in net N mineralization, net nitrification, or denitrification rates (Table 1.2). Time was a significant effect in rates of all three N cycling processes, reflecting expected seasonal changes in the effects of temperature on these processes, but there were no significant interactions between HGM class and time (Table 1.2).

There were no significant differences in net N mineralization rates between normal and altered sites (Table 1.3, Figure 1.3a). However, sites which had normal

Table 1.2. Differences in N cycling rates among 14 wetlands separated by HGM class. Measures were taken monthly over one year. Statistical results are from repeat measures ANOVAs using HGM class as the fixed factor, site as the random factor, and time as the between subjects factor. T tests were used to test for differences between pairs of HGM classes.

Factor	***N Mineralization***		***Nitrification***		***Denitrification***	
HGM Class	$F_{2,60.2}=0.77$	ns	$F_{2,65}=4.53$	*	$F_{2,57.6}=11.33$	****
Time	$F_{8,46.9}=5.34$	****	$F_{8,53.2}=7.59$	****	$F_{9,36.5}=2.32$	*
HGM Class * Time	$F_{16,73.6}=1.74$	ns	$F_{16,83.2}=1.22$	ns	$F_{18,58.5}=1.56$	ns
Riverine vs. Flat	t=1.18	ns	t=0.98	ns	t=0.31	ns
Riverine vs. Flat-Riv	t=0.22	ns	t=2.98	**	t=4.08	****
Flat vs. Flat-Riv	t=0.85	ns	t=2.09	*	t=4.37	****

ns not significant, * $p<0.05$, ** $p<0.01$, *** $p<0.001$, **** $p<0.0001$

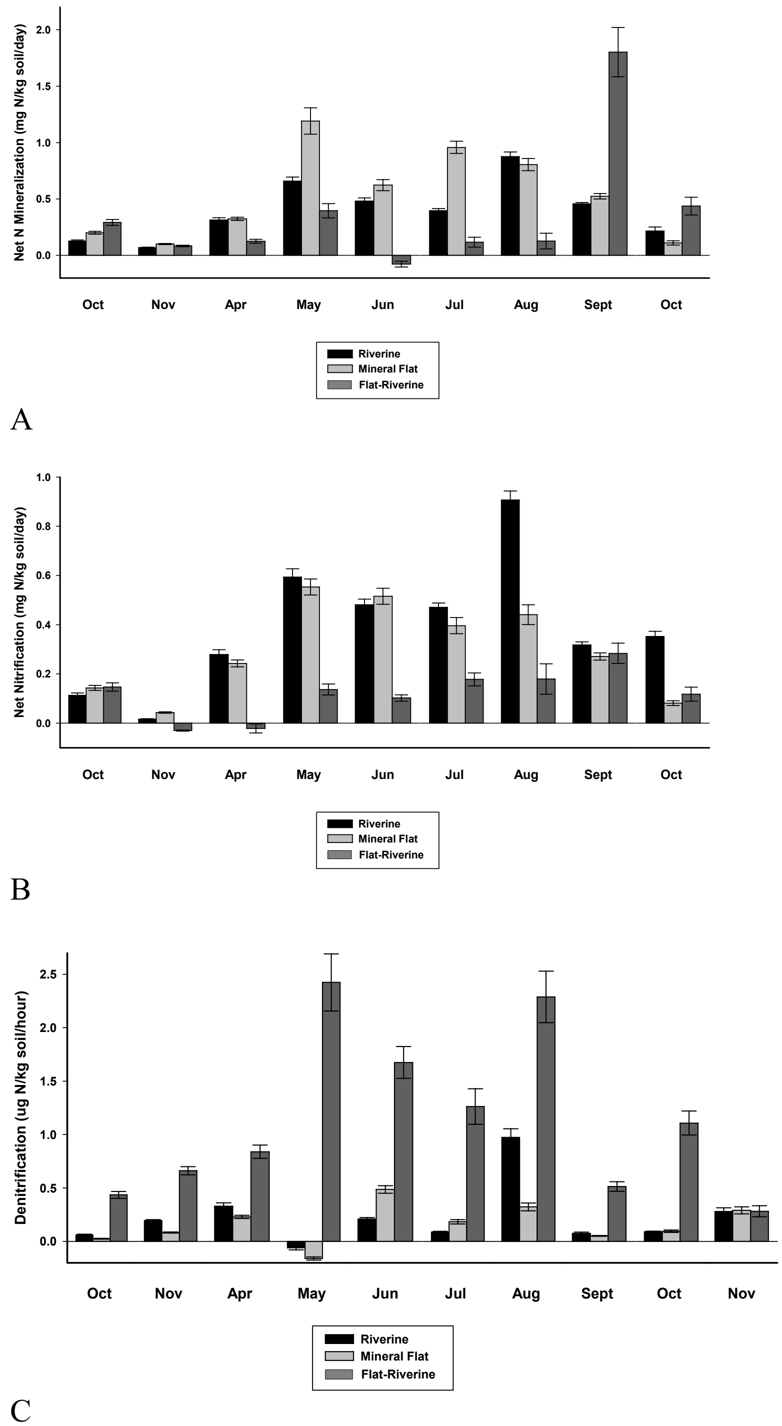
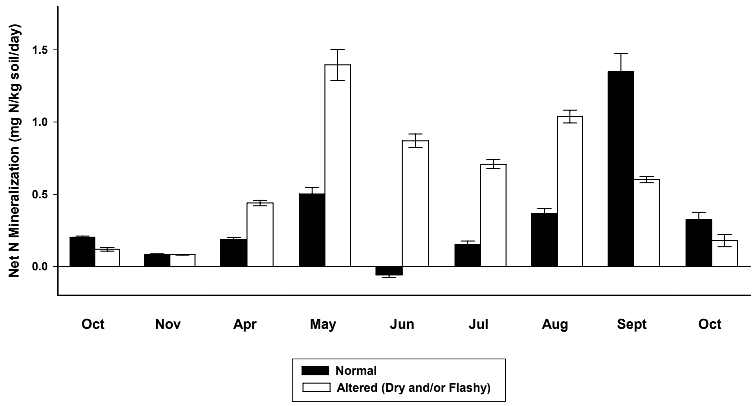


Figure 1.2. Mean rates of net N mineralization (A), net nitrification (B) and denitrification (C) in each HGM class per month. Error bars represent standard errors for each HGM class.

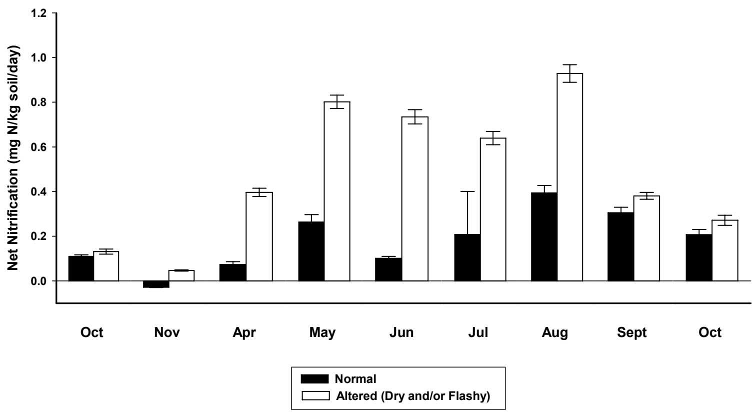
Table 1.3. Differences in N cycling rates among 12 wetlands classified according to hydrological patterns. Long-term measurements of water table levels were used to classify wetlands as having either normal or altered (dry and/or flashy) hydrology. Statistical results are from repeat measures ANOVAs using hydrology class as the fixed factor, site as the random factor, and time as the between subjects factor.

Factor	***N Mineralization***		***Nitrification***		***Denitrification***	
Hydrology Class (Normal vs. Altered)	$F_{1,52.9}$=1.79	ns	$F_{1,58.9}$=10.63	**	$F_{1,42.7}$=7.00	*
Time	$F_{8,40.5}$=5.71	****	$F_{8,45.9}$=7.86	****	$F_{9,25.6}$=1.47	ns
Hydrology Class * Time	$F_{8,40.5}$=2.59	*	$F_{8,45.9}$=2.01	ns	$F_{9,25.6}$=0.96	ns

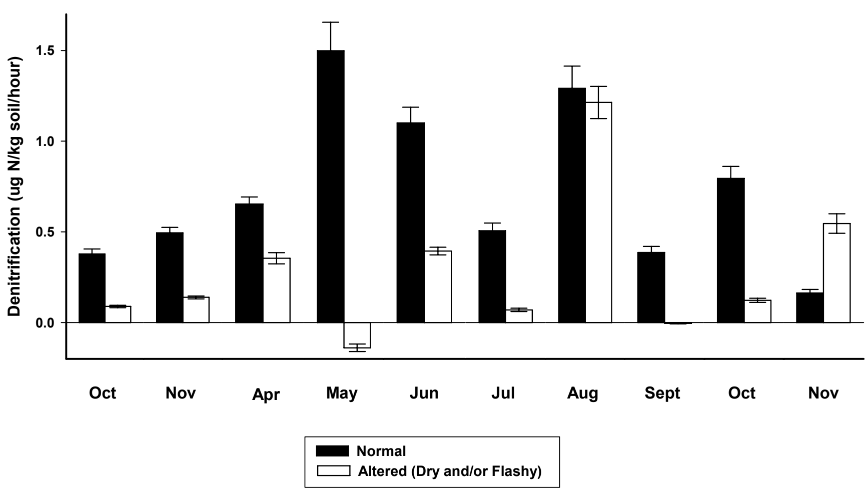
ns not significant, * $p<0.05$, ** $p<0.01$, *** $p<0.001$, **** $p<0.0001$



A



B



C

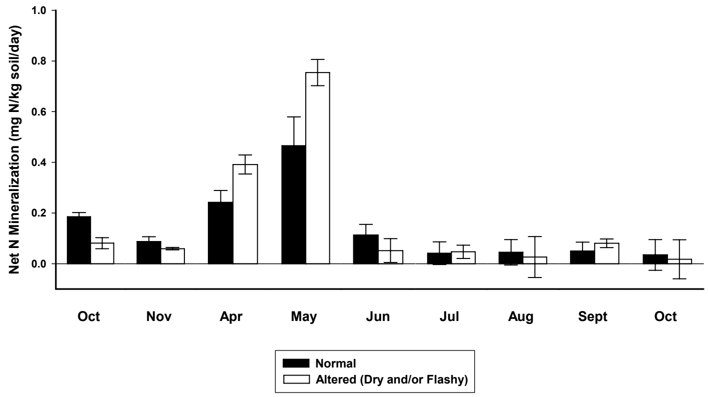
Figure 1.3. Mean rates of net N mineralization (A), net nitrification (B), and denitrification (C) in wetlands with normal versus altered hydrology. Two of the original 14 sites were not used in this analysis because there were no hydrological data on which to base an *a posteriori* designation. Error bars represent standard errors for both hydrological classes.

hydrology had higher rates of denitrification and lower rates of net nitrification than sites with dry and/or flashy hydrology (Table 1.3, Figures 1.3b-c). Rates of net nitrification and net N mineralization varied significantly over time, and the temporal patterns of net N mineralization rates differed (significant time x class interactions) between the two hydrological classes (Table 1.3). In contrast, denitrification rates did not show significant differences over time (Table 1.3).

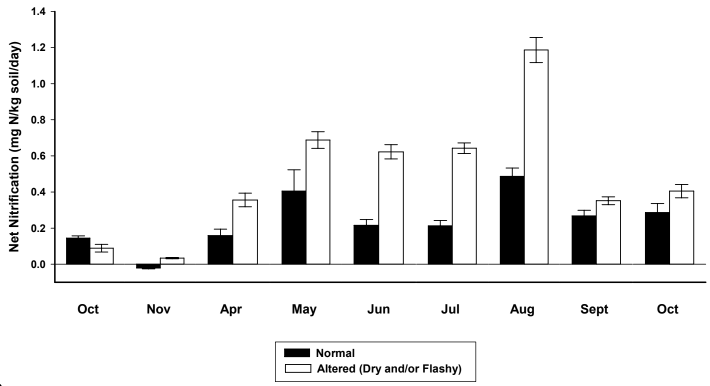
A priori vs. A posteriori Designation of Reference Standard Sites

Rates of denitrification were not significantly different between reference standard and non-reference (*a priori* designation) sites in the riverine and flat-riverine HGM classes (Table 1.4). There were significant differences in denitrification rates between reference standard and non-reference sites in the mineral flat class (Table 1.4). However, contrary to the assumed pattern (reference sites have the highest level of function), the reference standard sites had *lower* rates of denitrification than the non-reference sites (Table 1.4). There were no significant differences between reference standard and non-reference sites in net nitrification or net N mineralization rates in any of the three HGM classes (Table 1.4).

Reference standard sites did not significantly differ from non-reference sites in rankings of denitrification, net nitrification, or net N mineralization rates when tested over all HGM classes together ($S=44.0$, $p=0.417$; Table 1.5). Ranks of positive functions (net N mineralization and denitrification) were not significantly different between reference and non-reference sites ($S=47.0$, $p=0.240$; $S=44.0$, $p=0.438$, respectively). Ranks of the negative function (net nitrification) also were not significantly different



A



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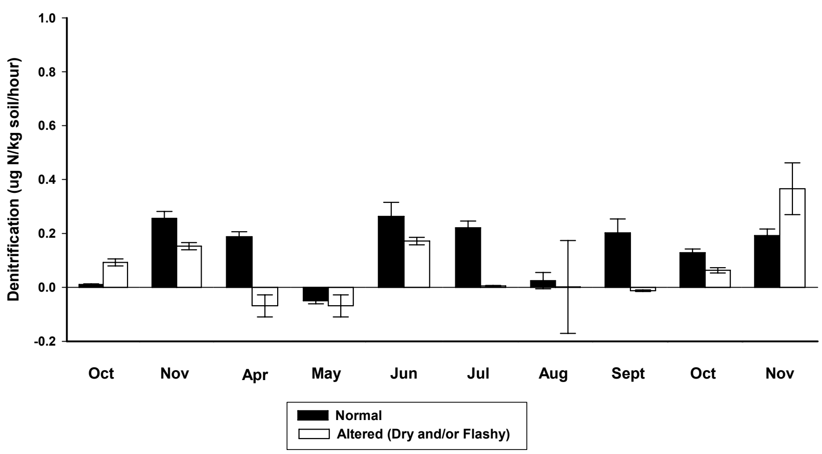

C

Figure 1.4. Sites in the riverine class were *a posteriori* reclassified according to normal or dry and/or flashy hydrological pattern. Only the riverine class sites had both normal and altered sites (the mineral flat class only had altered sites and the flat-riverine class only had normal sites). Rates of net N mineralization (A), net nitrification (B), and denitrification (C) are presented. Error bars represent standard errors for both hydrological classes.

Table 1.4. Differences in N cycling rates between *a priori* classified reference standard and non-reference wetlands in each of the three HGM classes. Statistical results are from repeat measures ANOVAs using *a priori* classification as the fixed factor, site as the random factor, and time as the between subjects factor.

Factor	***N Mineralization***		***Nitrification***		***Denitrification***	
Riverine Ref. vs. Non-Ref.	$F_{1,22.9}$=0.06	ns	$F_{1,24.3}$=0.10	ns	$F_{1,4.69}$=0.01	ns
Time	$F_{8,151}$=4.10	***	$F_{8,151}$=6.57	****	$F_{9,12.5}$=2.87	**
Riverine * Time	$F_{8,151}$=0.77	ns	$F_{8,151}$=1.14	ns	$F_{9,12.5}$=1.27	ns
Mineral Flat Ref. vs. Non-Ref.	$F_{1,24.2}$=1.98	ns	$F_{1,22.2}$=0.46	ns	$F_{1,22.9}$=18.10	***
Time	$F_{8,140}$=1.58	ns	$F_{8,139}$=2.31	*	$F_{9,15}$=2.05	*
Flat * Time	$F_{8,140}$=0.99	ns	$F_{8,139}$=0.76	ns	$F_{9,15}$=4.15	****
Flat-Riverine Ref. vs. Non-Ref.	$F_{1,13.3}$= 1.94	ns	$F_{1,16.1}$=2.65	ns	$F_{1,15.6}$=.01	ns
Time	$F_{8,89.7}$=1.22	ns	$F_{8,92.7}$=1.80	ns	$F_{9,128}$=1.69	ns
Flat-Riv * Time	$F_{8,89.7}$=1.01	ns	$F_{8,92.7}$=2.98	**	$F_{9,128}$=0.57	ns

ns not significant, * p<0.05, ** p<0.01, *** p<0.001, **** p<0.0001

Table 1.5. Ranks of nitrogen cycling functions for sites arranged by *a priori* designation of reference standard and non-reference sites according to criteria illustrated in Table 1.1. Ranks of all three N cycling processes are averaged for each site in the last column. By definition, reference standard sites should have higher ranks of positive functions, such as nitrogen mineralization and denitrification, and lower ranks of the negative function nitrification.

Site	*HGM Class*	*A Priori Designation*	*N Min. Rank*	*Nitrification Rank*	*Denitrification Rank*	*Mean Rank*
ML	**Riverine**	**Reference**	**9**	**7**	**7**	**7.67**
GR	**Riverine**	**Reference**	**8**	**9**	**8**	**8.33**
EZ	Riverine	Non-reference	4	14	9	9
OR	Riverine	Non-reference	6	10	11	9
MW	Riverine	Non-reference	13	5	12	10
M5f	**Mineral Flat**	**Reference**	**5**	**12**	**14**	**10.33**
BB	**Mineral Flat**	**Reference**	**11**	**3**	**13**	**9**
M6	Mineral Flat	Non-reference	1	11	4	5.33
PL	Mineral Flat	Non-reference	3	13	5	7
YK	Mineral Flat	Non-reference	10	4	6	6.67
M5 fr	**Flat-Riv**	**Reference**	**14**	**1**	**2**	**5.67**

CH	Flat-Riv	Non-reference	7	8	10	8.33
PA	Flat-Riv	Non-reference	12	2	3	5.67
RL	Flat-Riv	Non-reference	2	6	1	3

between reference standard and non-reference sites (S=32.0, p=0.519).

The reclassification of sites based on observed hydrology (Table 1.1) resulted in a complete reorganization of the set of sites. Only one HGM class, riverine, included both normal and altered sites; the mineral flat class included only altered sites and the flat-riverine class included only normal sites (Table 1.1). Within the riverine class rates of net N mineralization were significantly different between sites with normal versus altered hydrology ($F_{1,25}$=4.96, p=0.0352; Figure 1.4a). Rates of net nitrification were marginally significantly higher in altered sites compared with normal sites ($F_{1,25.4}$=3.83, p=0.0614; Figure 1.4b), and rates of denitrification were not significantly different between normal and altered sites ($F_{1,23.9}$=0.60, p=0.4460; Figure 1.4c). Denitrification rates were uniformly low within the riverine sites.

Sites with normal hydrology did not differ significantly from altered sites in the averaged ranks of the three nitrogen cycling rates (S=28.0, p=0.509; Table 1.6). Rankings of net nitrification rates were marginally significantly higher in normal sites (S=21.0, p=0.073). However, rankings of net N mineralization and denitrification did not differ significantly between the two hydrological groups of sites (S=40.0, p=0.268; S=27.0, p=0.432).

Only one site, GR, was classified as a reference standard site using both the *a priori* and *a posteriori* reference site criteria (Table 1.7). Notably, 3 out of 4 of the sites which were *a priori* designated as reference standard sites on the basis of apparent minimal human disturbance turned out to have altered hydrology (one additional reference standard site, M5fr, did not have adequate hydrological data to make an *a*

Table 1.6. Ranks of nitrogen cycling functions for sites arranged by *a posteriori* designation according to long-term hydrological data. Two of the original 14 sites were not used in this analysis because there were no hydrological data on which to base an a posteriori designation. Ranks of all three nitrogen cycling processes are averaged for each site in the last column.

Site	***A Posteriori Designation***	***N Min Rank***	***Nitrification Rank***	***Denitrification Rank***	***Mean Rank***
GR	**Normal**	**8**	**9**	**8**	**8.33**
MW	**Normal**	**13**	**5**	**12**	**10**
CH	**Normal**	**7**	**8**	**10**	**8.33**
PA	**Normal**	**12**	**2**	**3**	**5.67**
RL	**Normal**	**2**	**6**	**1**	**3**
ML	Altered	9	7	7	7.67
EZ	Altered	4	14	9	9
OR	Altered	6	10	11	9
M5f	Altered	5	12	14	10.33
BB	Altered	11	3	13	9
M6	Altered	1	11	4	5.33
PL	Altered	3	13	5	7

Table 1.7. Overlap between *a priori* and *a posteriori* designations of reference standard and non-reference sites. Two of the original 14 sites were not used in this analysis because there were no hydrological data on which to base an *a posteriori* designation.

	A Priori Reference Standard (# of sites)	***A Priori Non-reference (# of sites)***
***A Posteriori* Normal (# of sites)**	1	4
***A Posteriori* Altered (# of sites)**	3	4

posteriori designation). Conversely, four sites initially designated as non-reference, because of dense surrounding human population density and/or other evidence of human disturbance, had normal, non-flashy hydrology (Table 1.7).

Discussion

Neither the HGM classification nor the designation of reference standard sites based on *a priori* criteria of apparent minimum human disturbance were effective predictors of N cycling functions in these urban wetlands. The classification system did distinguish the flat-riverine class from the other classes, but it did not separate the riverine and mineral flat classes in terms of levels of N cycling function (Table 1.2, Figures 1.2a-c). A classification system should distinguish all three classes in order to be effectively used for management purposes. This is in accordance with the findings of Ehrenfeld et al. (2003) and Ehrenfeld (2005) in a partially overlapping set of sites in urban/suburban northeastern New Jersey. In those previous studies the flat-riverine class was the only HGM class of those tested that was distinguishable in terms of hydrology and vegetation patterns, mostly because those sites were, as a group, wetter than the other HGM classes. Indeed, despite differences in the apparent amount of human disturbance, all of the flat-riverine sites had normal hydrology, unlike the two other HGM classes. The mixture of sites with normal and altered hydrology within the riverine and mineral flat HGM classes (Table 1.1) resulted in too much hydrological variability for those classes to cluster well for rates of N cycling processes which are influenced by hydrology. The fact that HGM classification, which is based on hydrological inputs and hydrodynamics, cannot separate sites by hydrology speaks to the significance and extent of urban impacts on hydrology. This study demonstrates that urban influence extends to ecological functions which are, in turn, influenced by hydrological patterns. Whether or not wetlands had normal or altered hydrology, as determined from long-term water table measurements, was a more reliable indicator of N cycling function, regardless of HGM class (Table 1.3, Figures 1.3a-c). This suggests that in an urban/suburban region, hydrologic disturbance due to the urban condition is a better descriptor of N cycling function than a hypothesized characterization of hydrological patterns based on natural geomorphic setting.

The wetlands which fall into the flat-riverine class, however, remain wet despite exposure to the same types of urban stressors, including high population densities at the watershed scale and symptoms of urban hydrology such as noticeably downcut stream banks. I speculate that because the flat-riverine sites have more sources of wetness (precipitation and overbank riverine inputs) than either of the other two classes, there was a greater likelihood of both receiving and retaining water in this class. Piezometer data from a previous study (Ehrenfeld et al. 2003) suggested that there is relatively little groundwater discharge to the surface in these sites. This would suggest that saturated conditions are more dependent on temporally-variable precipitation and flooding events, rather than the steady delivery of water to the surface from regional groundwater discharge. In this case, having both sources of water would produce more wetness than either precipitation (as in the mineral flat) or overbank flooding (as in the riverine) sites alone. Thus the natural hydrogeomorphic setting of these sites may be driving wetter patterns in the flat-riverine sites. Other factors which may be responsible for wetter conditions in the flat-riverine sites include large wetland areas for three of the four sites, patterns of regional groundwater discharge, or a possible sampling effect. Wet conditions in two of the flat-riverine sites (RL and M5fr) may also be driven by much higher organic matter content at these two sites relative to the other 12 sites used in this study (see Chapter 2/Stander and Ehrenfeld submitted for analysis and discussion of soil properties).

The result of wet hydrology in these sites is characteristically lower rates of net nitrification and higher rates of denitrification (Figures 1.2b, c), and therefore, presumably higher N retention. For at least two of the flat-riverine sites (RL and M5fr) there were also important differences in soil properties that might explain some of the patterns in denitrification. I explore soil patterns and their relationship to denitrification rates in detail elsewhere (Chapter 2/Stander and Ehrenfeld submitted).

I also found that another component of HGM functional assessment, the *a priori* designation of reference standard sites using criteria of apparent human disturbance, did not work for these sites. Criteria I hypothesized would predict less alteration in an urban setting (i.e., size, surrounding human population density, and management) coupled with my qualitative assessment of alteration using best professional judgment did not select wetlands which were different from *a priori*-designated non-reference wetlands in N cycling rates (Tables 1.4 and 1.5). The only significant difference between reference standard and non-reference wetlands using *a priori* designation was for rates of denitrification in the mineral flat class. However, denitrification rates were *lower* in the reference standard sites compared to the non-reference sites, contrary to the assumptions of the HGM rapid assessment method. These results strongly suggest that at least in urbanized regions, it cannot be assumed that reference standard sites identified through visual assessment of condition have higher or better levels of wetland function than non-reference sites. I suggest that the use of *a priori* designation of reference standard sites needs to be quantitatively tested with detailed measurements of particular wetland functions in the landscapes for which they are to be used in wetland assessment.

A posteriori designation of reference standard sites using a long-term record of water table levels (i.e., normal versus altered sites) in general was more successful than *a priori* designation, (Tables 1.3 and 1.6; Figures 1.3a-c). However, when normal sites were compared to altered sites just within the riverine class, rates of denitrification were not significantly different (Figure 1.4c). These results suggest that controls on denitrification may be more complex, and less immediately responsive to hydrological condition, than controls on nitrification. Nitrification is carried out by a small group of microorganisms (primarily autotrophs in the genera *Nitrosomonas* and *Nitrobacter*) which are well known to have fairly specific requirements of oxygen availability, pH and temperature for activity. In contrast, denitrification is carried out by a larger group of unrelated bacteria, and a variety of microsites within the soil can provide adequate conditions for this process. The difference in sensitivity of nitrification and denitrification to environmental conditions suggests that wetland functions may differ in their performance levels even within reference standard sites, however established. This result again emphasizes the need for detailed quantitative measurements of processes in a population of wetlands to calibrate assessment models proposed for regional use in management. Another possible explanation is that a categorical description of hydrology may be unable to fully capture the variability in wetland functions which are influenced by hydrological processes. Elsewhere I explore a characterization of hydrology using a regression-based continuum of normal to altered conditions as a means of predicting nitrogen cycling processes (Chapter 2/Stander and Ehrenfeld submitted).

It is also possible that there is not a direct relationship between alteration and function, meaning that I should not necessarily expect to see higher rates of nitrification and lower rates of denitrification in more altered sites than less altered sites, whether alteration is assessed according to *a priori* or *a posteriori* criteria. Hruby (2001) found this to be true for forty-four wetlands in four HGM classes in Washington State which were rapidly assessed for 15 functions, including “Potential for removing nutrients (particularly phosphorus and nitrogen)”. Unaltered sites performed functions that spanned the range of the seven possible ratings in all four HGM classes, calling into question the underlying concept that unaltered wetlands perform functions at a “characteristic” level for an HGM class in a particular region. A lack of a significant difference in denitrification rates between normal and altered sites in the riverine class may be consistent with Hruby’s (2001) findings. It would also be consistent with the idea of the Tolstoy effect (Ehrenfeld et al. 2003, Ehrenfeld 2005) which compares the idiosyncratic nature of urban wetland hydrology to Tolstoy’s description of families in the novel *Anna Karenina*: “Happy families are all alike; every unhappy family is unhappy in its own way” (Tolstoy 1973). This concept suggests that due to the idiosyncratic nature of historical and more recent urban disturbances in urban/suburban wetland fragments, altered wetlands may be performing levels of N cycling functions that span the range of functional levels found in their HGM classes in this region (Whittecar and Daniels 1999, Ehrenfeld et al. 2003, Ehrenfeld 2004, Ehrenfeld 2005). This means that some altered wetlands may have high levels of function that overlap with functional levels in wetlands with normal hydrology.

Another problem with rapid assessment methods based on assumed relationships between HGM or disturbance classifications and function is that process rates vary over time, and the relative rates of processes among wetlands in different classes may change over time. This was clearly demonstrated in this study: net N mineralization and denitrification rates were higher in altered wetlands during some months (Figures 1.3a, c) and nitrification rates were lower in altered wetlands during some months (Figure 1.3b). The significant changes over time in all three N cycling functions suggest that it may not be legitimate to assess these functions rapidly. Results of rapid assessment would likely vary depending on what month of the year they were conducted.

My data support the conclusion that at least in urban regions, N retention function is strongly linked to hydrology, and that the hydrological determinants of this function cannot be deduced from visual assessment of the site and consideration of the land use and population density of the surrounding landscape. The lack of correspondence of normal hydrograph patterns and my *a priori* designation of least altered wetlands was striking (Table 1.7). I suggest that the establishment of reference standard sites in urban areas, at least for N cycling functions, must be based on sufficient hydrological data to judge the annual pattern of water level movements and the temporal variability of that pattern. Therefore, I recommend that at least in urban/suburban regions, a functional assessment of N cycling function should include the measurement of water table levels for at least one hydrologic year. This recommendation echoes that of Cole (2006), who made a similar recommendation based on a review of functional assessment conducted in four HGM classes in central Pennsylvania, intermontane prairie pothole wetlands in the Rocky Mountains, riverine wetlands in western Tennessee, and floodplain wetlands in a

Mississippi River alluvial valley; none of these regions are very urban compared to northeastern New Jersey. This underscores the need to more quantitatively test the assumption that HGM effectively predicts hydrologically-driven functions in non-urban landscapes as well as urban ones. To date there are few studies that evaluate the validity of this assumption using actual measurements of wetland functions in non-urban landscapes (but see Findlay et al. 2002). While I focused specifically on N retention processes as prominent wetland functions that are frequently used to justify wetland conservation and restoration, I suspect that other functions also will not vary simply with visually-determined assessments of disturbance and will require data acquisition to establish a reference condition for assessment purposes.

This recommendation, of course, implies a slowing of the assessment and permitting processes, which runs counter to the current mandate of regulatory agencies. Carletti et al. (2004) also address this issue, stating that time constraints lead to tradeoffs in the quality of the science which is used to make policy and management decisions. Cole (2006) suggests that it may be justifiable to use rapid assessments when the policy emphasis is on maintaining wetland area, but because the policy is specifically focused on protecting and replacing wetland function, a rapid assessment methodology is not appropriate. My findings support Cole's assertion, as a rapid assessment technique predicated on HGM classification is fundamentally flawed in the urban/suburban landscape of northeastern New Jersey and is likely to be inappropriate in other urbanized regions. I urge that the criteria for establishing reference conditions for other functions, in both urbanized and non-urban landscapes, be more critically examined and tested with quantitative data.

In summary, HGM classification and *a priori* designation of reference standard sites using a visual assessment of alteration, two major components of the HGM rapid assessment methodology, were not effective in predicting rates of nitrate production (nitrification) and removal (denitrification) in urban wetlands in northeastern New Jersey. An alternative designation of reference standard sites using *a posteriori* criteria of normal versus altered hydrology was more successful in predicting nitrification and denitrification rates. My results suggest that it is necessary to characterize hydrology using at least one water year of water table measurements in order to identify reference standard sites in urban landscapes. I recommend more quantitative evaluation of the basic assumptions of the HGM method in assessing a range of wetland functions in both urban and non-urban landscapes.

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CHAPTER 2

Rapid assessment of urban wetlands:

Functional assessment model development and evaluation

Introduction

The assessment of wetland functions is central to the implementation of several wetland management policies. Both federal and state regulatory agencies have emphasized the need for science-based methodologies for assessing functions. Such assessments are necessary under Clean Water Act Section 404 rules, which require the replacement of functions lost when wetlands are damaged or destroyed. Functional assessments are equally necessary to determine the success of wetlands specifically designed for the purpose of environmental remediation, such as created wetlands for the management of nutrient-enriched waters. The Hydrogeomorphic (HGM) functional assessment method developed by the US Army Corps of Engineers is currently the most widely adopted approach to functional assessment (Brinson 1993, Brinson et al. 1995, Smith et al. 1995). This method is based on the development of quantitative models, in which rapidly-measured components of wetland structure are arithmetically combined to produce a numeric estimate of wetland function, based on general scientific knowledge of the relationships between ecosystem structure and function. However, there have been very few specific tests of the validity of these models in which field measurements of function are compared with model estimates (Hruby 1999, Cole 2006). I have carried out such a test by comparing HGM models of nutrient removal, a critical water quality protection function, to field data on nitrogen (N) cycling and retention in a set of 14 forested wetlands.

The HGM assessment method is a major advance in the development of assessment methodologies, as it utilizes an ecosystem-level approach, incorporates landscape and site-specific components of hydrology as the primary drivers of wetland structure and function, and provides specific rationales for integrating multiple measures of wetland structure into functional assessment (Hauer and Smith 1998). Despite these advances the HGM functional assessment method has been the subject of much debate in the wetland scientific community (Hruby 1999, Hruby 2001, Arp and Cooper 2004, Cole 2002, 2006, and others). Much of the controversy centers on the justification for relating measurements derived from the brief, limited sampling obligatory within the regulatory arena (Fennessy et al. 2004) to complex functions (Hruby 1999, Cole 2006). Variables assessed by qualitative observations, such as amount of hydrological disturbance from ditching, evidence of flooding, or evidence of water table fluctuation, tend to vary among observers (Whigham et al. 1999). In addition, simple structural measurements (e.g., tree basal area, percent cover of herbaceous plants, depth of the litter layer) are combined to assess complex processes such as nutrient cycling and wetland hydrology, and the relationships between these measures of structure and function are unproven (Cole 2002, 2006).

Another criticism of the HGM rapid assessment methodology is that the functions are defined too broadly to be meaningful. For example, indefinite numbers and types of biogeochemical functions are potentially lumped together into one functional capacity index titled ‘Maintain characteristic nutrient removal and elemental cycling processes’ (Rheinhardt et al. 1997), ‘Remove elements and compounds’ (Smith and Klimas 2002), or ‘Biogeochemical cycling’ (Rheinhardt et al. 1999), to name a few. Structural variables representing vegetation, hydrology, and soil properties are included in these functions in order to rapidly assess the capability of wetlands to carry out a range of biogeochemical functions. Because different nutrients are removed and/or retained through very different biogeochemical mechanisms (Kadlec and Knight 1996, Mitsch and Gosselink 2000), a single expression may not adequately capture the function of a given wetland with respect to different elements and compounds. Moreover, variation among wetlands in process rates may not be well correlated with broad characterizations of structure (Cole 2006).

I have focused my study on N cycling as a group of functions that are prominent in all aspects of wetland management. Wetlands are widely created and restored for the purpose of reducing nitrate (NO_3^-) transfer from uplands to surface waters in recognition of the linkage between excess NO_3^- and the degradation of both inland and coastal waters (Lowrance et al. 1997, Mitsch et al. 2001). The N retention function of wetlands is similarly a prominent component in public controversies over wetland destruction for development and highway construction.

N cycling processes are also excellent functions for testing the validity of predictive models based on structure because there is a sophisticated understanding of the biological, physical and chemical mechanisms underlying N cycling process rates. Soil denitrification, a process by which the mobile anion NO_3^- is converted to nitrogen gases (NO, N_2O and N_2), is controlled by three main factors (Groffman and Tiedje 1989 and 1991, Brettar and Hofle 2002, Boyer et al. 2006). These include the concentration of NO_3^-, which functions as an electron acceptor; the concentration of metabolizable organic carbon, the source of electrons and energy to the denitrifying bacteria; and the absence or near-absence of O_2, because denitrification is an anaerobic metabolic process. The supply of NO_3^- may be endogenous, a result of nitrification within the soil in close proximity to the sites of denitrification, and/or may be exogenous, supplied by nitrate-enriched surface or ground waters entering the site (McClain et al. 2003). Nitrification rates reflect the supply of ammonium (NH_4^+) from N mineralization, the presence of oxic conditions, and moderate pH values, as nitrifying bacteria are restricted to these conditions (Schlesinger 1997, Fenn et al. 2005). Typically denitrification rates are optimized under alternating wet and dry conditions because these conditions allow for the coupling of nitrification and denitrification (Boyer et al. 2006, Robertson and Groffman 2007).

Because of the well-described mechanistic understanding of these processes, I hypothesized that readily-observable properties of soil, vegetation, and hydrology could be associated with the specific requirements of these biogeochemical processes, and therefore provide a means of developing clearly justified and testable assessment models. Measurements of both net nitrification and denitrification rates are time-consuming and require trained laboratory personnel, and thus cannot be used in the rapid assessments required for regulation and management. I propose that quantitative assessment models built from structural indicators that are clearly related to the factors mechanistically linked to N processes can be developed, and that these models will better describe the wetland function of N removal than models based on general concepts of “nutrient removal” or “element cycling.” For example, a number of hydric soils indicators, commonly measured as part of wetland delineations (USDA, NRCS 2003, Mid-Atlantic Hydric Soils Committee 2004), may serve as rapidly-measured indicators of oxic or sub-oxic conditions that influence nitrification and denitrification rates. If verified, the results will demonstrate that quantitative models based on structural, readily-observed wetland characteristics can be developed to describe wetland functions, but that these models need to be based on detailed mechanistic understanding of the underlying ecological processes, and therefore should be defined narrowly rather than broadly.

Wetlands in urbanized regions represent a unique challenge because high variability among sites in both exogenous sources of NO_3^- (e.g., presence of stormwater inputs, polluted groundwater inputs) and endogenous sources due to the urban stream syndrome (e.g., incised streambanks, lowered water tables, reduced watershed water storage, and increased surface water discharge during storm events (Meyer et al. 2005, Hollis 1975, Booth 1990, Owen 1995, Stromberg et al. 1996, Booth and Jackson 1997, Moscrip and Montgomery 1997, Groffman et al. 2002, Im et al. 2003)) are likely to produce a wide range of actual N cycling rates. Previous studies of riparian wetlands in urbanized areas have documented higher rates of net N mineralization and denitrification potential (Hanson et al. 1994, Groffman et al. 2002, Groffman et al. 2003) and higher rates of net nitrification and lower rates of denitrification (Chapter 1/Stander and Ehrenfeld submitted) as compared to riparian wetlands in less urban settings.

In this study, I 1) compare predictions from existing assessment models in the current HGM literature against measured net nitrification and denitrification rates in a set of wetlands located within a large urban region (New York metropolitan area), and 2) propose new rapid assessment models based on mechanistic relationships between structural characteristics and known controls on N cycling rates. I further test the suitability of basing assessment models solely on structural variables that can be rapidly measured and that are assumed to be indicators of environmental condition (“rapid” variables) versus models incorporating variables based on more detailed actual measurements (“non-rapid” variables).

Methods

Study Sites

Fourteen palustrine, forested wetland sites were selected in northeastern New Jersey. All sites are located within the Piedmont physiographic province. This places the sites in the most urbanized region of the state and within the third largest urban agglomeration in the world with a population of 18.7 million (UN 2005). Population densities range from 177 to 3,585 persons km^{-2}, and road densities range from 4.6 to 33.1 km km^{-2} in the watersheds containing the 14 sites. Site selection and location are more fully described in Chapter 1/Stander and Ehrenfeld (submitted). Sites were chosen to represent three HGM classes, riverine, mineral flat, and mineral flat-riverine (see Chapter 1/Stander and Ehrenfeld (submitted) for a description of these classes in the same set of sites). All sites had a mature canopy dominated by red maple (*Acer rubrum* L.) and plant communities as described by Ehrenfeld (2005).

Hydrology

Water table dynamics were measured in 12 of the 14 sites to determine the presence of oxic, sub-oxic, or anoxic conditions. Water table measurements were used to generate “non-rapid” indicators of controlling factors on nitrogen cycling process rates. These 12 sites were equipped with an automatically recording well (hereafter, autowell) (either a WL-40 or an Ecotone model, Remote Data Systems, Inc., Whiteville, NC). Details on location, installation, and use of autowells are presented in Chapter 1/Stander and Ehrenfeld (submitted). Due to problems with vandalism, wells had to be removed from two of the sites (YK and M5fr). Thus, there is a long-term hydrological record for only 12 of the 14 sites used in this study.

In Situ Soil Nitrogen Cycling Rates

Rates of net N mineralization, net nitrification, and denitrification were measured in all 14 sites to quantitatively determine levels of N cycling functions and their seasonal variations over a year's period. The intact static core technique developed by Robertson et al. (1999) was used to measure *in situ* rates of net N mineralization and net nitrification during month-long field incubations. The acetylene block technique (Tiedje et al. 1989) was used to measure denitrification rates on the same cores in six-hour laboratory incubations. Soils were measured for bulk density and moisture content and were extracted for inorganic nitrogen using a 2 M KCl solution. KCl extracts were analyzed colorimetrically for nitrate and ammonium concentrations. See Chapter 1/Stander and Ehrenfeld (submitted) for a more detailed description of these field and laboratory methods.

Quantitative Soil Description

Soils were analyzed quantitatively for various descriptive soil properties. A sample of the top ten cm of soil was taken from 12 sampling locations per site and bulked for each site. Soil samples were analyzed using standard procedures at the Rutgers Soil Testing Laboratory for pH, estimated CEC and cation saturation, soluble salts, organic matter content, percentages of sand, silt, and clay, soil textural class, extractable NO_3^- and NH_4^+, and total Kjeldahl nitrogen.

Structural Indicators Used in HGM Models

I followed the guidelines and procedures developed by Rheinhardt *et al.* (1997, 1999) to collect data on hydrological, soil, and vegetation variables used in existing assessment models. Site assessments took approximately 2.5-3 hours each; two sites were assessed per day. Methods used to measure vegetation structural variables were modified from Rheinhardt et al. (1997, 1999). Three circular plots of 10 m radius at each site were assessed for vegetation and soil structural variables. Two of the plots were located at each end of the transect used for the hydrological and N cycling measurements described above. The center point of the third plot was located 30 m from the center points of the other two plots in a triangular formation. All trees >10 cm diameter at breast height (dbh) were counted by species, and dbh was measured for each tree. Tree basal area was calculated from dbh measurements. All snags were counted, and coarse woody debris was counted by size class (small = >1 m and <5 m in length, large = ≥5 m in length). All shrubs within a five m nested circular plot within the main plot were counted by species. Four 1 m^2 quadrats were located at random within each 10 m radius plot and measured for percent cover of herbaceous plants, seedlings, litter, and fine woody debris (>2.5 cm diameter). Maximum herbaceous vegetation height was recorded for each quadrat. Soil variables were also measured in the 1 m^2 quadrats. Thickness of the litter layer was measured in two locations in each quadrat and averaged to generate one measurement per quadrat. The depth of the organic horizon was recorded, as was the presence/absence and depth of an A horizon with Munsell value ≤3. Soil matrix color of the B horizon was determined in one quadrat per plot, and presence/absence of a B horizon with chroma ≤2 (signifying reducing conditions) was noted for the remaining three quadrats. The presence and intensity of redoximorphic features (primarily mottling) was scored for each quadrat on a scale of 0 to 2; 0 indicates absence, 1=low frequency and/or intensity, and 2=high frequency and/or intensity. Presence/absence of channelized streams and cross-floodplain ditches within the study area were noted.

Indicators of N Cycling Functions

In order to develop assessment models specific to N cycling processes, I used the hydrological, N cycling, soil, and vegetation measurements above to define indicator values that could be well justified in terms of the known mechanisms of N cycling processes. These variables, their relationships to known controlling factors, the rationales for choosing them, and a description of how they were calculated are presented in Tables 2.1 and 2.2. In addition to the general knowledge of controls on N cycling functions, I used knowledge of the genesis of soil properties with respect to soil organic matter and oxygenation as described by Vepraskas (1996, 2001).

Data Analyses

Evaluation of Existing HGM Models

I searched the ecological literature and the Army Corps of Engineers website to find existing HGM guidebooks written for HGM classes comparable to the ones used in this study. Within those papers and guidebooks I identified functional models related to N cycling which I could evaluate given the non-rapid and rapid indicators I measured. I found three existing models which fit these criteria.

1. "Maintain characteristic nutrient and elemental cycling processes" (Rheinhardt *et al.* 1997):

Functional Capacity Index (FCI) $=\{(V_{tree} + V_{subc} + V_{sdlg} + [V_{gram} + V_{forb}]/2)/4 + (V_{ltr} + V_{snag} + V_{cwd})/3\}/2$

Table 2.1. Indicator variables used to assess net nitrification in assessment models. "Rapid" and "Non-Rapid" refer to the amount of time and expertise required for measurement. Rationales for soil variables are based on Vepraskas (1996, 2001).

Controlling Factors	*Indicators*	*Rapid vs. Non-Rapid*	*Method of Calculation*	*Justification*
NH_4^+ Availability	**Leaf Litter Thickness (cm)**	Rapid	Averaged two measurements of depth of litter layer per quadrat across all 12 quadrats/site	Litter represents the supply of readily-mineralizable organic nitrogen
NH_4^+ Availability	**Frequency of A Horizon Munsell Value ≤ 3 (%)**	Rapid	Visual assessment of each quadrat; converted to frequency of occurrence for all 12 quadrats/site	Dark A horizons result from high organic matter content, which is a source of readily-mineralizable organic N
NH_4^+ Availability	**% Soil Organic Matter (%)**	Non-Rapid	Composited soil samples from all 12 quadrats/site; analysis at Rutgers Soil Testing Lab	Organic matter in the surface horizons is a supply of readily-mineralizable organic N
NH_4^+ Availability	**N Mineralization Rates (mg N/kg soil/day)**	Non-Rapid	Monthly *in situ* measurements averaged across one year	Actual measurement of NH_4^+ supply rate
NH_4^+ Availability	**Extractable NH_4^+ (mg N/kg soil)**	Non-Rapid	Composited soil samples from all 12 quadrats/site; analysis at Rutgers Soil Testing Lab	Actual measurement of NH_4^+ concentration in the soil solution

Oxic Conditions	**Redoximorphic Feature Frequency (%)**	Rapid	Visual assessment of each quadrat; converted to frequency of occurrence for all 12 quadrats/site	Redox features are produced by alternating oxic/anoxic conditions and fluctuating water tables (Vepraskas 2001)
Oxic Conditions	**Soil Moisture**	Non-Rapid	Measured gravimetrically on monthly basis; averaged over one year	Soil moisture is directly related to saturation
Oxic Conditions	**% Water Table Observations < -30 cm (%)**	Non-Rapid	Percentage of entire record of daily means which are < -30 cm in depth	Direct observation of saturation within the soil zone
Oxic Conditions	**Median Water Table Level (cm)**	Non-Rapid	Median of entire record of water table readings	"
Oxic Conditions	**% Water Table Observations > 0 cm**	Non-Rapid	Percentage of entire record of daily means which are > 0 cm in depth	"
Oxic Conditions	**Flooding Frequency (# flood days/month)**	Non-Rapid	Number of flood days/month averaged over entire record of water table readings	"
Oxic Conditions	**% Crossings at -30 cm (%)**	Non-Rapid	Percentage of entire record in which consecutive daily means crossed the -30 cm line	Direct observation of fluctuating oxic and anoxic conditions

Table 2.2. Indicator variables used to assess denitrification in assessment models. “Rapid” and “Non-Rapid” refer to the amount of time and expertise required for measurement. Rationales for soil variables are based on Vepraskas (1996, 2001).

Controlling Factors	***Indicators***	***Rapid vs. Non-Rapid***	***Method of Calculation***	***Justification***
NO_3^- Availability	**Redoximorphic Feature Frequency (%)**	Rapid	Visual assessment of each quadrat; converted to frequency of occurrence for all 12 quadrats/site	Deposits of oxidized Fe result from periodic oxic conditions, allowing reduced Fe to be re-deposited (Vepraskas 2001); oxic conditions permit nitrification
NO_3^- Availability	**Nitrification Rates (mg N/kg soil/day)**	Non-Rapid	Monthly *in situ* measurements averaged across one year	Actual measurement of net nitrate production rate
NO_3^- Availability	**Extractable NO_3^- (mg N/kg soil)**	Non-Rapid	Composited soil samples from all 12 quadrats/site; analysis at Rutgers Soil Testing Lab	Actual measurement of nitrate concentration in the soil solution
NO_3^- Availability	**% Water Table Observations < -30 cm (%)**	Non-Rapid	Percentage of entire record of daily means which are < -30 cm in depth	Low water tables allow air entry into the soil and should promote nitrification
Soil Organic Carbon	**Leaf Litter Thickness (cm)**	Rapid	Averaged two measurements of depth of litter layer per quadrat across all 12 quadrats/site	Primary supply of readily-mineralizable organic matter and organic carbon leachate to

				the soil
Soil Organic Carbon	**Frequency of A Horizon Munsell Value ≤ 3 (%)**	Rapid	Visual assessment of each quadrat; converted to frequency of occurrence for all 12 quadrats/site	Primary supply of readily-mineralizable organic matter; dark A horizons reflect high organic matter content
Soil Organic Carbon	**% Soil Organic Matter (%)**	Non-Rapid	Composited soil samples from all 12 quadrats/site; analysis at Rutgers Soil Testing Lab	Direct measurement of soil organic carbon
Sub-Oxic Conditions	**Frequency of Matrix Munsell Chroma ≤ 2 (%)**	Rapid	Visual assessment of each quadrat; converted to frequency of occurrence for all 12 quadrats/site	Low chroma reflects dominance of reduction processes in the soil (absence of O_2)
Sub-Oxic Conditions	**Redoximorphic Feature Frequency (%)**	Rapid	Same as above	Depletions produced by periodic reducing (anoxic) conditions
Sub-Oxic Conditions	**Soil Moisture**	Non-Rapid	Measured gravimetrically on monthly basis; averaged over one year	High soil moisture implies lack of O_2 availability
Sub-Oxic Conditions	**Median Water Table Level (cm)**	Non-Rapid	Median of entire record of water table readings	High water tables imply lack of O_2 availability
Sub-Oxic Conditions	**% Water Table Observations > 0 cm (%)**	Non-Rapid	Percentage of entire record of daily means which are > 0 cm in depth	Flooded conditions imply lack of O_2 availability

Sub-Oxic Conditions	**Flooding Frequency (# flood days/month)**	Non-Rapid	Number of flood days/month averaged over entire record of water table readings	Ditto
Sub-Oxic Conditions	**% Crossings at -30 cm (%)**	Non-Rapid	Percentage of entire record in which consecutive daily means crossed the -30 cm line	Direct observation of fluctuating oxic and anoxic conditions
Sub-Oxic Conditions	**% Clay (%)**	Non-Rapid	Composited soil samples from all 12 quadrats/site; analysis at Rutgers Soil Testing Lab	High clay percentage implies high rates of water retention in pores and thus low O_2 availability

where:

V_{tree} = canopy biomass (absolute basal area of trees, m^2 ha^{-1})

V_{subc} = subcanopy biomass (absolute density of subcanopy shrubs and understory trees, # ha^{-1})

V_{forb} = forb biomass (% cover)

V_{gram} = graminoid biomass (% cover)

V_{sdlg} = seedling biomass (% woody seedling cover)

V_{lttr} = litter biomass (thickness of litter layer, cm)

V_{snag} = biomass of standing dead stems (density, # ha^{-1})

V_{cwd} = biomass of downed coarse woody debris (m^3 ha^{-1})

2. "Biogeochemical cycling" (Rheinhardt *et al.* 1999):

$FCI=[(((V_{chan} + V_{buff} + V_{ditc})/3)*((V_{tba} + ((V_{litr} + V_{cwd})/2))/2))]^{1/2}$

where:

V_{chan} = presence/absence of channelized stream

V_{buff} = condition of vegetation buffers

V_{ditc} = presence/absence of cross-floodplain ditches

V_{tba} = stand basal area

V_{litr} = litter cover

V_{cwd} = volume of coarse woody debris

3. "Remove elements and compounds" (Smith and Klimas 2002, hereafter referred to as the Yazoo Basin model):

$FCI= V_{freq} * [(V_{cec} + V_{ohor} + V_{ahor})/3]$

where:

V_{freq} = frequency of flooding

V_{cec} = cation exchange capacity (texture analysis by "feel method", convert to CEC using conversion chart)

V_{ohor} = O horizon thickness (cm)

V_{ahor} = A horizon thickness (cm)

I used data from my rapid assessments to calculate functional capacity index (FCI) scores for N cycling functions using all three models for each of my sites. The flooding frequency variable, V_{freq}, in the Yazoo Basin model (Smith and Klimas 2002) is expressed as overbank flood recurrence interval in years and is calculated from one of several possible data sets, including a nearby USGS stream gage, regional flood frequency curves, hydrological models, or local knowledge (Smith and Klimas 2002). I did not have access to these types of data, so I used data from my non-rapid, long-term water table measurements to generate a flooding frequency variable. Because I could not determine the occurrence of overbank flooding *per se* from autowell data, I calculated V_{freq} as number of flood days month^{-1}. In these cases only the twelve sites which were instrumented with autowells were used in the analysis. Scores for the Yazoo Basin model were calculated three different ways using different indicators for flooding frequency and cation exchange capacity. The first set of scores were calculated using flooding frequency calculated as number of flood days month^{-1} (according to non-rapid hydrological data) and cation exchange capacity as measured by the Rutgers University Soil Testing Laboratory (therefore a non-rapid, laboratory analysis). The second set of Yazoo scores was calculated using flooding frequency again calculated as number of flood days month^{-1} and cation exchange capacity estimated from texture, which was determined by feel and then converted to cation exchange capacity using a conversion chart published in the Yazoo Basin guidebook (Smith and Klimas 2002). The third set of scores was calculated using % of water table observations > 0 cm along with cation exchange capacity measured by the Soil Testing Laboratory. Values for each indicator for all models were scaled from 0 to 1 across sites prior to calculating scores according to Findlay et al. (2002), briefly (observed value – min value)/(max value – min value). This placed all the indicators in the same numerical range so that variables would be equally weighted in addition and multiplication functions.

FCI scores were regressed against net N mineralization, net nitrification, and denitrification rates to test the ability of the models to predict N cycling functions. Tests were performed as a series of simple, one parameter regressions. Tests were performed in Sigma Plot (Systat Software Inc., ver. 9.0). Sites from all three HGM classes were composited for these analyses in order to increase statistical power. Because N mineralization and denitrification are positive functions (i.e., highly functioning sites should have high scores), I expected positive regression slopes between FCI scores and these two functions. While nitrification is necessary to supply the substrate (NO_3^-) for denitrification, I consider nitrification to be a negative function because it produces the most mobile form of N which may be exported out of the system through leaching and thus contribute to eutrophication of coastal waters (Lowrance et al. 1997, Mitsch et al. 2001). High rates of net nitrification are often associated with highly disturbed systems (Hanson et al. 1994, Paul and Clark 1996, Groffman et al. 2002, Faulkner 2005). Slopes of regressions were thus expected to be negative for the relationship between FCI scores and net nitrification (i.e., highly functioning sites should have low rates of net nitrification and thus high scores should correlate with low rates of net nitrification).

Relationship of Indicators to N Cycling Functions

I tested the relationships of the indicators in Tables 2.1 and 2.2 with my measurements of net nitrification and denitrification rates using simple regressions. Tests of significance were performed in Sigma Plot (Systat Software Inc., ver. 9.0). Power analyses were run separately on each regression. When regression relationships were significant, the effects were strong enough to generate high power. In many cases where non-significant results were obtained, the power of the test was low (i.e., the lack of significance may not be a reliable result). Data points which were considered influential according to Cook's Distance and DFFITS tests were removed from the analysis and the correlation was rerun to determine the robustness of the original relationship. Regression equations, r^2 values, and p values are reported from tests which used all sites.

Nitrification I expected to see positive relationships between indicators of NH_4^+ availability and net nitrification rates as more available NH_4^+ should fuel nitrification. I expected to see negative relationships between soil moisture, median water table level, % observations > 0 cm, and flooding frequency with nitrification since higher levels of these indicators suggest sub-oxic or anoxic conditions which should inhibit nitrification. I expected to see positive relationships between % observations < -30 cm and potentially redox frequency and % crossings at -30 cm as high levels of these indicators should suggest oxic conditions, although redox frequency and % crossings at -30 cm may be associated with temporally variable levels of oxia.

Denitrification I expected to see positive relationships between indicators of NO_3^- availability and denitrification rates as higher levels of available NO_3^- should fuel denitrification, and also between indicators of organic carbon supply and denitrification rates for the same reason. I expected to see a positive relationship between redox frequency and denitrification, since mottling is an indicator of alternating oxic and anoxic conditions, and these conditions should promote a coupled relationship between nitrification and denitrification, thus maximizing denitrification rates. I expected to see positive linear or potentially positive unimodal relationships between soil moisture, median water table level, % observations > 0 cm, flooding frequency, % clay, and low chroma frequency with denitrification since very dry and very saturated conditions should inhibit denitrification (nitrification would be inhibited in very saturated conditions, thus producing less fuel for denitrification). I expected to see a negative relationship between % observations < -30 cm and denitrification, because oxic conditions, as indicated by high percentages of observations < -30 cm, should inhibit denitrification.

Development and Evaluation of Mechanistic Models

Lastly I created my own functional capacity indices for nitrification and denitrification (Table 2.3). My models were constructed from combinations of rapid and non-rapid indicators of known controlling factors on rates of these processes (Tables 2.1 and 2.2). Models were not intended to be rigorous, process-based models in the vein of DNDC (Li *et al.* 1992, 1996, 2000) or DAYCENT (Parton *et al.* 1994, Kelly *et al.* 2000) but rather to provide indicator values (Tables 2.1 and 2.2) similar to existing HGM assessment models (Rheinhardt et al 1997, 1999). Models were constructed using the simple logic statements as recommended by Smith et al. (1995) so that my models were equivalent in conceptual design to models in the literature (Table 2.3).

Table 2.3. Rapid and non-rapid models created to predict nitrification and denitrification rates. Abbreviations are: litter = litter layer thickness; A ≤ 3 = A horizon with Munsell value ≤ 3; redox = frequency of redoximorphic features; nmin = net N mineralization rate; SOM = % soil organic matter; % < -30 = % water table observations < -30 cm; NH4+ = extractable NH4+; moisture = soil moisture content; median wt = median water table; % > 0 = % water table observations > 0 cm; % crossings = % crossings at -30 cm; freq = flooding frequency as # days month-1; chroma = frequency of chroma ≤ 2; clay = % clay.

Type of Variables	Nitrification	Denitrification
Rapid	RN1. FCI=(litter + A ≤ 3 + redox)/3	RD1. FCI=(A ≤ 3 + redox + chroma)/3
Rapid		RD2. FCI=(litter + redox + chroma)/3
Rapid		RD3. FCI=(A ≤ 3 + redox + clay)/3
Non-Rapid	NN1. FCI=(nmin + SOM + % < -30)/3	ND1. FCI=(SOM + % < -30 + moisture)/3
Non-Rapid	NN2. FCI=(NH_4^+ + SOM + % < -30)/3	ND2. FCI=(SOM + % < -30 + median wt)/3
Non-Rapid	NN3. FCI=(nmin + SOM + (1-moisture))/3	ND3. FCI=(SOM + % < -30 + % > 0)/3
Non-Rapid	NN4. FCI=(nmin + SOM + (1-median wt))/3	ND4. FCI=(SOM + % < -30 + % crossings)/3
Non-Rapid	NN5. FCI=(nmin + SOM + (1-% > 0)/3	ND5. FCI=(SOM + % < -30 + freq)/3
Non-Rapid	NN6. FCI=(nmin + SOM + % crossings)/3	
Non-Rapid	NN7. FCI=(nmin + SOM + (1-freq))/3	

I used indicators which had medium to high levels ($r^2 > 0.30$) of correlation with the observed process rates (Table 2.4). Rapid models, coded as RN for rapid nitrification models and RD for rapid denitrification models, were constructed using only rapidly-assessed indicators, such as those that might be implemented as part of a rapid assessment or regulatory protocol (Table 2.3). Non-rapid models, coded as NN for non-rapid nitrification models and ND for non-rapid denitrification models, used only non-rapid indicators (Table 2.3). In constructing rapid models, I substituted rapid indicators of hydric soils for non-rapid hydrological indicators (Tables 2.1 and 2.2). These rapid indicators, which include redox frequency and matrix chroma ≤ 2, are indicators used to identify hydric soils as part of wetland delineation protocols (Mid-Atlantic Hydric Soils Committee 2004; USDA, NRCS 2003). Indicators which had an opposite relationship to a controlling factor, such as soil moisture as an indicator of oxic conditions in nitrification models, were included in the model as their additive inverse. In these cases indicators were not subtracted, as that could result in negative FCI scores. Indicator values were scaled from 0 to 1 prior to calculating FCI scores, as described above for the evaluation of existing models. Scores were then regressed against my measurements of net nitrification and denitrification rates using methods described above. I did not attempt to create models for N mineralization because I did not measure many of the indicators of controlling factors on this process, factors such as C/N, lignin/N or carbon quality (Aber and Melillo 2001).

In general I expected to see positive, linear relationships between FCI scores and rates of both net nitrification and denitrification. However, because denitrification is typically maximal when conditions are either sub-oxic or fluctuating rather than uniformly anoxic,

Table 2.4. Relationships between indicator variables and N cycling process rates. n=14 except in tests involving hydrological indicator variables (i.e., median water table level), in which case n=12.

N Process	Indicator Variable	Regression Model	r^2
Nitrification	**Leaf Litter Thickness**	ns	
	A Horizon Value ≤ 3	ns	
	% Soil Organic Matter	ns	
	Net N Mineralization Rates	y=0.6529x-0.0099	0.62 ***
	Extractable NH_4^+	y=0.0766x-0.1154	0.48 **
	Redox Frequency	ns	
	Soil Moisture	ns	
	% Observations < -30 cm	y=0.0053x+0.0098	0.66 **
	Median Water Table Level	$y=-0.0001x^2-0.0164x-0.1$	0.68 **
	% Observations > 0 cm	ns	
	Flooding Frequency	ns	
	% Crossings at -30 cm	ns	
Denitrification	**Redox Frequency**	ns	
	Net Nitrification Rates	ns	
		ns	

Extractable NO_3^-		
% Observations < -30 cm	ns	
Leaf Litter Thickness	ns	
Value ≤ 3	ns	
% Soil Organic Matter	$y=0.0018x^2-0.0215x+0.2329$	0.83 ****
% Soil Organic Matter w/out RL	ns	
Low Chroma Frequency	ns	
Soil Moisture	$y=17.1594x^2-11.8095x+2.1104$	0.95 ****
Soil Moisture w/out RL and M5fr	ns	
Median Water Table Level	ns	
% Observations > 0 cm	ns	
Flooding Frequency	ns	
% Crossings at -30 cm	ns	
% Clay	ns	

ns not significant, * p<0.05, ** p<0.01, *** p<0.001, **** p<0.0001

in order to permit coupled nitrification and denitrification, I also examined quadratic regression models to test for unimodal relationships.

Results

Evaluation of Existing HGM Models

None of the existing models of N cycling function that I evaluated (Rheinhardt et al 1997, 1999, Smith and Klimas 2002) were able to reliably predict rates of net N mineralization, net nitrification, or denitrification in my sample of river-influenced, urban wetlands. All regressions between FCI scores of the three models and N cycling rates were non-significant except for the relationship between the Yazoo Basin model (Smith and Klimas 2002) and denitrification. When calculating Yazoo FCI scores using quantitative hydrological data to describe flooding frequency (in this case, % observations > 0 cm water table depth), FCI scores explained 56% of the variation ($p<0.05$) in denitrification rates according to a positive unimodal relationship (Figure 2.1). The relationship was highly dependent on one point, however, which corresponded to a site which did not prove to be influential in nearly all of my other analyses. The two models developed by Rheinhardt and colleagues (Rheinhardt et al. 1997, 1999) generated relationships which were opposite from those expected. There were slightly positive trends for net nitrification and slightly negative trends with denitrification; there were either slightly positive or no trends for net N mineralization. These trends were not significant.

Relationship of Indicators to N Cycling Functions

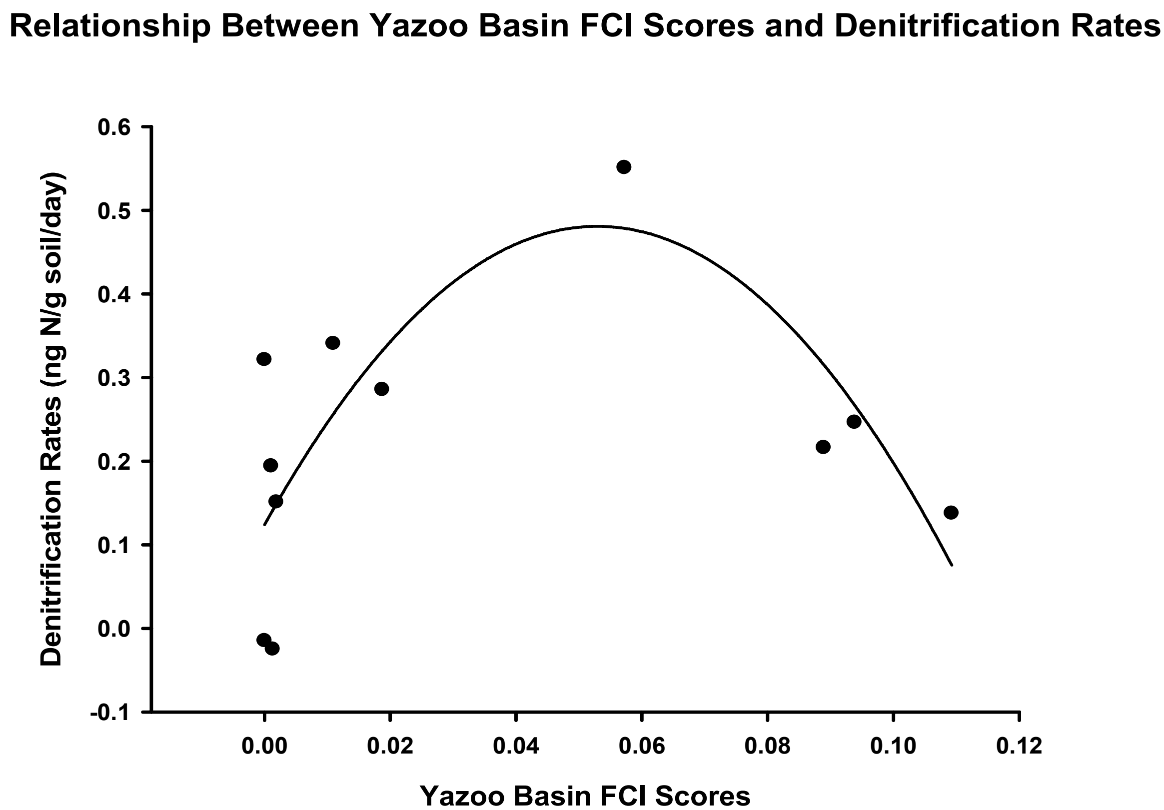

Figure 2.1. The relationship between scores generated by the Yazoo Basin FCI (Smith and Klimas 2002) and mean annual denitrification rates. FCI scores were calculated using % observations > 0 cm as an indicator of flooding; these indicator values were calculated from a long-term hydrological record. Model scores explained 56% of the variation in denitrification rates ($p<0.05$).

I tested the relationships of the indicator variables thought to be mechanistically related to nitrification and denitrification (Tables 2.1 and 2.2) to the actual process rates. Net nitrification rates increased with increasing net N mineralization rates and extractable NH_4^+, as expected (Table 2.4). Net nitrification also increased with increasing % water table observations < -30 cm. Only median water table level showed a quadratic relationship with net nitrification rates. Notably, none of the rapidly-assessed indicators were significantly related to net nitrification rates (Table 2.4). Similarly, none of the rapidly-assessed indicators were significantly related to denitrification rates (Table 2.4). In fact, denitrification rates were only related to two of the non-rapid indicators, soil moisture and percent soil organic matter, and in both cases showed quadratic relationships to these variables. However, when influential points, which correspond to sites with very high soil organic matter and moisture content, were removed from these analyses, neither of these indicators was significantly correlated with denitrification rates.

Correlations Among Indicators of Controlling Factors

There were no strong correlations among indicators of NH_4^+ availability. In general there were few strong relationships among indicators of oxic conditions, although, unsurprisingly, there was a very strong relationship between % of water table observations > 0 cm and flooding frequency (r^2=0.97, p<0.0001). There was also a relatively strong correlation between median water table level and redox frequency (r^2=0.38, p<0.05).

There were several strong relationships among indicators of NO_3^- availability, including between net nitrification rates and extractable NO_3^- (r^2=0.53, p<0.01), net nitrification rates and % observations < -30 cm (r^2=0.66, p<0.01), and extractable NO_3^-

and % observations < -30 cm (r^2=0.39, p<0.05). There were no strong relationships among indicators of organic carbon supply. Several relatively strong relationships occurred among indicators of sub-oxic conditions, including between median water table level and low chroma frequency (r^2=0.36, p<0.05), between median water table level and redox frequency (as above), between % observations > 0 cm and flooding frequency (as above), and between low chroma frequency and redox frequency (r^2=0.58, p<0.01).

Development and Evaluation of Mechanistic Models

I tested my proposed models (Table 2.3) by regressing the scaled FCI scores derived from each model against the observed process rates (Table 2.5). The nitrification model using only rapidly-assessed indicators (RN1) was unable to capture patterns in measured process rates. Some of the nitrification models using non-rapid indicators (NN1, NN2, NN3, NN4, and NN7) were successful in describing patterns in net nitrification rates (Table 2.5). The best model, NN2, used two indicators of NH_4^+ availability (extractable NH_4^+ and percent soil organic matter) and one indicator of oxic conditions (% observations < -30 cm) (Table 2.3). The first two indicators involve standard laboratory analyses of soil samples; the third demands more lengthy measurements of water table level over a period of time. In contrast, one of the three proposed rapid models for assessing denitrification (RD1) was moderately well correlated with the observed process rates (Table 2.5). However, the pattern of the relationship predicted low denitrification rates at intermediate FCI scores (negative coefficient, Table 2.5) which is opposite to the predicted pattern of highest denitrification rates at intermediate levels of oxygenation due to coupled nitrification and denitrification. Some of the denitrification models based on non-rapid indicators (ND1 and ND2) were

Table 2.5. Regressions testing the fit of new assessment models for N cycling functions to mean annual N cycling measurements. Models include those using only rapidly-determined structural indicators ('rapid') and those using only non-rapid field and laboratory measurements ('non-rapid'). Full model descriptions are given in Table 3. n=14 except in non-rapid models using hydrological variables, in which case n=12.

Model Type	**N Process**	**Assessment Model**	**Regression model**	**r^2**
Rapid	**Nitrification**	RN1	ns	
	Denitrification	RD1	$y=5.3998x^2-4.9272x+1.1183$	0.58 **
	Denitrification	RD2	ns	
	Denitrification	RD3	ns	
Non-rapid	**Nitrification**	NN1	$y=0.8259x-0.0707$	0.63 **
	Nitrification	NN2	$y=0.8983x-0.0195$	0.72 ***
	Nitrification	NN3	$y=1.3081x-0.4083$	0.59 *
	Nitrification	NN4	$y=0.79x-0.0195$	0.56 **
	Nitrification	NN5	ns	
	Nitrification	NN6	ns	
	Nitrification	NN7	$y=0.5682x+0.0214$	0.33 ms
	Denitrification	ND1+	$y=2.8798x-0.5841$	0.43 *
	Denitrification	ND2+	$y=4.3857x-1.6268$	0.38 *
	Denitrification	ND3	ns	
	Denitrification	ND4	ns	
	Denitrification	ND5	ns	

ns not significant, ms marginally significant, * p<0.05, ** p<0.01, *** p<0.001, **** p<0.0001

\+ models were not significant when one influential site (RL) was removed from the analysis significantly related to measured rates; however, these relationships depended on two influential sites, both of which had much higher organic matter content (42% and 20% soil organic matter, respectively, compared to a mean of 11% for all other sites) and were considerably wetter (0.726 and 0.582 g/g wet soil, respectively, compared to a mean of 0.429 for all other sites) than the other sites. These two models were not significantly related to actual denitrification rates when the high organic matter site was removed from the analyses.

Discussion

Rapid versus Non-rapid Models

Assessment models based on rapidly-assessed structural variables failed to provide reliable indicators of N cycling function. This was the case both for existing models proposed for broadly-defined ecosystem functions ('Remove elements and compounds' or 'Biogeochemical cycling') and my own models designed to assess specific N cycling processes. Some detailed measurement of ecosystem process, whether it was a hydrological record allowing true quantification of flooding frequency (e.g., Yazoo FCI scores calculated using % observations > 0 cm rather than annual flooding recurrence), inorganic N concentrations in soil extracts, or quantification of soil properties such as moisture content, was necessary to produce models that reliably reflected actual N cycling rates (Table 2.5). Although I created rapid models using variables, such as hydric soils indicators, with well-supported and specific associations with the conditions necessary for the two N cycling processes evaluated here, these models were unable to capture the differences among sites in actual process rates. These results suggest that rapid indicators of hydrology, soil carbon, and inorganic N availability cannot serve as surrogates for more quantitative, and thus non-rapid, N cycling indicators. Consequently, I echo the recommendation of Cole (2006) for at least one year of hydrological monitoring for wetland assessment methodologies.

Models based on non-rapid variables were successful in describing net nitrification rates (Table 2.5). This success can be attributed largely to the inclusion of quantitative hydrological indicators, many of which proved to be important controlling factors on net nitrification rates (Table 2.4). It is important to note that although these models used non-rapid indicators, some of these indicators, such as % soil organic matter and moisture content, require simple laboratory analyses which can be conducted with minimal training and equipment and at low to moderate cost. Soil testing laboratories associated with research universities routinely perform these inexpensive analyses. I recommend the inclusion of these analyses to strengthen the effectiveness of N cycling assessment models.

My non-rapid models failed to describe denitrification rates (Table 2.5). These models were not intended to be rigorous, comprehensive denitrification models; however, they were still unable to predict even relative levels of function among sites. This again points to the difficulty of attempting to quantify denitrification in a rapid assessment context. The ability of the denitrification models to capture measured rates depended strongly on a single site, RL, which had high rates of denitrification, a deep organic horizon, and was saturated to the surface or flooded for much of the study duration. These results suggest that assessment models should be developed and calibrated using sites with more similar soil (e.g., only mineral soils) and hydrological properties (e.g., within a narrower range of moisture conditions). It is also possible that models which contained specific indicators of site scale soil fertility, such as soil C:N, foliar N content, or litter quality, might have better predictive ability (Pastor et al. 1984).

Along the same lines, the lack of sufficient power in the non-significant analyses points to the need for more than 14 sites to capture the variability inherent in urban wetlands (Ehrenfeld et al. 2003, Ehrenfeld 2005). Although my wetland sites did span three different HGM classes, I have shown that rates of N cycling processes did not differ between sites in the riverine and mineral flat classes (Chapter 1/Stander and Ehrenfeld submitted). Rather, the presence or absence of urban-impacted hydrology (i.e., dry and/or flashy water table levels as determined from long-term measurements) is the most important predictor of rates of net N mineralization, net nitrification, and denitrification. Variability in soil and hydrological properties among this set of qualitatively similar palustrine, forested wetlands was high enough to hamper my ability to model denitrification rates, even using non-rapid indicators based on a mechanistic understanding of denitrification. Urban variability, due in part to the idiosyncrasies of historical and recent disturbances at the site and landscapes scales, has been well documented in freshwater wetlands in northeastern New Jersey (Ehrenfeld 2000, Ehrenfeld et al. 2003, Ehrenfeld 2005, Chapter 1/Stander and Ehrenfeld submitted) as well as other urban locations (Groffman and Crawford 2003). This variability must be specifically addressed in any assessment of wetlands in urbanized regions.

Specific versus General Models

My results strongly suggest that assessment models for ecosystem functions need to be developed in a radically different manner from current practice. First, models that are intended to capture generalized "nutrient cycling functions" are not useful in assessing specific ecosystem services, such as nitrate removal. Indeed, the high variability in the nature and mechanisms behind different ecosystem functions (Ehrenfeld 2000) make it unlikely that one equation can effectively capture any individual process. Similarly, one equation cannot be expected to describe a wide range of functions related to a variety of elements, including phosphorus, mercury, and heavy metals, which each have a different biological, chemical, and physical basis (Kadlec and Knight 1996). I thus suggest that the development of models for the assessment of wetland functions be carried out for specific process-based functions, as previously recommended by Findlay et al. (2002). Designing specific models for different elements and processes will require identifying and quantifying known controlling factors of the specific processes of interest. Hruby (1999) also calls for the use of specific functions, noting that if functions are defined broadly, such as ‘Remove nutrients and compounds,’ then wetlands would have to perform all nutrient removal functions at high levels in order to be considered highly functioning. Not all wetlands are capable of performing all functions at high levels due to inherent/natural hydrological and soil/geological properties. Thus it is appropriate to carefully identify the functions of interest which are likely to occur in a particular type of wetland in a particular region, and to design models which specifically target these functions (Findlay et al. 2002).

Structure of the Equations

Another possible explanation for the poor performance of my non-rapid denitrification models is that my models were built on linear relationships. Indicators of NO_3^- availability, organic carbon availability, and sub-oxic conditions were combined using additive functions to predict a linear relationship with denitrification rates. As a site scores higher for each variable included in the model, it scores higher overall. However, a number of the controlling factors on denitrification do not have a linear relationship with denitrification. Percent soil organic matter and moisture content, for example, displayed nonlinear relationships to denitrification rates (Table 2.4). Also, although hydrological indicators were not significantly correlated with denitrification rates, they should in theory have a nonlinear relationship with denitrification since intermediate values of wetness (and therefore, sub-oxic rather than anoxic conditions) should maximize denitrification rates through coupled nitrification and denitrification. The simplicity of the structure used in many current models does not account for nonlinear relationships between variables and the function of interest. In contrast, the Yazoo Basin model, which includes a multiplicative function between flooding and one other variable which represents an average of a several soil indicators, was successful in predicting denitrification rates when calculated using the non-rapid hydrologic indicator % observations > 0 cm. It is therefore necessary to understand the nature of the relationship between the assessment variable and the function (linear versus nonlinear) and to represent that relationship using the appropriate mathematical functions, as per Smith et al.'s published guidelines (1995). While the scientific community does have this understanding for a number of assessment variables and functions, my understanding is not complete across variables and functions, nor is it complete across systems. Detailed studies of populations of wetlands are necessary to validate the specific structure of model equations.

Finally, it must be acknowledged that modeling denitrification at the landscape scale has historically been challenging and has not generally produced unequivocal results (Boyer et al. 2006). Denitrification is a highly spatially and temporally variable process. Recommendations for improving models should be utilized with caution.

In summary, existing HGM rapid assessment models written for river-influenced sites were not effective predictors of N cycling functions in urban wetlands in northeastern New Jersey. Rapid models designed according to a more mechanistic understanding of specific N cycling functions also were not successful in predicting rates of nitrate production and removal. Non-rapid models which used long-term measurements of indicators of known controlling factors of N process rates were successful for predicting net nitrification rates, but I was still unable to capture the variation in denitrification rates. The complex and site-specific relationships between disturbance in urban watersheds, altered hydrology, and hydrologically-driven N cycling processes limits my ability to use simple models to describe denitrification in urban wetlands which display high variability in soil and hydrological properties. Also, the simple structure of these models may not account for complex, nonlinear relationships between controlling factors and denitrification rates. My results strongly suggest that assessment models for ecosystem functions need to incorporate hydrological monitoring data and simple laboratory analyses of soil properties in addition to rapidly-assessed structural indicator variables. I also recommend that assessment model development be carried out for specific process-based functions based on structural variables that are well linked to process rates. This requires detailed studies of populations of wetlands to validate specific forms of models based on such variables.

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CHAPTER 3

Landscape and local scale controlling factors on nitrogen cycling processes in urban wetlands

Introduction

The ability of ecosystems to retain nitrogen (N) is a critical ecosystem service for the maintenance of water quality (Vitousek et al. 1997, Costanza et al. 1997, Mitsch and Gosselink 2000, Ehrenfeld 2004, Hansson et al. 2005). As human land uses such as agriculture and urban development continue to act as nonpoint sources of N pollution to receiving streams and rivers, eutrophication of receiving waters will increasingly threaten the quality of water resources on a global scale (Lowrance et al. 1997, Mitsch et al. 2001). In many countries including the United States, managers have turned to natural systems such as wetlands and forests as tools for removing excess N released from upland land uses before it can reach receiving streams (Saunders and Kalff 2001, Ehrenfeld 2004, Groffman et al. 2004, Zedler and Kercher 2005, Hansson et al. 2005). The ability of forested riparian buffers to remove excess N from agricultural land uses is well documented (Lowrance et al. 1984, Cooper 1990, Lowrance 1992, Simmons *et al.* 1992, Haycock and Pinay 1993, Gilliam 1994, and Hill 1996). However, it is not clear whether wetlands in urban landscapes provide the same function. Urban land uses alter hydrological regimes in urban streams and wetlands (Hollis 1975, Booth 1990, Owen 1995, Booth and Jackson 1997, Moscrip and Montgomery 1997, Ehrenfeld 2000, Ehrenfeld et al. 2003, Im et al. 2003), and these hydrological changes may affect the ability of urban wetlands to perform critical N removal functions (Groffman et al. 2002, Ehrenfeld et al 2003, Stander and Ehrenfeld in prep), which may then have cascading effects on water quality of receiving streams and rivers. In this study I test the ability of wetlands to both produce and remove nitrate (NO_3^-), the most mobile form of N, in the context of urbanization as characterized on both local and landscape scales.

Wetlands are highly N-retentive systems because their saturated soils facilitate the anaerobic process of denitrification, which transforms the mobile anion NO_3^- to N_2 gas which is then released to the atmosphere (Mitsch and Gosselink 2000). This property of wetlands has been extensively exploited in constructed wetlands used for treating many kinds of wastewaters, including sewage effluent, agricultural water, and industrial water (Lowrance et al. 1984, Cooper 1990, Lowrance 1992, Simmons et al. 1992, Haycock and Pinay 1993, Gilliam 1994, Hill 1996, Kadlec and Knight 1996, and Boustany et al. 1997). However, there is reason to believe urban wetlands may behave differently than less impacted wetlands or riparian buffers downslope from agricultural fields (Faulkner 2004). It has been widely documented that urbanization causes a number of changes in stream hydrology, including streambank incision (Hollis 1975, Booth 1990, Booth and Jackson 1997, Moscrip and Montgomery 1997, Paul and Meyer 2001, Booth et al. 2004), increased river discharge during storm events (Moscrip and Montgomery 1997), and reduced baseflow and surface water storage (Im et al. 2003). These changes may impact wetland hydrology by increasing flooding frequencies (Moscrip and Montgomery 1997), decreasing groundwater and surface water inputs (Owen 1995), and causing water table levels to be drier and flashier than they have been historically (Golet et al. 1993, Groffman et al. 2002, Ehrenfeld et al. 2003). These changes in wetland hydrology may in turn cause changes in wetland N cycling processes. Drier soils in urban wetlands may facilitate the aerobic process of nitrification, which produces NO_3^-, and inhibit the anaerobic process of denitrification, which removes NO_3^- (Groffman et al. 2002, Chapter 1/Stander and Ehrenfeld submitted). In addition wetlands in urban areas often have extensive physical hydrological disturbances, including mosquito ditching, ditches that separate wetlands from road or railroad corridors, power line rights-of-way, berms resulting from adjacent construction that alter water movements within the wetland, and impervious surfaces such as parking lots immediately adjacent to the wetland edge that funnel stormwater flows directly into the wetland.

In an attempt to identify universally applicable factors which explain the effects of urbanization on ecological patterns and processes, investigators have focused on landscape level metrics which characterize the intensity of urbanization at the watershed scale. Popularly used metrics include percent impervious cover, percent of various land cover classes, road density, and human population density (Arnold and Gibbons 1996, Brabec et al. 2002, King et al. 2005, McBride and Booth 2005, Kauffman et al. 2006). On smaller scales, such as the neighborhood or city block, urban areas can be very heterogeneous in the qualities and amount of impervious surfaces (size and shape of buildings and paved surfaces), types of vegetation, and soil conditions, ranging from eroded grass on compacted soils of ballfields to forested yards behind houses built at low densities (Cadenasso et al. 2007). On larger scales, such as the watershed scale, it may be easier to generalize the intensity of the urban condition by evaluating metrics such as percent impervious cover and road density, which in effect integrate the spatial extent of the various types of small-scale, idiosyncratic land uses and the degree of urban intensity they represent.

Extensive research has demonstrated the negative effects of urban land use, characterized using the aforementioned metrics, in the upgradient watershed on stream structure (Booth et al 2004, McBride and Booth 2005, Chadwick et al. 2006, White and Greer 2006) and function (Mallin et al 2000, Rhodes et al. 2001, Huryn et al. 2002, Booth et al. 2004, Kleppel et al. 2004, Pellerin et al. 2004, Burns et al. 2005, McBride and Booth 2005, Chadwick et al. 2006, and many others; see Gergel et al. 2002 for a review of this literature). Only a small handful of studies have analyzed various aspects of wetland structure and function in relation to watershed-scale land use/land cover patterns (Houlahan and Findlay 2004). Also, many of these studies focused on watersheds which were more impacted by agriculture and forestry than urban development, and few used measurements of actual denitrification as the response variable of interest. Stander and Ehrenfeld (submitted/Chapter 1) analyzed the relative ability of urbanization (described qualitatively) versus hydrogeomorphic landscape setting to predict rates of denitrification in urban wetlands. This study used a categorical description (urban versus non-urban) of urbanization. Merrill and Benning (2006) found that potential denitrification was explained by a combination of within site characteristics, such as soil moisture and redox, and landscape level factors like ecosystem type as characterized by topography and vegetation communities. This study was conducted in pristine, montane watersheds in the western US. Ullah and Faulkner (2006) found that landscape position and land use type (i.e., vegetated versus non-vegetated ditches, constructed wetlands, and depressional wetlands) in addition to local scale soil properties such as soil organic matter and soil moisture were important descriptors of potential denitrification rates. Other studies related landscape scale land cover patterns to nutrient concentrations (Galbraith and

Burns 2007), sediment accumulation rates (Noe and Hupp 2005), occurrence of vernal pools (Grant 2005), metal and organic sediment contamination (Paul et al. 2002), PAH's in wetland sediments (Kimbrough and Dickhut 2006), and abundance and composition of wetland vegetation communities (Mensing et al 1998, Zhu and Ehrenfeld 1999, Lopez et al 2002, Ehrenfeld 2005, Houlahan et al. 2006, and White and Greer 2006). In a palynological study Elliot and Brush (2006) found enrichment of ^{15}N with increasing land use intensity over time in sediment cores.

There is currently little consensus in the literature as to the relative importance of local versus landscape scale factors in explaining variation in wetland patterns and processes. Several studies have found that the local scale is more important for a range of wetland organisms, including plants (Houlahan et al. 2006) and birds (Mensing et al. 1998, DeLuca et al. 2004); wetland habitat for fish (Snyder et al. 2003); and wetland functions such as nitrification (Merrill and Benning 2006). On the other hand, several studies have found that landscape scale factors have more explanatory power for response variables such as potential denitrification (Merrill and Benning 2006), riparian vegetation (Tabacchi et al. 1998), fish abundance and diversity (Mensing et al. 1998), and macroinvertebrate IBI scores (Snyder et al. 2003). Other studies reported mixed results (Mensing et al. 1998, McBride and Booth 2005, Arscott et al. 2006, Ullah and Faulkner 2006). It is a critical distinction, because in theory landscape metrics that describe degree of urban intensity, such as % impervious cover, % urban land cover, road density, and population density, should characterize hydrologic alteration and water table dynamics in urban wetlands (Brabec et al. 2002). Since there should be a link between water table dynamics and N cycling processes (Groffman et al. 2002, Stander and Ehrenfeld submitted/Chapter 1), there should then be a cascading relationship between landscape scale metrics and levels of N cycling functions. However, there may be a tighter mechanistic link between local scale factors (Booth et al. 2004) and N cycling rates, since water tables are influenced on a local scale by soil properties, such as soil moisture and texture, both of which are also controlling factors on rates of nitrification and denitrification (Groffman and Tiedje 1989 and 1991, Brettar and Hofle 2002, Boyer et al. 2006).

In comparison to local scale factors, landscape level metrics are more descriptive of patterns rather than processes, although McBride and Booth (2005) note that road density is a measure of connectivity between impervious surfaces and streams and thus serves as a mechanistic link between urban intensity and NO_3^- releases in streams. Also, Houlahan et al. (2006) found a mechanistic link between landscape metrics and vegetation community structure through landscape scale plant dispersal. However, many landscape metrics such as % urban land cover represent a suite of stressors related to the urban context (Allan 2004). Despite the general de-emphasis on mechanistic links between landscape scale metrics and wetland processes, several investigators argue that the watershed scale is more important than the local scale because the watershed scale integrates the effects of multiple land uses (Rhodes et al. 2001) and because management decisions regarding any *one* wetland in a watershed should be made in the context of the condition of *all* the wetlands in that watershed (Torbick et al. 2006). Also, I acknowledge that local scale factors which may not necessarily be affected by urbanization, such as soil texture and pH, are well documented as important controlling factors on rates of N cycling processes in wetlands (Groffman and Tiedje 1989 and 1991, Brettar and Hofle 2002, Boyer et al. 2006). However, these studies employ laboratory incubations to examine the relationships between soil properties and N cycling process rates. It is not known how well these relationships apply to field conditions, particularly in human-impacted systems. It is possible that the effects of landscape scale urbanization on hydrology may outweigh the effects of soil properties, but this idea must be tested. Vegetation properties, such as shrub density and herbaceous cover, which themselves may be indicative of hydrological conditions (i.e., lower shrub densities under wetter conditions), may affect N cycling processes as well (Ehrenfeld et al. 2001, Kourtev et al. 2003).

I propose a conceptual model to illustrate the potential relationships of landscape and local level factors with N cycling processes in urban wetlands.

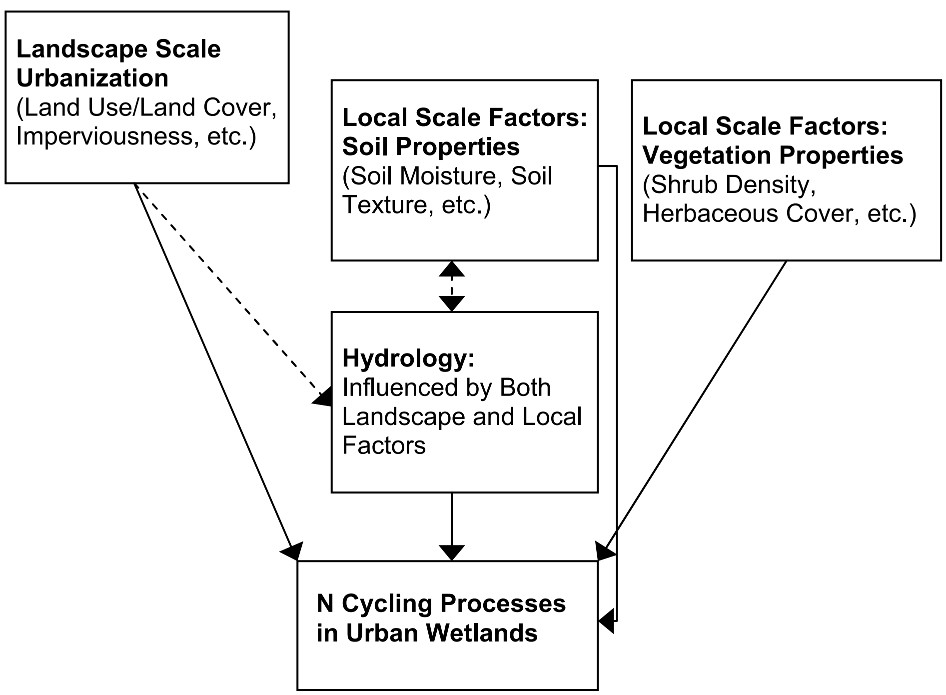


Figure 3.1. Conceptual model outlining the possible relationships of landscape and local scale factors with N cycling processes. Landscape and local scale factors may have direct effects on N cycling (solid arrows) or indirect effects as mediated through wetland hydrology (dashed arrows).

There may be a pattern of direct relationships between landscape scale urbanization and N cycling processes although the mechanism(s) may not be clear, or there may be indirect effects of watershed scale urbanization mediated through altered hydrology (i.e., stream incision and decreased baseflow causing lowered water tables in wetlands). Local scale factors (both soil and vegetation properties) may directly influence N cycling, soil properties such as texture may indirectly affect N cycling through changes in hydrology, or hydrology may indirectly affect N cycling by changing soil properties such as soil moisture and organic matter content. In this study I evaluated the presence of these potential relationships by regressing landscape urbanization metrics, soil properties, vegetation properties, and hydrological variables with *in situ* measurements of net N mineralization, net nitrification, and denitrification rates. I previously categorized these sites as “normal” or “dry/flashy” based on the presence or absence of hydrological alteration (Stander and Ehrenfeld submitted/Chapters 1 and 2). In this study I am interested in the effects of the *degree* of urban intensity on ecological patterns and processes, and so I employ a continuous, regression-based analysis rather than a categorical one to look for trends and relationships. This study suggests whether management efforts aimed at increasing the ability of urban wetlands to retain N should be targeted at the local or the landscape scale.

METHODS

Study Sites

Fourteen palustrine, forested wetland sites were selected in northeastern New Jersey. All sites are located within the Piedmont physiographic province. This places the sites in the most urbanized region of the state and within the third largest urban agglomeration in the world with a population of 18.7 million (UN 2005). Population densities range from 177 to 3,585 persons km^{-2}, and road densities range from 4.6 to 33.1 km km^{-2} in the watersheds containing the 14 sites (Table 3.1).

Study sites were chosen from the population of palustrine, forested wetlands (Cowardin *et al.* 1979) in the region, as identified by the New Jersey Freshwater Wetlands Inventory maps (http://www.state.nj.us/dep/gis/). These wetlands are in most cases naturally-occurring fragments remaining from larger wetland complexes created by the deposition of dense clays in two large glacial lakes, glacial lake Passaic and glacial lake Hackensack, which covered much of northeastern New Jersey following the retreat of the Wisconsin glaciation (Wolfe 1977). These wetland fragments persist despite close to 400 years of human land use and development in the region (Ehrenfeld 2004). All sites had a closed-canopy deciduous forest dominated by red maple (*Acer rubrum* L.) and were adjacent to streams (1^{st} to 4^{th} order) that were forested on both sides.

Hydrology

Water table dynamics were measured in 12 of the 14 sites (wells had to be removed from two of the sites due to vandalism problems). These 12 sites were equipped with an automatically recording well (hereafter, autowell) (either a WL-40 or an Ecotone model, Remote Data Systems, Inc., Whiteville, NC). Specific locations for each autowell were chosen based on the presence of typical wetland soils (i.e., redoximorphic features, peat accumulation) and forested conditions on both sides of the stream. Autowells were installed to a depth of 100 cm at a distance of 25 m from the stream bank. Autowells were programmed to collect water table measurements four times daily. The autowells' data loggers were downloaded bimonthly. Measurements of hydrology were taken

Table 3.1. Means and ranges of variables measured in 14 palustrine, forested wetlands in northeastern New Jersey. Hydrological variables were measured in 12 of the 14 sites. Landscape variables were measured on the subwatershed scale (HUC 14).

Variable	***Mean***	***Range***
Extractable NO_3^- (mg N/kg soil)	1.54	0.228-3.76
Extractable NH_4^+ (mg N/kg soil)	6.70	3.59-14.4
Net N Mineralization (mg N/kg soil/day)	0.442	-0.0136-0.811
Net Nitrification (mg N/kg soil/day)	0.263	-0.0383-0.696
Denitrification (µg N/kg soil/hour)	0.447	-0.0250-2.54
Population Density (people/km^2)	1,000	177-3,590
% Impervious Cover	22.9	5.96-46.2
Road Density (km/km^2)	14.3	4.60-33.1
% Urban Land Cover	61.5	31.2-92.7
% Forested Land Cover	16.9	4.24-49.9
% Wetland Land Cover	16.9	1.87-52.3
Watershed Area (ha)	2,290	1,300-3,680
Median Water Table Level (cm depth)	-43.0	-95.0 - -5.02

% Observations < -30 cm	56.4	2.24-100
% Observations > 0 cm	3.99	0-22.5
% Crossings at -30 cm	3.88	0-9.25
Water Table Interquartile Range (cm)	26.1	0.254-52.7
Bankfull Height (m)	1.82	1.51-2.15
% Soil Organic Matter	13.99	4.80-42.14
Soil Moisture (g/g dry soil)	0.926	0.596-2.75
% Clay	25.9	13-47
% Clay + % Silt	65.7	44-90
Soil pH	5.25	4.30-6.40
Basal Area (m^2/ha)	26.2	14.5-38.3
Tree Density (#/ha)	389	64-658
Shrub Density (#/ha)	11,180	0-4,460
% Herbaceous Cover	28	0-100
Wetland Area (ha)	127	5.18-302

between October 2002 and May 2006, with sporadic gaps at different times from site to site when wells stopped collecting data due to dead batteries or repairs. Hydrological variables, listed in Table 3.1, were calculated from the long-term water table record. The variables were chosen to characterize the dryness and/or flashiness of the water table at each site on a local scale. Justification for most of the variables chosen is presented in Chapter 1/Stander and Ehrenfeld (submitted). An additional variable, interquartile range of the water table, is used to characterize the variability and some degree of flashiness of the water table record. Bankfull height is also used as a measure of streambank incision.

In Situ Soil Nitrogen Cycling Rates

Rates of net N mineralization, net nitrification, and denitrification were measured in all 14 sites from November 2002 through November 2003. The intact static core technique developed by Robertson et al. (1999) was used to measure *in situ* rates of net N mineralization and net nitrification during month-long field incubations. The acetylene block technique (Tiedje et al. 1989) was used to measure denitrification rates on the same cores in six-hour laboratory incubations. Soils were measured for bulk density and moisture content and were extracted for inorganic nitrogen using a 2 M KCl solution. KCl extracts were analyzed colorimetrically for NO_3^- and ammonium concentrations. See Chapter 1/Stander and Ehrenfeld (submitted) for a more detailed description of these field and laboratory methods.

Landscape Scale Metrics

A GIS based spatial analysis was used to characterize the degree of urbanization at the landscape scale surrounding each site. I quantified commonly used indicators of both amount of urban area (i.e., % urban land cover) and degree of connectivity of urban land (i.e., road density and % impervious cover). Human population density was also utilized as an indicator of urban intensity. Landscape scale variables are listed in Table 3.1. Indicator values were generated at the watershed scale using 14 digit hydrologic unit codes (HUC), the smallest USGS subwatershed classification. Some sites were located in the same HUC 14 subwatershed. I quantified the sub-watershed in its entirety, including portions both upstream and downstream of the study sites.

Percent impervious cover and land cover indicators, including % forest, % urban, and % wetland, were calculated for each HUC 14 using a 2002 Land Use/Land Cover (LU/LC) data set from the New Jersey Department of Environmental Protection (NJDEP 2007). The 2002 LU/LC data set was created by comparing NJDEP's 1995 LU/LC data set with 2002 digital color infrared orthophotography at a scale of 1:2400 with a 1 foot pixel resolution. Polygons were classified by land cover according to a modified Anderson level III classification (Anderson et al. 1976); percent impervious cover was also included for each polygon. Using ArcMap 9.2 (ESRI, Redlands, CA) I clipped the landcover layer based on HUC polygons, then tabulated the area of each land cover class for the HUC 14 subwatersheds. Percent impervious cover was calculated by summing the products of area and % impervious cover for developed land cover classes.

Population densities were calculated using Census 2000 TIGER information at the block level for New Jersey (US Census Bureau 2000, NJDEP 2000). I used the POP2000 attribute to obtain population numbers at the census block scale. I clipped census blocks by HUC 14 subwatersheds. Then, because populations can occur anywhere within a census block and clipped census blocks may not accurately reflect population density by area alone, I calculated the percentage of developed land by census block within HUC 14 subwatersheds and multiplied that by census block population numbers. Land cover was quantified using a 2001 Land Use/Land Cover data set in raster format prepared by the Rutgers Center for Remote Sensing and Spatial Analysis (CRSSA 2004). The 2001 LU/LC data set uses Landsat 7 ETM+ satellite imagery from 2001 which was terrain corrected by USGS with a positional error of +/- 1 pixel (30 m). Cloud covered areas were replaced using 1999 imagery. Each 30x30 m pixel was assigned a land cover value according to Anderson level I categories as mapped by CRSSA. Developed classes included high intensity (>75% impervious surface), medium intensity (50-75% impervious), low intensity (<50% impervious) wooded, and low intensity un-wooded. Percent developed land was calculated by converting census blocks into GRID format and using the "combine" function in ArcToolBox to find all unique pixel combinations for whole census blocks and landcover types at 30 m resolution. The procedure was performed a second time using clipped census blocks in order to calculate the percentage of developed land within census blocks limited by the HUC 14 boundaries. Population density at the HUC 14 scale was calculated as the census block population number multiplied by % developed land and divided by HUC 14 area.

Road density was quantified using the New Jersey Department of Transportation's NJ Roadway Network (NJDOT 2005). NJDOT digitized roads using 2002 statewide orthophotos at a scale of 1:2400 with a 1 foot pixel resolution. Orthophotos were ortho-rectified to a +/- 4.0 foot horizontal accuracy at a 95% confidence level. I clipped roads by HUC 14 boundaries and divided resulting road lengths by watershed area to calculate road densities.

HUC 14 watershed area was also used as a landscape scale metric.

Local Scale Metrics

Vegetation

Three circular plots of 10 m radius at each site were assessed for vegetation variables. Two of the plots were located at each end of the transect used for the hydrological and N cycling measurements described above. The center point of the third plot was located 30 m from the center points of the other two plots in a triangular formation. All trees >10 cm diameter at breast height (dbh) were counted by species to measure tree density, and dbh was measured for each tree. Tree basal area was calculated from dbh measurements. All shrubs within a five m nested circular plot within the main plot were counted by species to determine shrub density. Four 1 m^2 quadrats were located at random within each 10 m radius plot and measured for percent cover of herbaceous plants. Vegetation variables, which were treated as local metrics in analyses, are listed in Table 3.1.

Quantitative Soil Description

Soils were analyzed quantitatively for descriptive soil properties. A sample of the top ten cm of soil was taken from the 12 quadrats used in the vegetation analysis and bulked for each site. Soil samples were analyzed using standard procedures at the Rutgers Soil Testing Laboratory for pH, estimated CEC and cation saturation, soluble salts, organic matter content, percentages of sand, silt, and clay, soil textural class, extractable NO_3^- and ammonium (NH_4^+), and total Kjeldahl nitrogen. Soil variables, which were treated as local metrics in analyses, are listed in Table 3.1.

Wetland Area

Wetland area was also a local scale metric used in analyses.

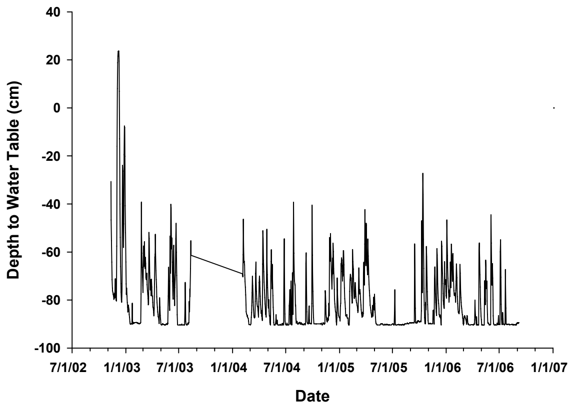
Data Analyses

I tested the relationships of landscape (i.e., % urban land cover, population density, etc.) and local metrics (i.e., soils and vegetation) with hydrological and N cycling patterns processes in urban wetlands using simple, one parameter regressions. Direct relationships with N cycling were tested (i.e., landscape metrics versus N, hydrology metrics versus N, soil metrics versus N, and vegetation metrics versus N) (Figure 3.1). Vegetation metrics were tested against N concentrations and process rates averaged over the growing season only. I also looked for relationships of landscape and soil variables with hydrology to determine the indirect effects of these variables on N cycling as mediated through hydrology, as well as effects of hydrology on soil properties to see indirect effects on N cycling mediated through soil (Figure 3.1). I tested relationships with both concentrations of extractable NO_3^- and NH_4^+ as well as with rates of net N mineralization, net nitrification, and denitrification. I also tested all relationships with these five N variables expressed on a per gram organic matter basis in order to control for the influence of organic matter content on N concentrations and process rates. Tests of significance were performed in Sigma Plot (Systat Software Inc., ver. 9.0). Power analyses were run separately on each regression. When regression relationships were significant, the effects were strong enough to generate high power. In many cases where non-significant results were obtained, the power of the test was low (i.e., the lack of significance may not be a reliable result). Analyses which produced significant results, however, did have sufficient power. Data points which were considered influential according to Cook's Distance and DFFITS tests were removed from the analysis and the correlation was rerun to determine the robustness of the original relationship. Regression equations, r^2 values, and p values are reported from tests which used all sites. Response variables expressed as percentages or proportions (i.e., % soil organic matter, soil moisture, % water table crossings at -30 cm, % water table observations < -30 cm, and % water table observations > 0 cm) were arcsine square root transformed before performing analyses. Denitrification rates were $\log_{10}$ transformed to improve normality and homogenize variances. Regressions of all transformed variables were also run untransformed; in most cases differences were minimal. Results using transformed variables are reported.

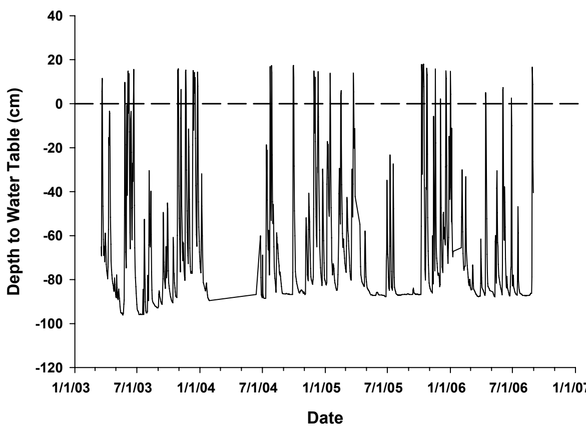
RESULTS

Patterns of Hydrology, N Dynamics, Soil, and Vegetation in Urban Wetlands

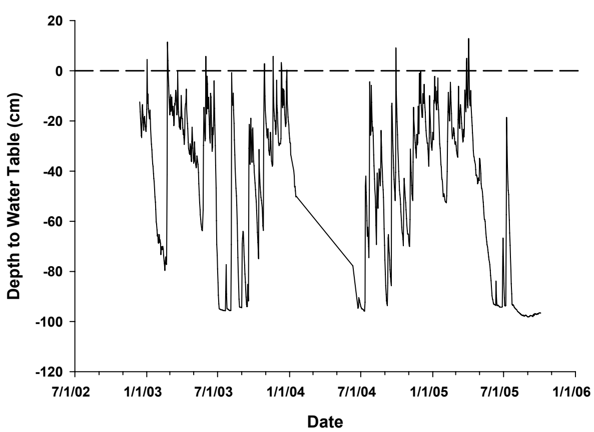
Median water tables averaged 43 cm below the surface across the 12 sites and ranged from below detection (~1 m) at the driest site to 5 cm below the surface at the wettest site (Table 3.1). Water tables showed four general patterns: dry (Figure 3.2a), flashy (Figure 3.2b), both dry and flashy (Figure 3.2c), and normal (Figure 3.3a, b). Normal water table levels are defined as occurring within 30 cm of the surface most of the year with a summer drawdown and with few large or rapid fluctuations (Golet et al. 1993). Water table levels were very variable among the set of wetlands, as demonstrated by the range of values for interquartile range and percent of water table observations < -30 cm (Table 3.1). Bankfull height, representing the depth of stream incision, varied little among the sites (Table 3.1). Concentrations of inorganic N varied over an order of magnitude, from 0.228 to 3.76 mg kg^{-1} for NO_3^- and from 3.59-14.4 mg kg^{-1} for NH_4^+



A.

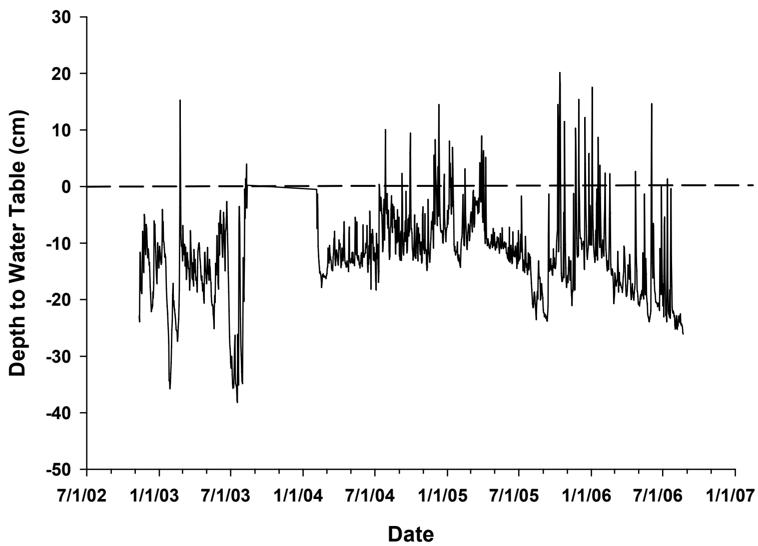


B.

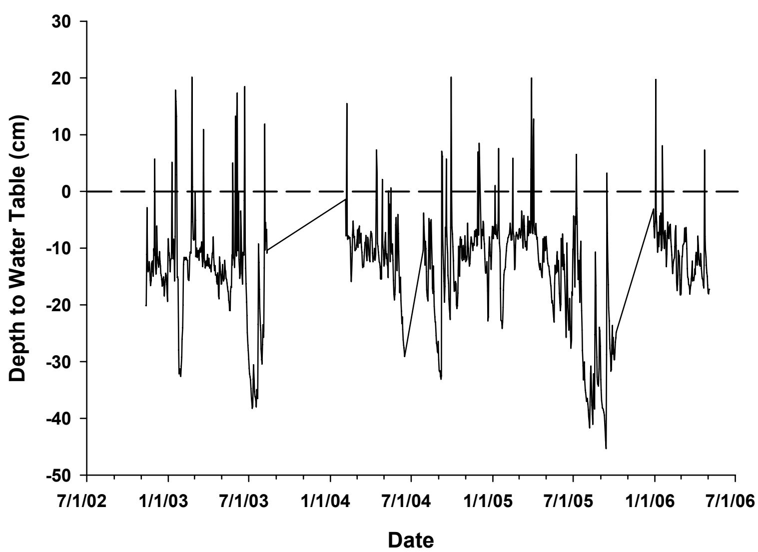


C.

Figure 3.2. Examples of water table hydrographs that represent dry (3.2a), flashy (3.2b) or both dry and flashy (3.2c) hydrological regimes. Water table depths are daily means; date is represented as M/D/YY.



A.



B.

Figure 3.3. Examples of water table hydrograph representing characteristic hydrological regimes for palustrine, forested wetlands in the Mid-Atlantic region. Water table depths are daily means; date is represented as M/D/YY.

(Table 3.1). Rates of N cycling processes were generally low but showed at least an order of magnitude difference over the set of study sites (Table 3.1). Landscape variables spanned a considerable range for all six variables measured, suggesting that my study sites represent a wide range of urban intensity in a developed region (Table 3.1). Soil moisture and organic matter content were low at most sites, but two sites had much higher values for both variables than the rest of the population (Table 3.1). Soil texture was very variable among the sites, as were all measures of vegetation cover (Table 3.1).

Relationships of Landscape and Local Variables with N Cycling

There were very few significant relationships of any of the six landscape variables (listed in Table 3.1) with N concentrations and rates, expressed as both per gram dry soil and per gram organic matter (Table 3.2). The only exceptions were weak correlations between percent urban land cover and percent residential land cover with concentrations of extractable NH_4^+ (Table 3.2). There were also very few relationships between landscape variables and hydrological variables (listed in Table 3.1) except for a weak correlation between population density and percent water table crossings at -30 cm (Table 3.2). Landscape variables thus did not demonstrate direct or indirect effects on N cycling. There were some correlations among landscape variables (Table 3.3).

Since hydrological patterns in these wetlands (Figures 3.2 and 3.3) were not explained by landscape scale urbanization patterns, I also looked for an influence of soil properties, particularly soil texture, on water table levels (Figure 3.1, Table 3.2). There was a strong relationship between percent clay and percent water table crossings at -30 cm (Table 3.2), but otherwise there were no relationships between texture, expressed as % clay and also % clay + % silt, and hydrological variables (Table 3.2).

Table 3.2. Significant relationships between variables. r^2 values are presented with significance level. OM is an abbreviation for organic matter. n=14 or 12 for tests which include hydrological variables.

Predictor Variable	***Response Variable***	***Regression Model***	r^2
	Landscape versus N Concentrations and Rates		
% Urban Land Cover	**Extractable NH_4^+**	y=0.0927x +1.002	0.30 *
% Residential Land Cover	**Extractable NH_4^+**	y=0.1459x +0.5253	0.42 *
	Landscape versus Hydrological Variables		
Population Density	**% Crossings at -30 cm**	y=-0.00005x +0.2472	0.36 *
	Soil versus Hydrological Variables		
% Clay	**% Crossings at -30 cm**	y=0.2169x -1.525	0.69 **
	Hydrological Variables versus N Concentrations and Rates		
Bankfull Height	**Net N Mineralization**	y=-0.8876x +2.097	0.42 *
Bankfull Height	**Extractable NO_3^-**	y=-2.796 +6.597	0.47 *
% Observations < -30 cm	**Extractable NH_4^+**	y=-0.0678x +10.51	0.47 *
Median Water Table	**Extractable NO_3^- (per gram OM)**	y=-.2070x +4.005	0.57 **
% Observations < -30 cm	**Extractable NO_3^- (per gram OM)**	y=0.1879x +2.310	0.61 **
Median Water Table	**Net Nitrification**	y=0.0055x +0.0714	0.55 **
% Observations < -30 cm	**Net Nitrification**	y=0.0053x +0.0098	0.66 **

Median Water Table	**Net N Mineralization (per gram OM)**	y=-0.0689x +0.7476	0.68 **
% Observations < -30 cm	**Net N Mineralization (per gram OM)**	y=0.0609x +0.2478	0.69 **
Median Water Table	**Net Nitrification (per gram OM)**	y=-0.0722x -0.1466	0.66 **
% Observations < -30 cm	**Net Nitrification (per gram OM)**	y=0.0611x -0.4849	0.62 *
Median Water Table	**% Observations < -30 cm**	y=-0.8074x +2.53	0.85 ****
Soil Variables versus N Concentrations and Rates			
% Soil Organic Matter	**Denitrification**	$y=-1.169x^2 +0.6345x+0.8594$	0.74 **** +
Soil Moisture	**Denitrification**	y=1.154x -0.6218	0.91 ****
% Soil Organic Matter	**Soil Moisture**	y=0.2052x +0.1778	0.78 **** +
Vegetation Variables versus N Concentrations and Rates			
% Herbaceous Cover	**Growing Season NH_4^+ (per gram OM)**	y=0.6560x +40.56	0.35 *
% Herbaceous Cover	**Growing Season Net N Mineralization**	y=-0.0079x +0.8522	0.33 *
N Variables versus N Variables			
Net N Mineralization	**Net Nitrification**	y=0.6415x -0.0202	0.65 ****
Extractable NH_4^+	**Denitrification**	y=0.1277x -0.4089	0.39 *

* p<0.05, ** p<0.01, *** p<0.001, **** p<0.0001

\+ relationships was not significant when one influential site (RL) was removed from the analysis

Table 3.3. Correlation matrix of relationships among landscape variables. r^2 values are presented along with indications of significance. Variable names are abbreviated for space; abbreviated variables are % impervious cover (% impervious), % urban land cover (% urban), % forest land cover (% forest), and population density (pop density). Significant results are bolded. n=14 for all tests.

Landscape Variables	***% Impervious***	***% Urban***	***% Forest***	***Road Density***
% Impervious	--		ns	**0.8045 ******
% Urban	**0.8202 ******	--	ns	**0.5869 ****
Pop Density	**0.7968 *****	**0.6898 ****	ns	**0.902 ******

ns not significant, * p<0.05, ** p<0.01, *** p<0.001, **** p<0.0001

Although I was unable to document the causes of hydrological alteration, the data do demonstrate the influence of hydrological patterns on N concentrations and rates. Median water table level and percent of water table observations < -30 cm had the most explanatory power of all the hydrological variables, as they were correlated with concentrations of extractable NH_4^+ and net nitrification rates and also concentrations of extractable NO_3^-, net N mineralization rates, and net nitrification rates as expressed on a per gram organic matter basis (Table 3.2). Median water table level and percent observations < -30 cm were also highly correlated with each other (Table 3.2). Bankfull height, an indicator of streambank incision, was significantly correlated with concentrations of extractable NO_3^- and net N mineralization rates, although these relationships were weaker (Table 3.2). There were no significant relationships between percent water table observations > 0 cm, an indicator of flooding, and interquartile range, an indicator of water table variability, with any of the N concentrations or rates. None of the hydrological variables were correlated with denitrification rates.

Local scale factors such as soil and vegetation properties were also tested against N concentrations and rates. Percent soil organic matter and soil moisture were both highly correlated with denitrification rates (Table 3.2), although when one site with highly organic soils, RL, was removed from the analysis, percent soil organic matter was no longer significantly correlated with denitrification (Table 3.2). Thus soil moisture was the best predictor of denitrification rates. Percent soil organic matter and soil moisture were also highly correlated with each other, although this relationship was also dependent on the highly organic site, RL. Soil texture and pH were not effective predictors of N variables. Only one of the four vegetation properties showed any significant relationships with N concentrations or rates (Table 3.2). Percent herbaceous cover was significantly correlated with both extractable NH_4^+ as expressed on a per gram organic matter and net N mineralization rates, although these relationships were weak (Table 3.2). Also, rates of net N mineralization were strongly correlated with net nitrification rates, and extractable NH_4^+ was weakly correlated with denitrification rates (Table 3.2). Net N mineralization and net nitrification rates did not effectively predict denitrification rates. Hydrological variables did not explain soil moisture or percent soil organic matter. Wetland area was also not significantly correlated with N concentrations or rates.

DISCUSSION

Hydrological and soil properties were better descriptors of N cycling rates in urban wetlands than landscape level metrics. Hydrological variables, particularly median water table levels and % water table observations < -30 cm, which describe dry and/or flashy hydrological regimes in urban wetlands, were good predictors of net nitrification rates, but they were less effective in describing net N mineralization rates and were not effective at all in predicting denitrification rates (Table 3.2). This is in accordance with Merrill and Benning's (2006) finding that variation in net nitrification rates was better explained by local scale rather than landscape scale metrics. Soil properties, specifically % soil organic matter and soil moisture, were excellent predictors of denitrification rates (Table 3.2). Ullah and Faulkner (2005) and Merrill and Benning (2006) also found these same soil properties to be important predictors of potential denitrification rates, but in contrast with my findings, both studies also suggested that landscape level metrics were important additional predictors of this N removal function. It is possible that the landscape level metrics which were evaluated in these two studies, including ecosystem type and landscape position, are good descriptors of *potential* denitrification rates rather than *actual* denitrification rates, as were measured in my study. Ecosystem type and landscape position are in theory important controlling factors on denitrification, and potential denitrification is a measure of NO_3^- removal that would occur in a soil given ideal organic substrate availability and reducing conditions. However, in urban landscapes in which urban wetlands may be hydrologically disconnected from both uplands and streams, actual denitrification rates may not be reflective of landscape metrics such as ecosystem type and landscape position. However, landscape level metrics measured in this study, such as % impervious cover, % urban land cover, and road density, which in theory should describe the degree of hydrological alteration and/or lack of connectivity between uplands and urban wetlands, were also not good predictors of denitrification rates.

Concentrations of extractable inorganic N and N cycling rates were indeed generally lower than in comparable urban systems as well as agricultural and natural systems. Extractable NO_3^- concentrations (Table 3.1) in this set of urban wetlands were considerably lower than urban riparian soils in Baltimore which ranged from 2 to 8 mg kg^{-1} (Groffman et al. 2002), although NH_4^+ pools in New Jersey wetlands were higher (3.59-14.4 mg kg^{-1}, Table 3.1) than in Baltimore (1.7-4.7 mg kg^{-1}) (Groffman and Crawford 2003). My measured rates of N cycling processes (Table 3.1) were typically lower than those measured in urban riparian zones in Baltimore (Groffman et al. 2002, Groffman and Crawford 2003); however, Baltimore measurements were potential rates, while I measured actual rates. I am not aware of other studies which measured actual rates of N cycling in urban wetlands to use for comparative purposes; however, comparisons can also be made with wetlands located in natural and agricultural settings. Denitrification rates in New Jersey were on the lower end of rates measured in a riparian forest in Georgia which was exposed to experimental N additions (Ettema et al. 1999). The static core acetylene block technique was also used in this study. New Jersey denitrification rates were in some cases an order of magnitude lower than potential denitrification rates in the same Georgia riparian forest measured using the denitrification enzyme activity procedure (Lowrance 1992). *In situ* denitrification rates in forested, shrub, and grassy sections of a riparian wetland in an agricultural region in northwestern France (Clement et al. 2002) and in 15 riparian wetlands along a flooding gradient in agricultural southwestern France (Pinay et al. 2000) were up to one order of magnitude higher than in New Jersey wetlands. In the same study average extractable concentrations of NO_3^- and NH_4^+ were similar or up to an order of magnitude higher than in New Jersey. The same pattern held in 13 riparian wetlands in agricultural landscapes along a climatic gradient in central and western Europe in terms of *in situ* denitrification rates, but net nitrification rates, in contrast, were in the same range as in New Jersey wetlands (Hefting et al. 2004).

My results show that there is a tighter mechanistic link between water table levels, and thus symptoms of altered urban hydrologic regimes, and rates of net nitrification than rates of denitrification. In particular, hydrological variables which described dryness (and thus aerobic soil conditions), such as % water table observations < -30 cm, were more effective predictors of nitrification than variables which described flashiness, such as % water table crossings at -30 cm (Table 3.2). This suggests that net nitrification rates in urban wetlands increase as water table levels decrease and as dry conditions increase.

However, median water table level and % observations < -30 cm explained only 55% and 66% of the variation in net nitrification rates (Table 3.2). Since these two variables were highly correlated with each other (Table 3.2), they clearly explain much of the same variation in net nitrification rates. Therefore some other factor besides altered hydrology must explain the remaining ~40% of variation in net nitrification rates. Rates of net N mineralization, and thus supply of NH_4^+ (the substrate for the nitrification reaction), appears to be this other factor, explaining 65% of the variation in net nitrification rates (Table 3.2). Also, net N mineralization rates were not highly correlated with mean water table levels or % observations < -30 cm, suggesting that net N mineralization rates mostly explain different variability in net nitrification rates than those hydrological variables.

Denitrification, on the other hand, was best explained by soil properties on the local, wetland scale (Table 3.2). The effect of soil properties on denitrification rates was direct, as there were strong correlations of soil moisture and organic matter content with denitrification rates. I was surprised to find that hydrological variables were not good predictors of denitrification rates and that there was little relationship between altered hydrological regimes and soil properties. Soil did not, therefore, have an indirect effect on N cycling as mediated through hydrology. There were also no evidence of a connection between indicators of watershed urbanization at the landscape scale and hydrologic alteration at the wetland scale. Thus I also did not find an indirect link between landscape urbanization and N cycling as mediated through hydrology. Based on the variables I measured, I was unable to elucidate the causes of dry and flashy hydrological patterns in these urban wetlands. It is possible that altered urban hydrology is thus driven not by landscape urbanization or soil properties, but rather by local disturbances such as ditches and berms, which I did not quantify in this study. Further testing would be required to confirm the existence of this mechanistic link. It is also possible that I did not capture the effect of stream incision on hydrology because I monitored water table levels 25 m from the stream; a stronger response might only be visible closer to the stream. Water table levels measured at this distance may reflect more complex relationships with local and regional groundwater dynamics. Another possible explanation is that the high explanatory power of the two soil properties, organic matter content and soil moisture, masked the presence of relationships of denitrification with other variables. These relationships would no doubt be weaker, but they might be important in understanding patterns of variability in denitrification rates. I attempted to remove the influence of organic matter content by testing local and landscape variables against N concentrations and rates expressed on a per gram organic matter basis. Because organic matter content and soil moisture were highly correlated (Table 3.2), this approach should also account for much of the influence of soil moisture as well. However, this approach was not successful in elucidating relationships that had been previously unseen.

Perhaps a better explanation is that patterns of hydrology and soil, and consequently N cycling rates, may be strongly influenced by the idiosyncrasies of land use history. While there are broad scale patterns of historical agricultural and forestry practices in northeastern New Jersey (Wacker and Clemens 1995), historical uses of wetlands for crops, pasture, and wood production and the timing of specific practices may have varied enough from place to place that the lasting legacy is current patterns of hydrology, soil, and N cycling rates that are difficult to generalize on a landscape or regional basis. For example, the production of leguminous crops could have increased soil fertility levels, leading to an agricultural legacy of soils with higher C:N, concentrations of extractable inorganic N, and rates of N mineralization and nitrification (Pastor et al. 1984). Soils with higher NO_3^- production may also have higher denitrification rates. N status and soil fertility may of course differ among sites as a result of natural differences in geology and soil parent material (Groffman et al. 2006). Ehrenfeld et al. (2003) described idiosyncratic hydrological patterns among urban wetlands as the "Tolstoy Effect"; here I extend the Tolstoy Effect to soil properties and N cycling rates among wetland sites representing a gradient of urban conditions. In a review of the effects of land use on stream ecosystems, Allan (2004) acknowledges that it has been difficult to identify clear patterns for several reasons, including the difficulties of separating modern and historical influences. The palynological work of Elliott and Brush (2006) also points to the importance of land use history as a confounding factor in interpreting modern soil N dynamics. I suggest that land use history and/or natural causes of soil fertility differences is a likely driver of hydrological and N cycling patterns in my urban wetlands, although this assertion requires additional testing.

Another difficulty that must be addressed when working with landscape metrics is that many of these metrics are correlated with each other. In this study I found correlations between a number of landscape metrics, including % urban land cover, % impervious cover, population density, and road density (Table 3.3). A related problem is the non-independence of land cover class percentages. An increase in the percentage of one class is by definition associated with a decrease in the percentage of another class (Snyder et al. 2003, King et al. 2005), and this can confound the effects of simple, one-parameter regressions. Neither of these problems came into play in this study for several reasons. First, the land cover classes used in my analyses were not correlated with each other (Table 3.3). Also, the explanatory power of all the landscape metrics was low for the response variables measured with a small handful of exceptions. Finally, because the regression relationships in this study are descriptive and are not meant to be employed in predictive models, simple one-parameter regressions should be sufficient to analyze the relative strength of various relationships despite problems of covariance and non-independence (Snyder et al. 2003).

Are urban wetlands acting as buffers for excess N from upland land uses? It is difficult to answer this question emphatically in the context of N retention without further research into actual N retention rates. This would require quantification of N input and outputs budgets, which was beyond the scope of this study. My findings of higher net nitrification rates and lower denitrification rates in dryer soils, however, do raise concerns that urban-impacted wetlands may be releasing NO_3^- to receiving streams and thus contributing to eutrophication of downstream water bodies. However, the ultimate control of denitrification rates by soil properties suggests that management efforts targeted at maintaining soil moisture content characteristic of saturated but not inundated soils may effectively maximize the ability of these wetlands to perform denitrification and thus remove excess N. It is not clear what the best strategy is for maintaining soil moisture, as my results suggest that soil moisture is not directly controlled by either water table levels, hydrological regimes, or landscape level % imperviousness. My results suggest that management efforts aimed at enhancing NO_3^- removal capacity of urban wetlands should be targeted at the local level. These efforts, though, should be organized at the watershed level in order to maintain a regional perspective for wetland and water quality protection. It is also critical to make explicit connections between NO_3^- sources and sinks to target important sources of NO_3^- as well as the mechanisms which lead to NO_3^- removal or leaching loss. This type of connection may be difficult to elucidate in many field situations which have spatially variable groundwater and surface runoff inputs as well as complex groundwater flowpaths; however, the task should be easier in more controlled settings such as constructed wetlands or stormwater detention basins (Kadlec and Knight 1996, Zhu et al. 2004).

In summary, I find that local scale factors are better predictors of NO_3^- production and removal in urban, forested wetlands than landscape level variables. In particular, hydrological variables which serve as indicators of dry conditions (median water table level and percent water table observations < -30 cm) were highly correlated with net nitrification rates. Net N mineralization rates were also strongly correlated with net nitrification rates. Local scale soil properties, in particular soil moisture and percent soil organic matter, were the best predictors of denitrification rates. Surprisingly, hydrological patterns were not correlated with denitrification rates or soil properties like soil moisture or percent soil organic matter. I also did not find a relationship between landscape level urbanization indicators and hydrological variables, nor did I find an influence of soil texture on hydrology. I was thus unable to explain the variability of water table levels among sites. It is possible that local hydrological conditions I did not measure, such as ditches and berms, are the major drivers of water tables in urban wetlands. Land use history may also play an important role in determining present day patterns of hydrology. My findings suggest that management efforts aimed at maximizing NO_3^- removal functions in urban wetlands should focus on the local scale, and on soil moisture in particular.

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CHAPTER 4

Evaluating the relative contributions of atmospheric nitrogen deposition and endogenous nitrate deposition on nitrate leaching from urban wetlands

Introduction

Human activities, in particular food and energy production, have resulted in dramatically increased rates and amounts of nitrogen (N) inputs to the terrestrial N cycle (Vitousek et al. 1997, Jaworski et al. 1997, Smil et al. 2001, Howarth et al. 2002, Van Breeman et al. 2002, Galloway et al. 2003). Elevated anthropogenic N inputs can have negative consequences for the integrity of atmospheric, terrestrial, freshwater, and coastal marine systems, as demonstrated by elevated atmospheric ozone production, N saturation of historically N limited terrestrial systems, acidification and loss of biodiversity in lakes and streams, and eutrophication and hypoxia of coastal waters (Vitousek et al. 1997, Lowrance et al. 1997, Mitsch et al. 2001, Aber et al. 2003, Driscoll et al. 2003, Galloway et al. 2003). N saturation of terrestrial systems, which occurs when the microbial and plant demand for inorganic N is exceeded, is thought to increase soil acidification, rates of nitrification, and rates of nitrate (NO_3^-) leaching to shallow groundwater and eventually surface waters, as well as cause forest decline and species composition shifts (Aber et al. 1989, Stoddard 1994, Aber et al. 1998, Aber et al. 2003). NO_3^- leaching losses due to N saturation may in part be responsible for N loading of surface waters and estuaries common throughout much of the world (Vitousek et al. 1997, Lowrance et al. 1997, Caraco and Cole 1999, Mitsch et al. 2001, Van Breeman et al. 2002, Van Drecht et al. 2005, Boyer et al. 2006).

The interrelated issues of atmospheric N deposition, forest decline, and eutrophication of coastal waters have put an increased emphasis on documenting and understanding mechanisms of watershed N retention and loss in a variety of landscapes. As global trends in urbanization are predicted to continue well into the 21st century (UN 2006), additional attention has recently been focused on urban landscapes (Pickett et al. 2001, Groffman et al. 2004). It might be expected that urban ecosystems would be less N retentive than less human-dominated systems due to multiple types and scales of disturbance combined with ubiquitous and large nonpoint N sources. In particular, urban ecosystems are subjected to widespread hydrological alterations due to engineered stormwater management structures which rapidly remove stormwater from impervious surfaces to receiving streams. This has multiple effects on urban streams, including incision of streambanks from higher peak flows, and reduced infiltration causing a regional lowering of water tables and thus reduced baseflow (Paul and Meyer 2001, Meyer et al. 2005, Walsh et al. 2005). Lower water retention times in biological systems may result in less biological processing of NO_3^- (Zhu et al. 2004). Impervious surfaces may then act as conduits for NO_3^- transport via surface flow to surface waters (Arnold and Gibbons 1996). Nonpoint sources of N are likely larger in urban watersheds due to chemical fertilizer use in lawn and landscaping management, pet waste, and leaky sewage and septic systems (Zhu et al. 2004, Groffman et al. 2004, Law et al. 2004, Kaye et al. 2006). However, despite these pervasive disturbances and nonpoint N sources, the few studies which have documented watershed scale N dynamics in urban ecosystems have found surprisingly high retention rates. Although N fluxes were high, 75% of inputs were retained in a suburban watershed in Baltimore, MD, which is similar to rates reported for several forested systems (Groffman et al. 2004). Wollheim et al. (2005) found that 65-85% of estimated N inputs were retained in an urbanizing headwater watershed in Massachusetts, compared to 93-97% in a paired forested watershed. Riverine export of NO_3^- represented only 3% of total exports in Phoenix, AZ, and the city experiences a net N accumulation of 21% of inputs (Baker et al. 2001). These findings suggest that N saturation is not occurring in urban ecosystems, although it is not clear whether this pattern is universal across urban landscapes or what exactly the mechanisms are for this retention.

Wetland ecosystems are commonly perceived as N sinks in landscapes because their saturated soils promote NO_3^- removal as nitrogen gases to the atmosphere through the anaerobic microbial process of denitrification. Thus wetlands are thought to promote watershed N retention by acting as buffers which intercept NO_3^- runoff from upland land uses before it drains to surface waters. This function has been widely documented in riparian zones receiving runoff from agricultural landscapes (Lowrance et al. 1984, Cooper 1990, Lowrance 1992, Simmons et al. 1992, Haycock and Pinay 1993, Gilliam 1994, and Hill 1996). Several studies of wetlands in urbanized landscapes, however, have found changes in N cycling process rates such as higher rates of net N mineralization and net nitrification (Hanson et al. 1994, Zhu and Ehrenfeld 1999, Groffman et al. 2002, Chapter 1/Stander and Ehrenfeld submitted) due to lowered water tables and thus aerobic soils (Groffman et al. 2002, Ehrenfeld et al. 2003, Chapter 1/Stander and Ehrenfeld submitted), higher NO_3^- inputs from upland urban land uses (Hanson et al. 1994), and higher pH and mineral content of wetland peat soils in developed versus undeveloped watersheds (Zhu and Ehrenfeld 1999). Physical modifications, including ditches and berms, of the wetland itself may also affect hydrological patterns and thus N cycling rates (Ehrenfeld 2000). While my previous work documented lower rates of denitrification in hydrologically-altered wetlands (Chapter 1/Stander and Ehrenfeld submitted), other studies have found high denitrification potential in urban riparian zones (Groffman and Crawford 2003) and a range of NO_3^- removal rates in forested and mowed riparian zones (Addy et al. 1999). My previous research has also demonstrated that the influence of watershed scale urbanization can be mediated by wetland scale soil properties, such as high soil organic matter content which promotes NO_3^- removal functions (Chapter 3). Although I have documented higher rates of net nitrification and lower rates of denitrification in sites with dry and/or flashy hydrology compared to sites with wetter hydrology, I do not have direct evidence of N retention or loss in urban wetlands in northeastern New Jersey. In this study I measure NO_3^- outputs via leaching to shallow groundwater to determine whether changes in N cycling process rates are resulting in NO_3^- loss.

If urban wetlands are in fact leaching NO_3^-, it may also be a direct effect of atmospheric N deposition. If N saturation has been reached in urban wetlands in northeastern New Jersey, N inputs from atmospheric deposition could leach directly to groundwater and discharge to streams without being first processed by soil microbes (Jaworski et al. 1997). Rates of atmospheric N deposition have increased as much as 90% in the northeastern United States over historical levels as a result of human activities, particularly fossil fuel combustion (Vitousek et al. 1997). Atmospheric N deposition represented 31% of N inputs and was the largest single N source to the combined area of 16 watersheds in the northeastern US (Boyer et al. 2002). Few studies have attempted to quantify rates of atmospheric N deposition specifically in urban areas, although Lovett et al. (2000) did document throughfall deposition of inorganic N that was twice as high at the urban end of an urban to rural gradient from New York City north into less developed landscapes. Additionally, there is a rich literature on N cycling processes in forested ecosystems in Europe and North America which are exposed to elevated levels of atmospheric N deposition. While the majority of studies have found that most of the deposited NO_3^- is retained by a combination of plant uptake and microbial incorporation into forest floor or soil organic matter (Nadelhoffer et al. 1995, Stuanes et al. 1995, Tietema et al. 1998, Magill et al. 2000, Providoli et al. 2005) or by abiotic retention (Edwards and Williard 2006), forests with high initial soil N availability and rapid rates of soil N cycling may be less retentive of high atmospheric N inputs (Emmett et al. 1998, Aber et al. 1998). Substantial and chronic NO_3^- leaching losses have been observed in chaparral and mixed conifer stands in the Los Angeles region of California (Bytnerowicz and Fenn 1996), undisturbed forested catchments in Finland (Lepisto 1995), high elevation spruce-fir forests in the Appalachians (Johnson et al. 1991), eastern hardwood watersheds in West Virginia (Gilliam et al. 1996), and high elevation alpine watersheds in Colorado's Front Range (Williams et al. 1996). In a review of data from 139 European forests, Dise et al. (1998) found that 50% of inorganic N leaching losses were explained by inorganic N fluxes in throughfall. NO_3^- losses in leachate can, however, be attributed to other factors, including natural succession and stand age (Cairns and Lajtha 2005), C:N ratio (Lovett et al. 2002), pH (Dise et al. 1998), and tree species composition (Lovett et al. 2002), especially the presence of N-fixing tree species such as alder (Compton et al. 2003).

Recent methodological advances have made it possible to use dual isotope technology to distinguish between atmospheric N deposition and soil nitrification as sources of NO_3^- in soil water. Because there is little isotopic separation in $\partial^{15}N$ values between atmospheric NO_3^- compared to NO_3^- generated by nitrification, it is necessary to also use ^{18}O isotopes in NO_3^-, which range from +25 to +90 ‰ in atmospheric NO_3^- (Kendall et al. 1998, Ohte et al. 2004) and -5 to +15 ‰ in nitrified NO_3^- (Mayer et al. 2001). Previous analytical techniques, in particular the combustion method (Chang et al. 1999, Silva et al. 2000) required large volumes (> 1 L) of low concentration material, which is impractical for studies involving soil water. The recently developed denitrifier method (Sigman et al. 2001, Casciotti et al. 2002) represents a major improvement. In the denitrifier method a known quantity of sample NO_3^- is denitrified to nitrous oxide (N_2O) using bacterial strains which lack the N_2O reductase enzyme and thus cannot reduce NO_3^- completely to N_2. The resulting N_2O is analyzed for stable isotopes of nitrogen and oxygen. In comparison with the combustion method, the denitrifier method has much lower sample volume requirements as well as improvements in precision and analysis time. Most studies which have used dual isotope analysis to compare the contributions of atmospheric NO_3^- versus nitrified NO_3^- in NO_3^- exports, typically in stream water, have found that NO_3^- which is exported from watersheds has been microbially-processed and has not leached directly from atmospheric inputs (Williard et al. 2001, Sickman et al. 2003, Pardo et al. 2004, Piatek et al. 2005, Mitchell et al. 2006, Campbell et al. 2006). However, several studies have found an atmospheric signal in NO_3^- exports, including Durka et al. (1994) in springwater in northwestern Germany, Spoelstra et al. (2001) in streams and groundwater in Ontario, Chang et al. (2002) in rivers draining urban land uses in the Mississippi River Basin, and Campbell et al. (2002) in streams when snowmelt likely entered streams from overland flow. Few of these studies have investigated isotope dynamics in urban systems and only one study evaluated flowpath dynamics in a riparian zone (McGlynn et al. 1999). Almost all existing studies used the combustion method. I used the denitrifier method to evaluate the relative contributions of atmospheric NO_3^- versus nitrified NO_3^- as sources of NO_3^- export in soil water below the rooting zone in urban wetlands.

The objective of this study was to investigate patterns of NO_3^- retention and loss in urban wetlands along a gradient from very urban to less urban conditions. I hypothesized that concentrations and fluxes of NO_3^- would be higher in both throughfall and leachate in sites located in more urban watersheds. I also predicted that overall nitrification would be a more important contributor to NO_3^- export, but I expected to see a higher contribution of atmospheric inputs in these urban sites than in studies of less human-dominated systems. I measured concentrations and fluxes of NO_3^- in throughfall and leachate over the course of one year to determine whether NO_3^- inputs and outputs increased with increasing urbanization. There are other possible types of NO_3^- inputs and outputs, including groundwater discharge and surface runoff; the purpose of this study was not to quantify a rigorous mass balance but rather to characterize inputs and outputs of interest. I also measured NO_3^- isotope values in throughfall and soil water samples to compare the contributions of exogenous atmospheric NO_3^- inputs and NO_3^- produced endogenously by soil nitrification to NO_3^- in soil water and leachate.

Methods

Study Sites

Nine palustrine, forested wetland sites were selected in northeastern New Jersey (Figure 4.1). Hydrology, soil properties, N cycling processes, and watershed urbanization have all previously been characterized (Chapters 1-3, Stander and Ehrenfeld submitted). All sites are located within the Piedmont physiographic province. This places the sites in the most urbanized region of the state and within the third largest urban agglomeration in the world with a population of 18.7 million (UN 2005). Sites were chosen to represent a gradient of very urban to less urban conditions according to the results of a Principal Components Analysis (PCA) (Figure 4.2) of the urbanization indicator values listed for the nine sites in Table 4.1. There were two gradients of urbanization represented by the two axes. The first axis (PC 1) represents a gradient of land cover from a high percentage of upland forest to a high percentage of residential land cover. The second axis (PC 2) represent a gradient of land cover from a high percentage of urban land cover to a high percentage of wetland land cover. Urban land cover is very closely associated with other measures of urbanization, including population density, road density, industrial land cover, etc. Sites which cluster on both axes with indicators associated with urbanization, including residential and urban land cover, fall on the very urban end of the urbanization gradient in this study (Figure 4.2). EZ is thus the most urban site, and OR, PA, and CH fall next on the gradient towards decreasing urban intensity (Figure 4.2, Table 4.1). Sites which cluster on both axes with upland forested and wetland land cover indicators fall on the less urban end of the urbanization gradient. Sites BB and GR are the least urban, and M5 and MW are next on the gradient towards increasing urban intensity (Figure 4.2, Table 4.1). M6 falls in between with intermediate amounts of upland forest, urban, wetland, and residential land

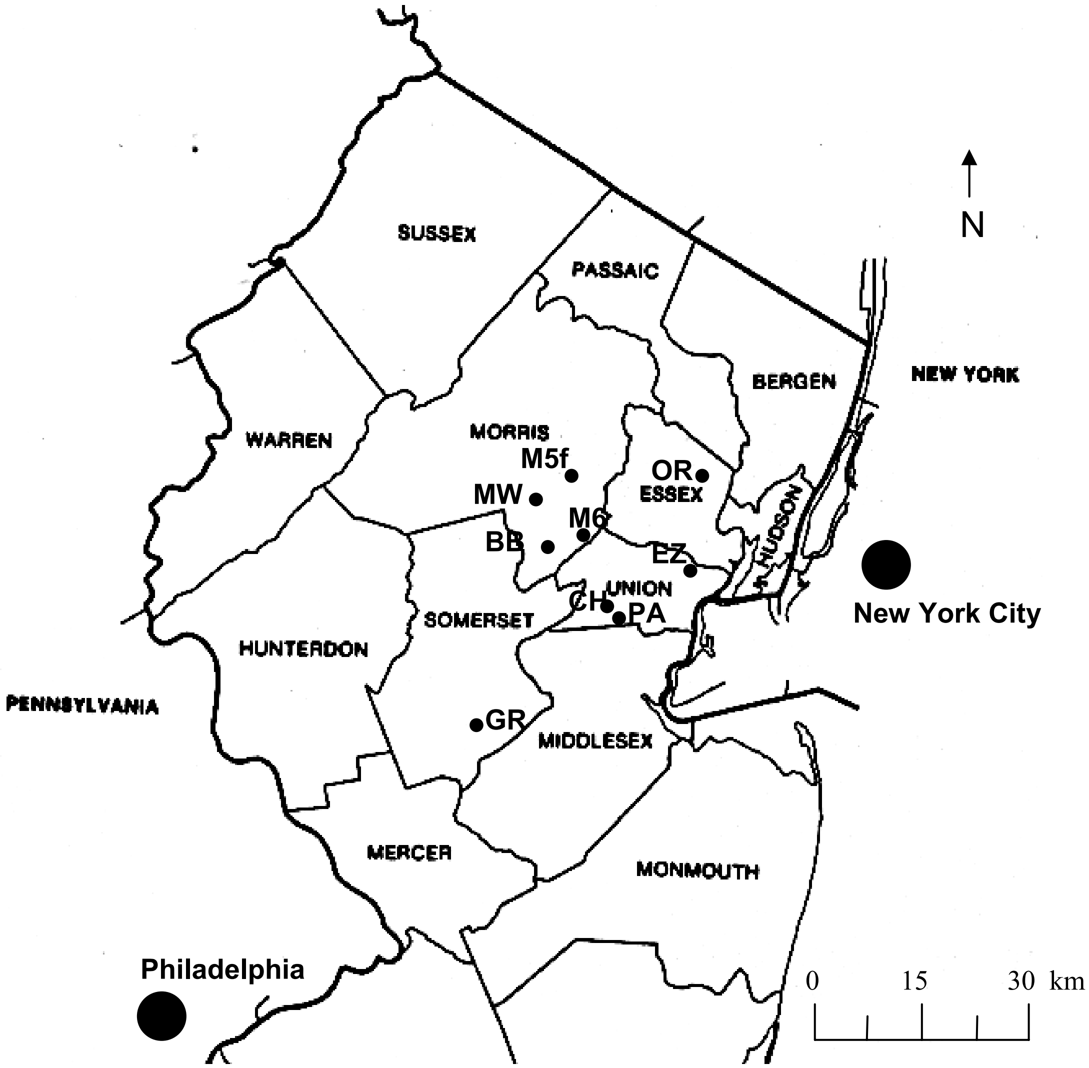

Figure 4.1. Location of study sites in northeastern New Jersey. This figure is modified from Chapter 1/Stander and Ehrenfeld (submitted).

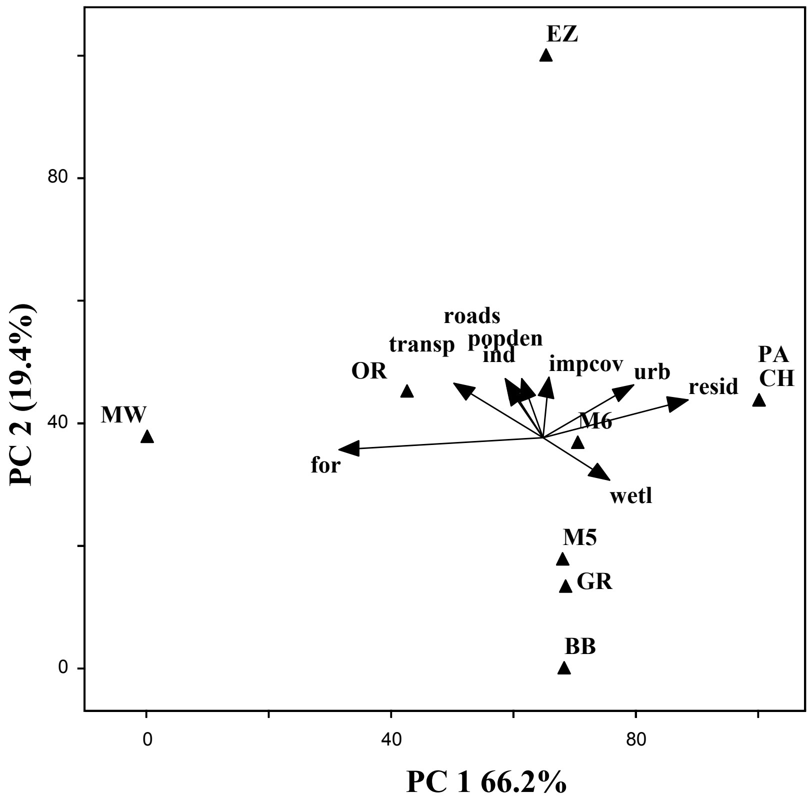

Figure 4.2. Ordination of urbanization indicators and sites. Indicator abbreviations are as follows: for = upland forest, transp = % transportation land cover, roads = road density, popden = population density, ind = % industrial land cover, impcov = % impervious cover, wetl = % wetland land cover, urb = % urban land cover, and resid = % residential land cover.

Table 4.1. Values of indicators of watershed urbanization for all study sites.

Urbanization Indicator	*EZ*	*OR*	*CH*	*PA*	*M5*	*M6*	*MW*	*BB*	*GR*
% Impervious Cover	**46.2**	**25.5**	**23.6**	**23.6**	**16.2**	**25.8**	**20.3**	**8.9**	**9.3**
% Forested Land Cover	**4.25**	**29.7**	**6.39**	**6.39**	**15.8**	**10.8**	**49.9**	**12.3**	**19.1**
% Urban Land Cover	**92.7**	**66.7**	**79.2**	**79.2**	**47.4**	**72.2**	**46.4**	**31.2**	**46.0**
% Wetland Land Cover	**2.39**	**2.53**	**13.5**	**13.5**	**34.9**	**15.9**	**1.86**	**52.3**	**14.7**
% Residential Land Cover	**59.9**	**43.8**	**66.0**	**66.0**	**35.2**	**36.4**	**28.6**	**26.1**	**42.0**
% Transportation Land Cover	**1.05**	**0.75**	**0.45**	**0.45**	**0.31**	**0.52**	**0.73**	**.34**	**0.18**
% Industrial Land Cover	**8.34**	**0.68**	**0.42**	**0.42**	**0.54**	**2.35**	**2.17**	**0.03**	**NA**
Population Density (people/km^2)	**3931**	**1722**	**1262**	**1262**	**663**	**687**	**1332**	**270**	**484**
Road Density (km/km^2)	**33.1**	**14.6**	**14.9**	**14.9**	**12.8**	**11.5**	**19.0**	**4.6**	**7.7**

cover (Figure 4.2, Table 4.1). Sites are more fully described in Chapter 1/Stander and Ehrenfeld (submitted). All sites had a mature canopy dominated by red maple (*Acer rubrum* L.) and plant communities as described by Ehrenfeld (2005).

Throughfall Collection and Analysis

Throughfall was collected in three locations in each of the nine sites. Collectors were placed 30 m apart in a triangular formation, with two collectors on either end of an existing transect used for long-term hydrological monitoring. Collector design was modified from Lovett et al. (2000). One 20 cm diameter polyethylene funnel was affixed approximately one m off the ground on a PVC stake to minimize splashing from the ground into the funnel. The funnel was connected with inert, flexible tubing to a four L polyethylene collection carboy. The carboy was wrapped in duct tape and buried halfway in the ground to keep collected sample cool and dark. A glass fiber plug was placed in the funnel stem to filter out large particulate material. During the winter months (December through March) snow and ice were collected in 20 L buckets lined with plastic bags. One collector was used in each site. Samples were melted in the laboratory to obtain volumes. Bulk collectors were not deployed due to limited access to open areas and vandalism concerns.

Weekly collections were made once per month from June 2005 through May 2006 in all sites except MW, which was initiated in July 2005. During one month each season, weekly collections were made each week of the month. All nine sites were visited within 24 hours of each other. Following each collection all funnels and carboys were replaced with acid washed funnels and carboys, tubing was rinsed with deionized water, and filter plugs were replaced. Throughfall volumes were measured in the field using a graduated cylinder, and a 20 ml aliquot was taken in a glass, borosilicate scintillation vial for inorganic N and pH analysis. During one week per month an additional 20 ml aliquot was taken for isotope analysis. Samples were kept on ice and immediately filtered through pre-combusted GF/F filters upon return to the laboratory. Samples were then transferred to polyethylene bottles and frozen until analysis.

Samples were analyzed colorimetrically for NO_3^- and ammonium concentrations on a QuikChem® Flow Injection Analyzer+ 8000 Series (Lachat Instruments, Loveland, CO). NO_3^- concentrations for each collector on each sampling date were weighted by precipitation amount to account for different collector sizes in the winter versus the other seasons. I refer to these as volume-weighted concentrations. Mean volume-weighted concentrations were taken as the average for each site of the three collectors over the entire sampling period. Throughfall NO_3^- fluxes, which reflect the transport of NO_3^- to the forest floor, were calculated over the entire sampling period as the sum of volume-weighted NO_3^- concentrations divided by the total precipitation amount over the course of the year. Fluxes are not presented on a per unit time basis because collections were not continuous over the course of the year.

Soil Water Collection and Analysis

In each of the nine sites, three tension lysimeters equipped with a porous ceramic cup (Soilmoisture Equipment Corporation, Santa Barbara, CA) were installed vertically to a depth of 50 cm (below the rooting zone). Installation was completed during the fall prior to initiation of collection the following summer to allow lysimeters to equilibrate during fall and spring rains. Lysimeters at GR were installed during the spring of 2005; sampling at this site commenced in October. Lysimeters were sealed using bentonite to avoid seepage of rainwater down the sides of the lysimeter and were located in close proximity to the three throughfall collectors. Zero-tension lysimeters were not used because they are not practical in sites which may be saturated or inundated for extended periods of time. Tension lysimeters also have an advantage in that they collect interstitial soil water during periods of little or no macropore flow. Lysimeters were sampled in conjunction with throughfall collectors. As described above for throughfall collection, soil water volumes were measured in the field, and 20 ml aliquots were filtered upon return to the laboratory and frozen until colorimetric analysis for inorganic N. NO_3^- concentrations were volume-weighted for each lysimeter and each sampling date, then summed over all lysimeters and dates and averaged per site, then finally divided by total site volume to generate volume-weighted mean concentrations of soil water NO_3^-. To calculate leachate NO_3^- fluxes, I first calculated soil water fluxes for each lysimeter over the entire collection period. Soil water fluxes were estimated as the difference between weekly bulk precipitation amounts and weekly evapotranspiration amounts. Bulk precipitation amounts were estimated from throughfall amounts assuming that throughfall amounts are approximately 80% of bulk precipitation during spring, summer, and fall and approximately 96% of bulk precipitation during winter (Lovett et al. 2000, Levia 2004, Hafner et al. 2005, Pryor and Barthelmie 2005, Levia and Frost 2006, Starr et al 2007). Evapotranspiration estimates for six nearby airports were obtained from the Northeast Regional Climate Center (Cornell University). Estimates were modeled using a modification of the British Meteorological Office Rainfall and Evaporation Calculation System (MORECS) for vegetation types in the northeast United States. MORECS uses a variation of the Penman-Monteith Equation which accounts for solar radiation, air temperature, vapor pressure and wind speed in calculations of evaporation (DeGaetano et al. 1994). Leachate NO_3^- fluxes were calculated for sampling dates which had a positive value of recharge (precipitation amount minus evapotranspiration amount). Fluxes were calculated as the product of soil water NO_3^- concentrations and recharge amounts for each lysimeter and each collection date, summed over all collection dates, divided by the total amount of recharge, and averaged over all lysimeters for each site. As for throughfall, fluxes are not presented on a per unit time basis because collections were not continuous over the course of the year. These fluxes are likely underestimates because in wetlands which are saturated through much of the year, upwelling of the shallow groundwater to surface soils likely causes soil to be wetter than evapotranspiration estimates allow (Gold and Kellogg 1997). This means that wetland soils are more often at field capacity, and that smaller precipitation amounts may be able to initiate leaching. However, because water tables are lower than 30 cm in some sites, particularly EZ and OR over long periods of time (Chapter 1/Stander and Ehrenfeld submitted), I used conservative estimates for soil water fluxes and thus recharge.

Isotope Analysis

Monthly samples of throughfall and soil water were analyzed for natural abundance $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios of NO_3^- at Princeton University using the denitrifier method (Sigman et al. 2001, Casciotti et al. 2002). Sealed vials containing media inoculated with *Pseudomonas aureofaciens*, a denitrifying bacterium which lacks the N_2O reductase enzyme, were purged with N_2 gas for five hours to remove oxygen. *P. aureofaciens* was used for this analysis because its low levels of oxygen exchange with water (~3-10%) compared to another commonly used bacterial strain, *Pseudomonas* *chlororaphis* (~60-80%), produce more accurate values of $\partial^{18}O$ (Hastings et al. 2003). Throughfall and soil water NO_3^- separate more clearly by $\partial^{18}O$ values than $\partial^{15}N$ values, so I was more interested in the accuracy of $\partial^{18}O$ measurements. Analysis of $\partial^{15}N$ values using *P. aureofaciens*, however, may overestimate the true $\partial^{15}N$ by 1-2 ‰ due to a mass-independent contribution of ^{17}O (Sigman et al. 2001, Hastings et al. 2004). Sample volumes which contained 20 nmol of NO_3^- were added to the vials, which were then stored inverted to reduce leaks in the dark overnight. The sample NO_3^- is thus quantitatively converted to N_2O. The isotopic composition of the N_2O is then measured on a DeltaPlus IRMS in continuous flow mode. $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios are determined from the 45/44 and 46/44 ion current ratios, respectively. The denitrifier method was critical for this analysis because higher sensitivity relative to the combustion method allowed for the analysis of soil water samples with NO_3^- concentrations as low as 0.7 μM even when sample volume was limited. Samples with concentrations lower than 5 μM were first concentrated using a Turbo Vap LV evaporator (Caliper Life Sciences, Inc., Hopkinton, MA). Because NO_2^- can also be converted to N_2O by *P. aureofaciens* and thus overestimate isotope values, NO_2^- was first removed from samples in which NO_2^- concentrations were 3% or more of the NO_3^- concentrations, using methods developed by Granger et al. (2003).

$\partial^{15}N$ values were referenced to atmospheric N_2, and $\partial^{18}O$ values were referenced to Vienna Standard Mean Ocean Water (VSMOW) using the internationally recognized standard IAEA-NO-3, which has an assigned value of 4.7‰ versus atmospheric N_2 for $\partial^{15}N$ (Bohlke and Coplen 1995) and a reported range of 22.7 to 25.6‰ for $\partial^{18}O$ versus VSMOW (Bohlke et al. 2003). USGS34 and USGS35 reference materials were used as secondary checks on the correction scheme. $\partial^{15}N$ values were corrected for a blank associated with the bacterial culture; blanks were analyzed with each run. A correction was also made for the contribution of ^{17}O to the peak at mass 45. $\partial^{18}O$ values were corrected for the blank and also for exchange of oxygen atoms with water during denitrification (Casciotti et al. 2002). Isotope values throughout the text are presented using the delta (∂) notation in units of per mil (‰), which means:

$\partial^{15}\text{Nsample} = ((^{15}N/^{14}N)_{\text{sample}}/(^{15}N/^{14}N)_{\text{reference}} - 1) \times 1000$ ‰

and

$\partial^{18}\text{Osample} = ((^{18}O/^{16}O)_{\text{sample}}/(^{18}O/^{16}O)_{\text{reference}} - 1) \times 1000$ ‰

where the $^{15}N/^{14}N$ reference is N_2 in air and the $^{18}O/^{16}O$ reference is VSMOW.

Data Analysis

Throughfall and soil water NO_3^- concentrations and fluxes were regressed against nine indicators of watershed urbanization (Table 4.1). Lysimeters only successfully collected soil water in six of the nine sites. Therefore, soil water NO_3^- concentrations and leachate fluxes were not analyzed in the remaining three sites (CH, PA, and BB), and these sites were removed from all analyses which involved soil water parameters. Since precipitation amounts are an important controlling factor on throughfall fluxes (Lovett et al. 2000), throughfall and soil water variables were also regressed against precipitation fluxes. Throughfall NO_3^- concentrations and fluxes were also tested as predictor variables of soil water NO_3^- concentrations and leachate fluxes. Soil water NO_3^- concentrations and leachate fluxes were also regressed as response variables against previous measurements of hydrological variables, soil properties, and N cycling process rates for each site, as reported in Chapter 1/Stander and Ehrenfeld submitted. I also regressed $\partial^{15}N$ and $\partial^{18}O$ values in throughfall and soil water against throughfall and soil water NO_3^- concentrations and fluxes, watershed urbanization indicators, and precipitation amounts. Tests were performed in Sigma Plot (Systat Software Inc., ver. 9.0) as a series of simple, one-parameter regressions.

A simple two end member mixing model analysis (Kendall 1998, Phillips and Gregg 2001, 2003) was used to quantify the relative contributions of atmospheric NO_3^- compared to NO_3^- (source 1) from soil nitrification (source 2) to NO_3^- in soil water below the rooting zone and thus potentially available for leaching. Because I did not measure $\partial^{18}O$ of NO_3^- generated from nitrification, I used the accepted range of -5 to +15‰ for nitrified NO_3^- (Kendall et al. 1998, Mayer et al. 2001, Pardo et al. 2004). The mixing model was run multiple times using both ends of the nitrification $\partial^{18}O$ range, thus generating a range of possible values for the proportional contribution of each source. $\partial^{15}N$: $\partial^{18}O$ ratios were also analyzed to qualitatively assess source contributions to soil water as well as look for evidence of fractionation due to denitrification. The presence of denitrification was also evaluated based on comparisons of $\partial^{15}N$ and NO_3^- concentration values. Seasonal patterns in throughfall and leachate concentrations and isotope values were qualitatively evaluated to gain insight on possible changes in source patterns or atmospheric chemistry by season.

Results

Throughfall and Leachate Concentrations and Fluxes

Volume-weighted mean concentrations of throughfall NO_3^- varied more than throughfall NO_3^- fluxes (Table 4.2). Throughfall NO_3^- concentrations were positively correlated with two, and throughfall fluxes with six, of nine total indicators of watershed

Table 4.2. Means and standard error (SE) of volume-weighted mean concentrations and fluxes of NO_3^- in throughfall and soil water, and precipitation amounts for each site. Lysimeters did not collect soil water at CH, PA, and BB. Standard errors are not presented for leachate fluxes for M6 and MW because leaching occurred in only one of the three lysimeters at both sites.

Site	***Throughfall NO_3^- Concentra-tion (umol/L)***	***Throughfall NO_3^- Flux (mmol/m^2)***	***Soil Water NO_3^- Concentration (umol/L)***	***Leachate NO_3^- Flux (mmol/m^2)***	***Precipitation Amount (cm)***
EZ	46.2 (2.9)	6.92 (0.60)	14.2 (2.9)	0.641 (0.016)	15.0 (0.98)
OR	36.4 (1.8)	3.40 (0.21)	114.9 (13.3)	7.16 (2.8)	9.33 (0.30)
CH	46.9 (1.4)	5.43 (0.13)	N/A	N/A	11.6 (0.087)
PA	34.4 (8.9)	4.53 (1.2)	N/A	N/A	12.6 (1.4)
M5	39.9 (1.2)	3.61 (0.21)	10.7 (3.7)	0.498 (0.15)	9.06 (0.51)
M6	43.2 (1.9)	3.45 (0.070)	30.6 (2.1)	1.97	8.11 (0.46)
MW	31.2 (2.6)	2.30 (0.14)	0.716 (0.058)	0.00753	7.49 (0.30)
BB	25.6 (1.7)	2.83 (0.29)	N/A	N/A	10.9 (0.39)
GR	17.5 (0.77)	2.84 (0.040)	33.8 (8.8)	4.51 (1.2)	16.4 (0.61)

urbanization (Table 4.3). Although NO_3^- concentrations were not correlated with as many of the urban indicators, higher slopes in the regression models suggest that concentrations responded more dramatically to urbanization than fluxes (Table 4.3). Higher r^2 values for the correlations involving fluxes, however, demonstrate stronger relationships between fluxes and urban indicators (Table 4.3). Some of these urban indicators were correlated with each other (Figure 4.2, Chapter 3 Figure 3.3). Neither throughfall NO_3^- concentrations nor fluxes were correlated with precipitation amounts, suggesting that changes in fluxes along the urbanization gradient are related more to NO_3^- concentrations than precipitation amounts (Table 4.2). At most sites concentrations were typically lower and much less variable during the winter than the other seasons (Figure 4.3).

Volume-weighted mean soil water concentrations of NO_3^- and leachate NO_3^- fluxes both varied over three orders of magnitude (Table 4.2). Soil water concentrations varied over a wider range than throughfall concentrations (Table 4.2). Neither soil water concentrations nor leachate fluxes of NO_3^- were correlated with any indicators of watershed urbanization. Variability in concentrations and fluxes also were not explained by rates of N cycling processes, soil properties, or hydrological variables (measurements described in Chapters 1-3). Soil water concentrations were uniformly low over time in all sites except OR (Figure 4.4). Leachate fluxes were lower than throughfall fluxes in four of the six sites (Table 4.2, Figure 4.5), suggesting overall N retention in most sites (except OR and GR). There were no significant relationships between throughfall and soil water NO_3^- concentrations or between throughfall and leachate NO_3^- fluxes, giving some evidence for a lack of a direct atmospheric influence on NO_3^- leaching loss.

Table 4.3. Significant relationships between volume-weighted mean throughfall NO_3^- concentrations and throughfall NO_3^- fluxes with indicators of watershed urbanization. r^2 values are presented with significance levels (* = $p<0.05$, ** = $p<0.01$).

Throughfall Variable	*Indicator Variable*	*Regression Model*	*r^2*
Volume-Weighted NO_3^- Concentration	**% Impervious Cover**	y=0.6564x+21.1419	0.55 *
Volume-Weighted NO_3^- Concentration	**% Urban Land Cover**	y=0.3562x+13.4765	0.55 *
NO_3^- Flux	**% Impervious Cover**	y=0.1063x+1.5691	0.65 **
NO_3^- Flux	**% Forested Land Cover**	y=-0.0674x+5.0825	0.45 *
NO_3^- Flux	**% Urban Land Cover**	y=0.0608x+0.1306	0.71 **
NO_3^- Flux	**% Residential Land Cover**	y=0.0772x+0.4577	0.66 **
NO_3^- Flux	**Population Density**	y=0.0010x+2.5770	0.61 *
NO_3^- Flux	**Road Density**	y=133.3068x+1.9495	0.54 *

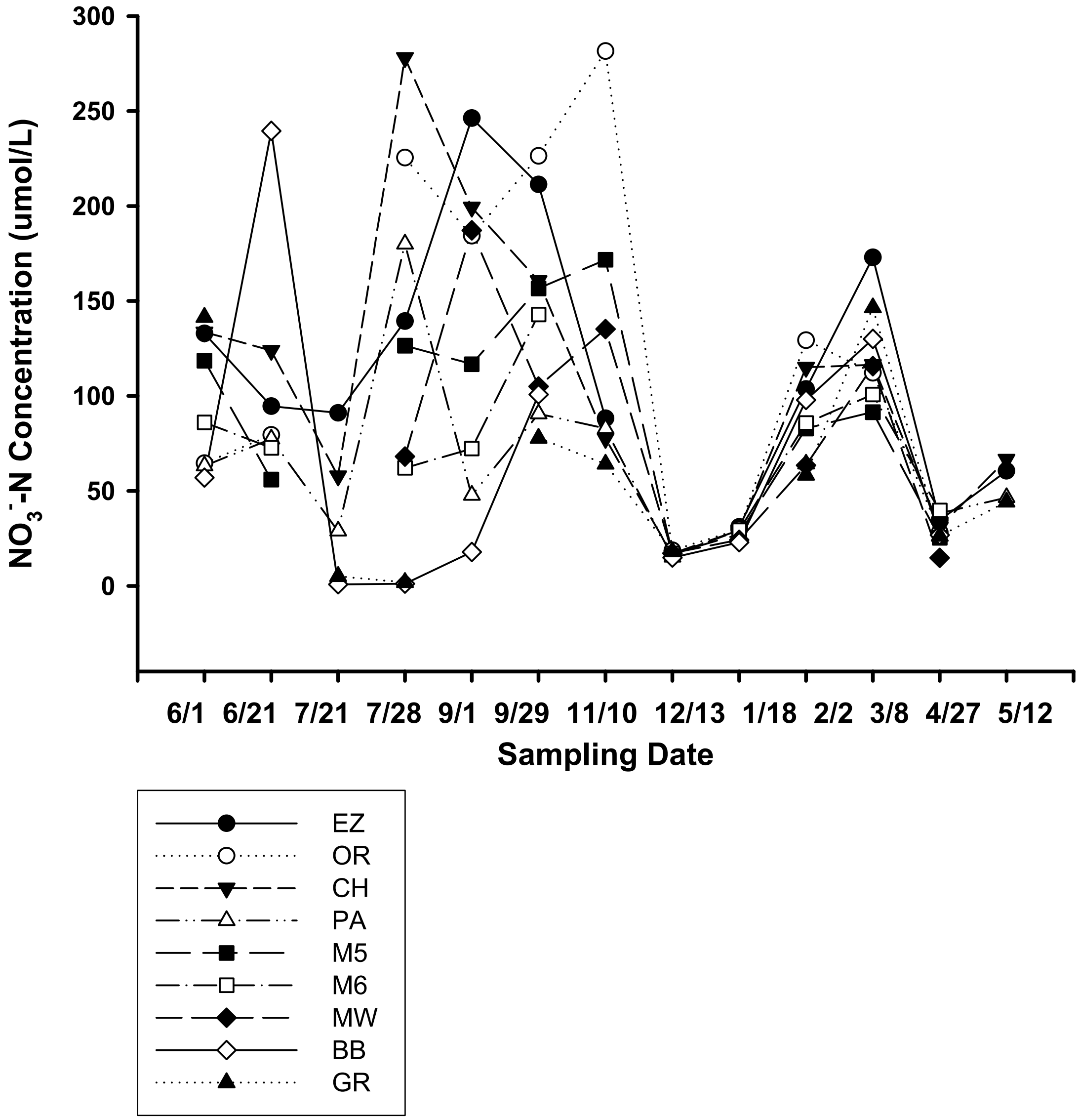

Figure 4.3. NO_3^--N concentrations in throughfall from June 2005 through May 2006.

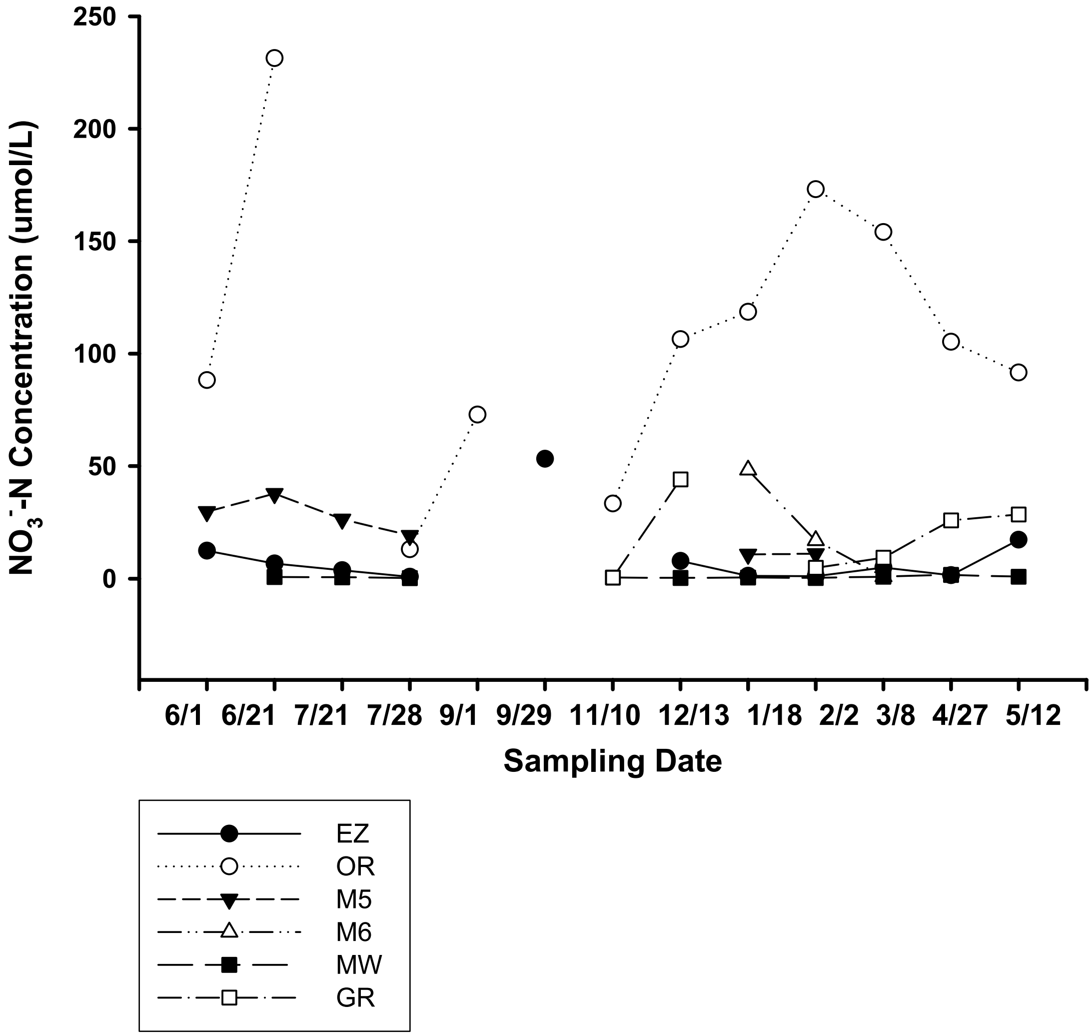

Figure 4.4. NO_3^--N concentrations in soil water from June 2005 through May 2006.

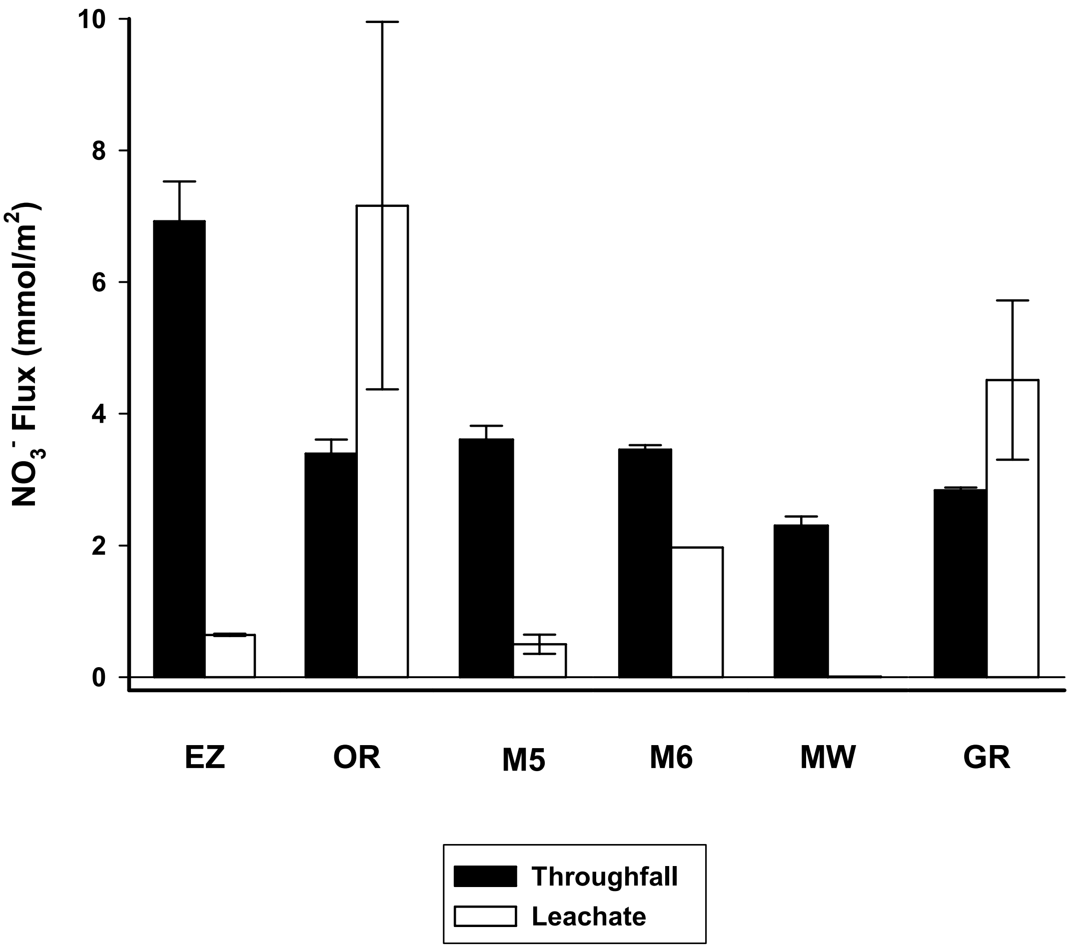

Figure 4.5. Mean throughfall and leachate fluxes of NO_3^- across sites.

Throughfall and Leachate Isotope Values

As expected, there was little isotopic separation in ∂^{15}N values of throughfall and leachate NO_3^-. ∂^{15}N-NO_3^- of throughfall ranged from -5.3 to +8.8‰ and ∂^{15}N-NO_3^- of soil water ranged from -7.7 to +13.2‰ (Figures 4.6 and 4.7). However, ∂^{18}O isotope values showed adequate separation for use in quantifying source contributions to soil water NO_3^-. ∂^{18}O-NO_3^- of throughfall varied from +53.6 to +87.8‰ and ∂^{18}O-NO_3^- of soil water ranged from -7.8 to +62.7‰, with all but four samples falling within the -7.8 to +4.3‰ range (Figure 4.8). Nitrification, and not atmospheric deposition, was the main source of NO_3^- in soil water that was either leaching or available for leaching, as is demonstrated by the clustering of ∂^{18}O values from leachate NO_3^- close to the accepted range of ∂^{18}O-NO_3^- values generated from nitrification (Figure 4.8). However, four soil water samples, three from the MW site corresponding to the March, April, and May 2006 collections, and one from the EZ site corresponding to the May 2006 collection, clustered much closer to the ∂^{18}O values of throughfall NO_3^-, which are atmospherically-derived (Figure 4.9). The proximity of these four samples to the throughfall ∂^{18}O values combined with their distance from the other soil water ∂^{18}O values is strongly suggestive of a higher contribution of atmospherically-derived, rather than nitrification-derived, NO_3^- in those samples. The results of the two end member mixing analysis show that for the winter months, 95-100%, and for the remainder of the year 94-100%, of soil water NO_3^- was microbially processed in the soil and thus generated by nitrification. This analysis did not include the four soil water samples with high (>30‰) ∂^{18}O values. In separately analyzing the four high ∂^{18}O samples, nitrification was the source of 33-43%

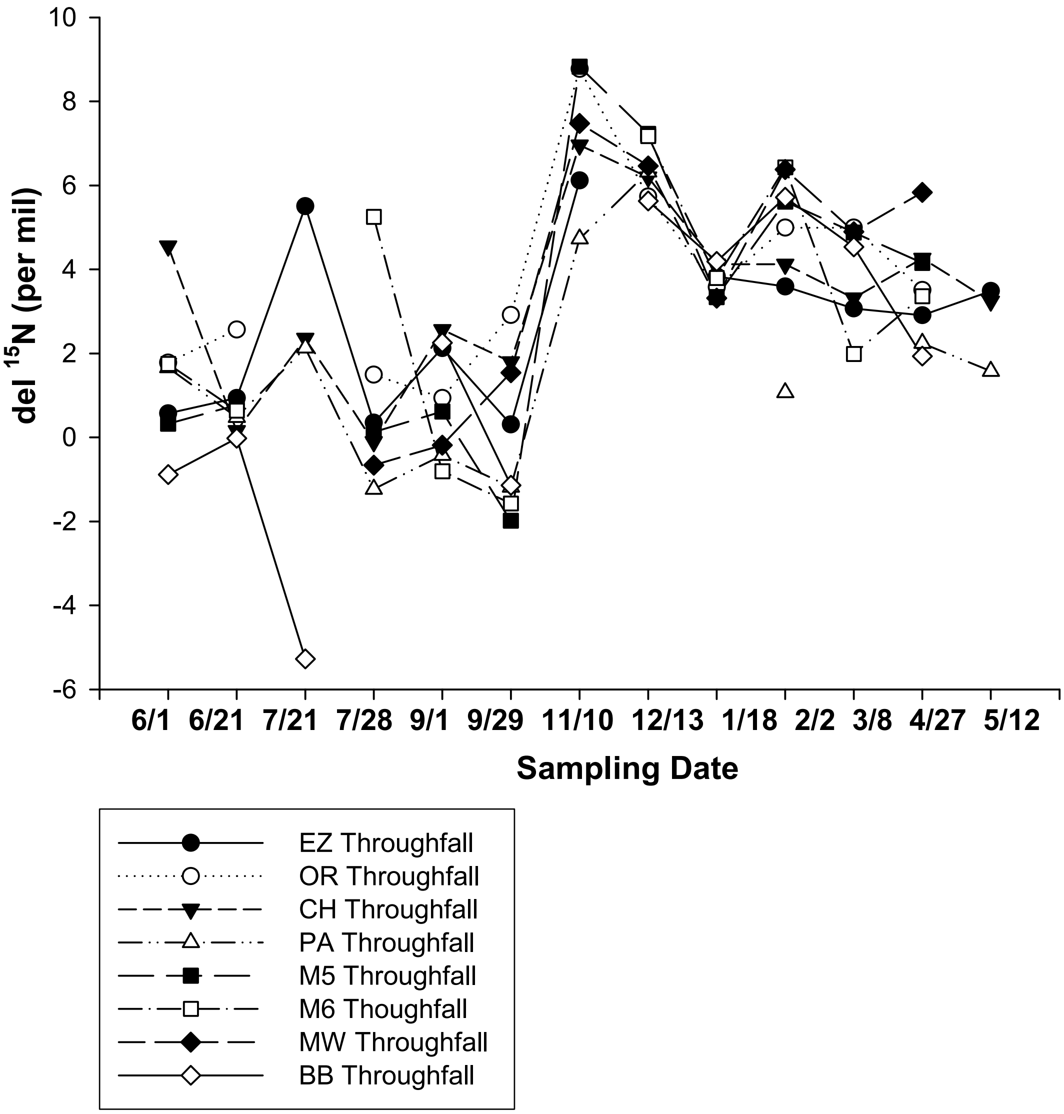

Figure 4.6. ∂^{15}N values in throughfall from June 2005 to May 2006.

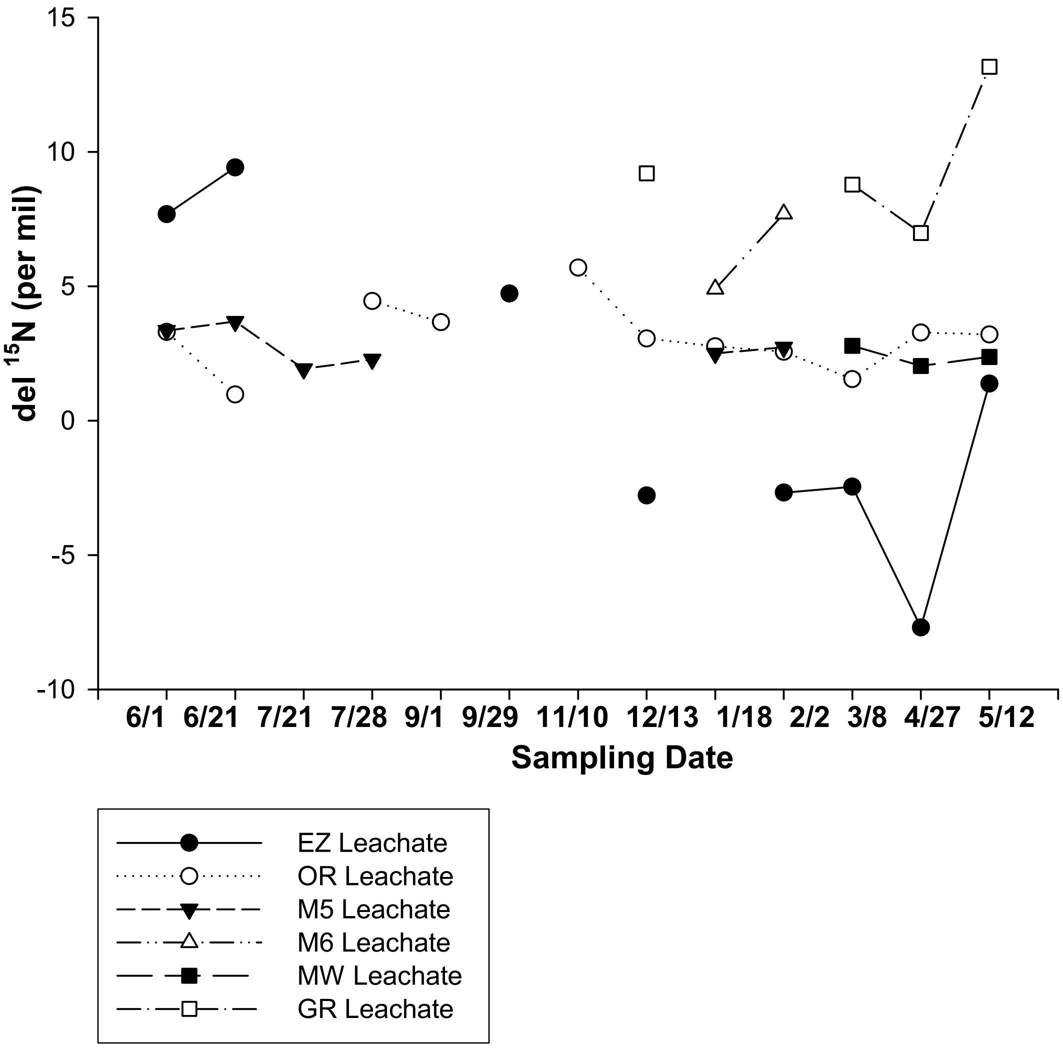

Figure 4.7. ∂^{15}N values in soil water from June 2005 to May 2006.

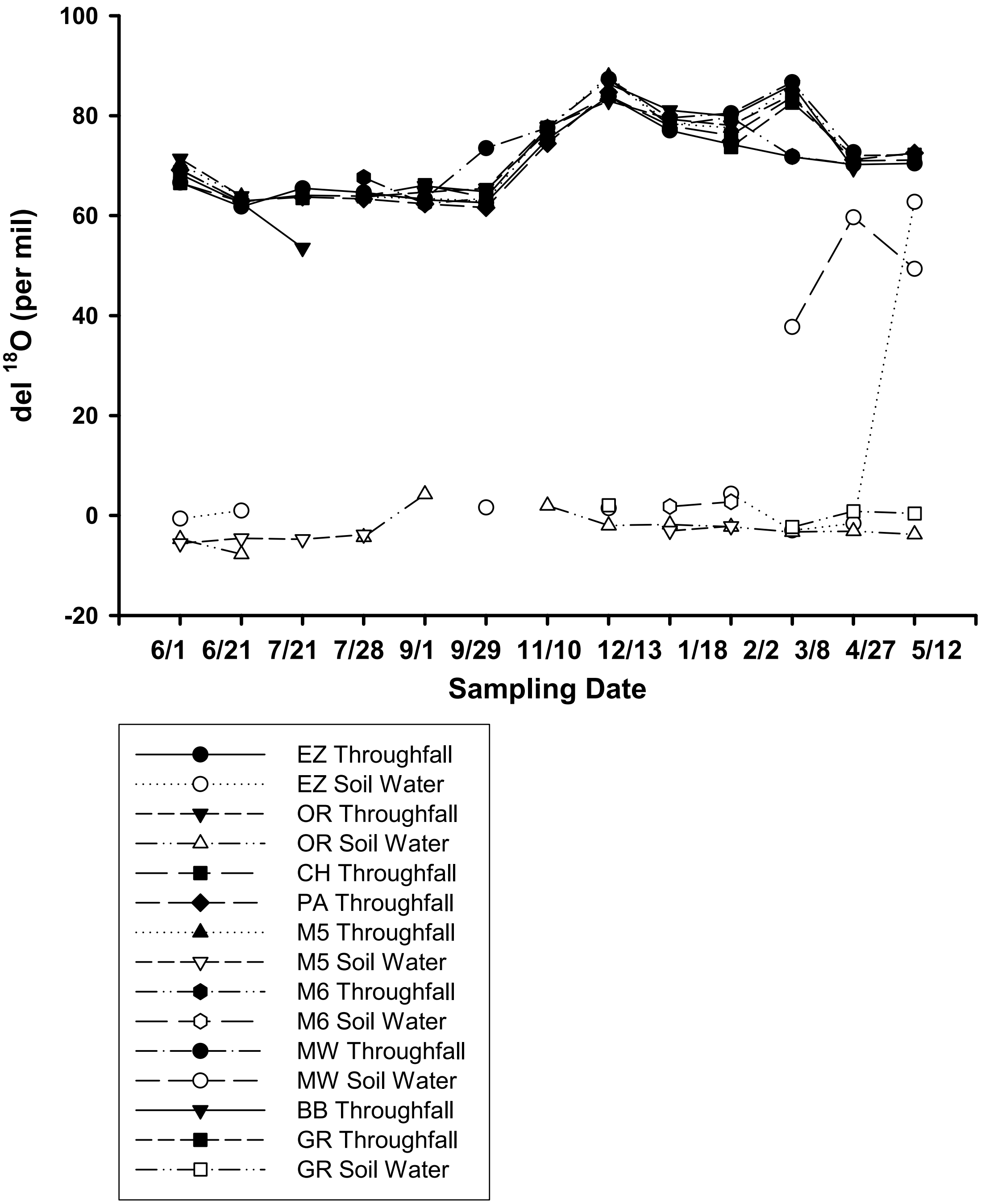

Figure 4.8. $\partial^{18}O$ values in throughfall and soil water from June 2005 to May 2006. Throughfall isotope values are represented by filled symbols; soil water isotope values are represented by open symbols.

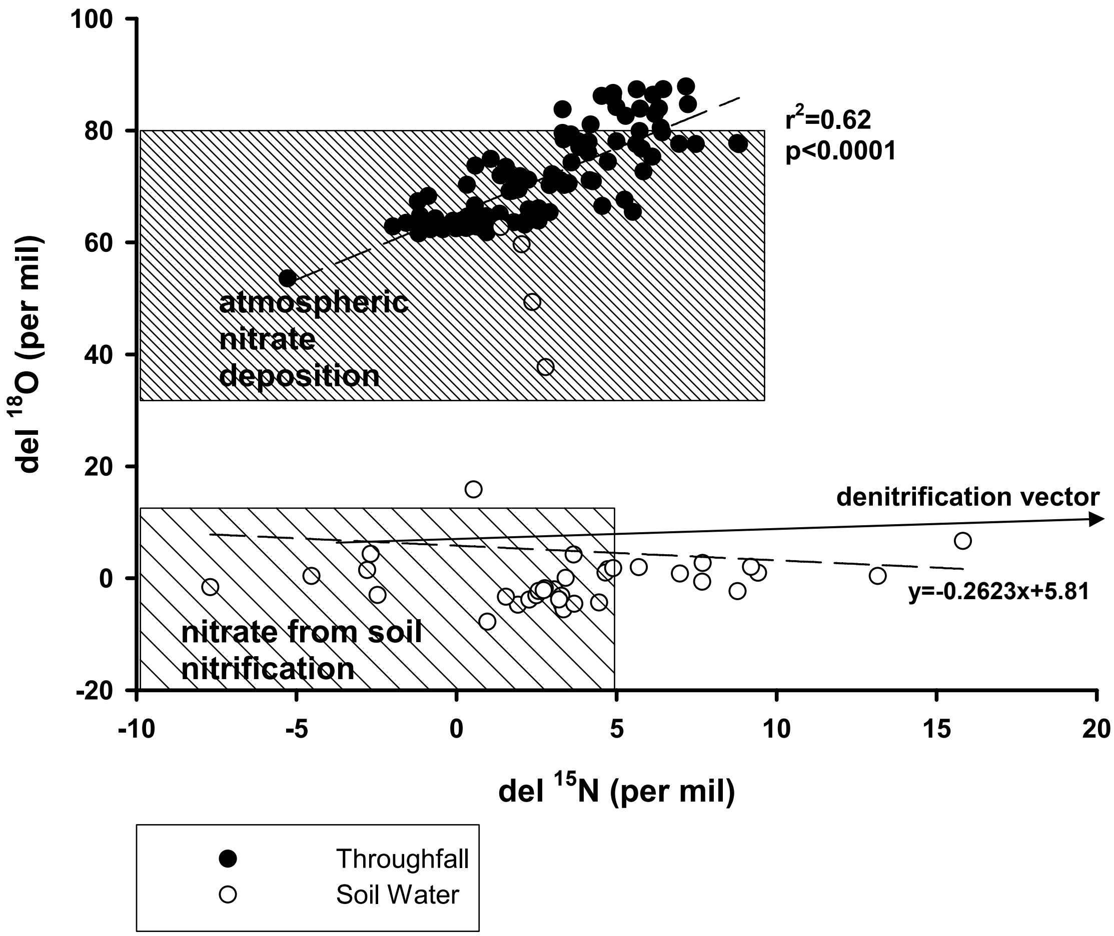

Figure 4.9. ∂^{15}N and ∂^{18}O values of NO_3^- in throughfall and soil water samples. Literature ranges of isotopic composition of atmospheric NO_3^- deposition and NO_3^- derived from soil nitrification are indicated in boxes. The denitrification vector indicates the 2:1 relationship between ∂^{15}N and ∂^{18}O values which has been ascribed to fractionation that occurs during denitrification (Bottcher et al. 1998, Wassenaar et al. 1995, Aravena and Robertson 1998, Cey et al. 1999, Battaglin et al. 2001, Spoelstra et al. 2001, Mayer et al. 2002, Panno et al. 2006).

of the NO_3^- in the MW sample from winter 2006 and 21-29% of the NO_3^- in the three other high $\partial^{18}O$ samples from spring 2006. Thus, atmospherically-derived NO_3^- accounted for 57-79% of the NO_3^- in soil water in the high $\partial^{18}O$ soil water samples.

$\partial^{15}N$ and $\partial^{18}O$ values in throughfall NO_3^- were very similar across sites (Figures 4.6 and 4.8), suggesting similar sources of NO_3^- and similar atmospheric processes prior to deposition across the study gradient. Seasonal differences were marked, with higher isotope values for both isotopes in the winter compared to the other seasons (Figures 4.6 and 4.8). $\partial^{15}N$ values for soil water samples showed some separation among sites, with EZ showing higher values than the other sites in June 2005 but lower values during winter and spring 2006, and GR showing higher values than the other sites during winter and spring 2006 (Figure 4.7). $\partial^{18}O$ values in soil water were mostly uniform across sites excepting the four aforementioned high values in EZ and MW (Figure 4.8). There were no overall seasonal differences in soil water isotope values (Figures 4.7 and 4.8). There were no correlations of isotope values of both throughfall and soil water NO_3^- with indicators of watershed urbanization, excepting a strong correlation between $\partial^{18}O$ in throughfall NO_3^- and % forest land cover ($r^2=0.84$, $p<0.001$). Throughfall and soil water NO_3^- isotopes were also not correlated with precipitation amounts, with the exception of $\partial^{18}O$ in throughfall NO_3^- ($r^2=0.63$, $p<0.05$).

The isotope values in soil water NO_3^- showed no evidence of fractionation due to denitrification (Figure 4.9). $\partial^{15}N$: $\partial^{18}O$ ratios of soil water NO_3^- did not show the typical 2:1 ratio commonly ascribed to denitrification fractionation (Bottcher et al. 1998, Wassenaar et al. 1995, Aravena and Robertson 1998, Cey et al. 1999, Battaglin et al. 2001, Spoelstra et al. 2001, Mayer et al. 2002, Panno et al. 2006) (Figure 4.9). Also, there was no evidence of increasing $\partial^{15}N$ values with decreasing NO_3^- concentrations, another commonly used indicator for the presence of denitrification (Figure 4.10).

Discussion

Four out of the six sites with measurable leachate along the very urban to less urban gradient showed overall NO_3^- retention, as demonstrated by lower NO_3^- outputs in leachate than NO_3^- inputs in throughfall (Table 4.2, Figure 4.5). However, in sites OR and GR, which have very different urban intensities (Figure 4.2, Table 4.1), NO_3^- fluxes were higher in leachate than throughfall, indicating overall NO_3^- loss to shallow groundwater. As there are other possible types of NO_3^- inputs and outputs to and from these sites, the results of a complete mass balance could show different patterns of retention and loss across this population of wetlands. For the purposes of this study, however, NO_3^- retention is defined as higher NO_3^- inputs in throughfall than outputs in leachate. NO_3^- concentrations in throughfall were generally higher in sites such as EZ, OR, and CH which are located at the more urban end of the gradient (Table 4.1, Figure 4.2), and there were significant positive correlations between throughfall NO_3^- fluxes and a number of watershed urbanization indicators (Table 4.3). These results suggest that wetlands in more urbanized watersheds do have higher NO_3^- inputs than wetlands in less urbanized watersheds. However, higher inputs in more urban areas do not result in higher NO_3^- concentrations in soil water (Figure 4.4) or higher NO_3^- outputs in leachate (Figure 4.5) except in the aforementioned sites, OR and GR. Isotopic evidence, combined with a lack of relationship between throughfall and leachate fluxes, indicate that atmospheric NO_3^- inputs very rarely leached directly but were first processed by soil microbes before being exported from the system. The results of the mixing model

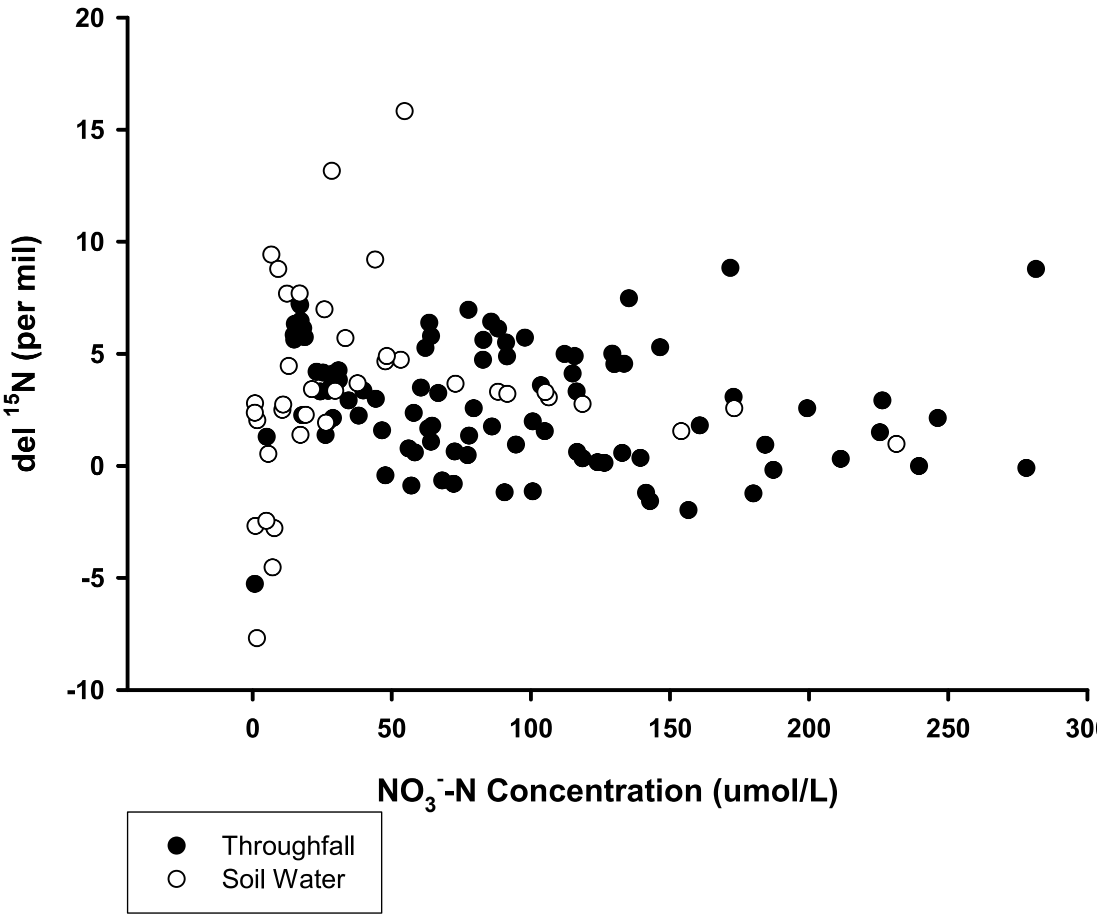

Figure 4.10. NO_3^--N concentration versus ∂^{15}N isotope values of throughfall (filled circles) and soil water (open circles).

analysis supports this conclusion. However, there was an apparent atmospheric signal in soil water in EZ and MW during the spring of 2006, suggesting that a direct loss of atmospheric NO_3^- is possible in urban wetlands. This is an unusual result; the only previous report of direct leaching of atmospheric NO_3^- to groundwater is from springwater in declining forest stands exposed to high rates of atmospheric N deposition in Germany (Durka et al. 1994).

Throughfall Patterns

$\partial^{15}N$ and $\partial^{18}O$ values of NO_3^- in throughfall ($\partial^{15}N$ ranged from -5.3 to +8.8‰ and $\partial^{18}O$ ranged from +53.6 to +87.8‰, Figure 4.9) fall within the range reported in the literature, which is -16 to +10‰ for $\partial^{15}N$ (Kendall et al. 1998) and +25 to +90‰ for $\partial^{18}O$ according to Kendall et al. (1998) and Ohte et al. (2004). These studies analyzed bulk deposition, but the few studies which did measure throughfall NO_3^- isotopes found mostly comparable values. Durka et al. (1994) found a ^{15}N range of +2.6 to +6.3‰ and an $\partial^{18}O$ range of +60.3 to +73.4‰ in throughfall NO_3^-, and Campbell et al. (2006) found a range of about +75 to +85‰ in throughfall $\partial^{18}O\text{-}NO_3^-$. Two studies found less enriched ^{18}O values, including Williard et al. (2001) who found $\partial^{18}O$ in throughfall to vary between +17 to +76‰ and Mayer et al. (2001) who found $\partial^{18}O$ in throughfall to average +39.5‰ under a deciduous canopy and +36.1‰ under a coniferous canopy.

Although NO_3^- concentrations and fluxes in throughfall varied with urban intensity at the watershed scale (Figure 4.3, Tables 4.2 and 4.3), isotope values in throughfall $\partial^{15}N\text{-}NO_3^-$ and $\partial^{18}O\text{-}NO_3^-$ showed little variability among sites (Figures 4.6 and 4.8). This suggests that air masses over the region are well-mixed and homogenous, thus the same NO_3^- is deposited along the length of the very urban to less urban gradient.

However, more of that same NO_3^- is deposited as urban conditions increase, as indicated by patterns in throughfall NO_3^- concentrations and fluxes (Figure 4.3, Tables 4.2 and 4.3). This is not explained by an increase in precipitation amounts (Table 4.2), as amounts were not correlated with urban indicators. The reason for this increased deposition is unclear. Possible explanations include greater canopy leaching and/or interactions with increasing urbanization or perhaps more atmospheric particulates in more urban areas resulting in more deposition. Further research would be required to resolve this issue. Seasonal variations were much more prominent than site variations in both $\partial^{15}N$ and $\partial^{18}O$ throughfall NO_3^- (Figures 4.6 and 4.8); Hastings et al. (2003) found similar seasonal patterns in throughfall isotope values in Bermuda. $\partial^{15}N$ values, which are thought to be determined by the source of oxidized nitrogen, the temperature and completeness of fossil fuel combustion in power plants and vehicle exhaust, and fractionation during atmospheric N reactions (Pardo et al. 2004), may be higher in the winter than other seasons due to changes in sources of emissions (for example, a change in the proportion of emissions from power plants versus vehicles during the winter compared to other seasons). They may also be higher due to seasonal changes in storm tracks and thus geographical sources. An analysis of the back trajectories of storm events is necessary to distinguish between these explanatory factors (Campbell et al. 2002, Hastings et al. 2003, Pardo et al. 2004).

Factors influencing $\partial^{18}O$-NO_3^- values in throughfall include fractionation during NO_3^- formation by lightning, isotopic values of the reactive atmospheric oxygen which combines with NO_x emissions to form atmospheric NO_3^-, and fractionation during atmospheric reactions (Hastings et al. 2003, Pardo et al. 2004). Due to rapid exchange of oxygen in NO_x with atmospheric ozone, particularly during daytime photolytic reactions, $\partial^{18}O$ of atmospheric NO_3^- is controlled more by atmospheric chemistry than the original source of the NO_x emissions (Hastings et al. 2003). Ozone has a range of $\partial^{18}O$ values from ~+90 to +122‰ (Johnston and Thiemens 1997, Krankowsky et al. 1995); my high $\partial^{18}O$ values in throughfall may thus reflect a dominance of atmospheric ozone-related processes. Seasonal variations in $\partial^{18}O$ values may reflect seasonal patterns of atmospheric chemistry, with more influence of photolytic processes during the longer daylengths of summer versus predominance of the N_2O_5 pathway for HNO_3^- and thus atmospheric NO_3^- formation during the colder seasons (Hastings et al. 2003).

Throughfall NO_3^- fluxes showed an even stronger relationship to watershed urbanization than throughfall NO_3^- concentrations (Tables 4.2 and 4.3); however, fluxes over the entire collection period were lower than expected (Table 4.2, Figure 4.5). Fluxes ranged from 2.30 to 6.92 mmol m^{-2} over 22 weekly collections over the course of one year (Table 4.2). Lovett et al. (2000) found much higher rates over just 11 weeks of collections during the summer of 1996 in an urban to rural gradient from New York City north into New York State. In that study throughfall NO_3^- fluxes ranged between 7.18 and 18.11 mmol m^{-2}. There are several possible explanations for this apparent discrepancy. First and foremost, a lack of rain events during a number of weekly collection periods, ranging from four collection periods in some sites to eight in others, resulted in reduced throughfall volumes and thus lower fluxes (Table 4.2). Total precipitation amounts in throughfall, which ranged from 7.49 to 16.4 cm (Table 4.2, were lower over my 22 collection periods than Lovett et al.'s (2000) total throughfall amounts, which ranged from 13.8 to 30.3 cm, over only 11 weeks of collection. Thus fluxes were considerably lower in this study than Lovett et al.'s (2000). According to monthly precipitation data from New Jersey, the period from June 2005 to June 2006 was not especially dry (http://climate.rutgers.edu/stateclim_v1/data/njhistprecip.html). The explanation for the low precipitation amounts I measured is that by chance there were several collection periods during the course of my study in which there were no rain events. Another possible explanation for the discrepancy in flux data is that throughfall NO_3^- concentrations and fluxes are notoriously variable and understudied (Levia and Frost 2006), especially in urban areas. Numerous biotic and abiotic processes may alter NO_3^- concentrations as precipitation filters through tree canopies, including canopy interception of precipitation water, canopy uptake and leaching of inorganic N, precipitation event magnitude, duration, and intensity, and wind speed and direction (Levia and Frost 2006). The greater variability in throughfall NO_3^- concentrations during the growing season compared to the winter leaf-off period (Figure 4.3) point to the likely influence of canopy uptake and leaching. Canopy interactions themselves are influenced by species composition, three-dimensional canopy structure, and plant area index (which includes area of branches and stems in addition to leaves) (Levia and Frost 2006). Stemflow, another component of precipitation that fractionates from bulk deposition, can vary widely in volume by season, and thus can change dramatically in proportion to both bulk deposition and throughfall over time (Levia 2004). As a result, recent reviews of the throughfall literature suggest using many more collectors per site than were employed in this study (Levia and Frost 2006, Starr et al. 2007). However, throughfall fluxes were not particularly variable per site (see standard errors Table 4.2), although throughfall concentrations were.

Soil Water Patterns

Most soil water isotope values fell within the ranges reported by other studies. In my study $\partial^{15}N$ ranged from -7.7 to +13.2‰ and $\partial^{18}O$ ranged from -7.8 to +4.3‰ in all samples except the four from MW and EZ which were much higher in $\partial^{18}O$ (+37.7 to +62.7‰) (Figures 4.7-9). Springwater values in Germany ranged from -2 to +2‰ for $\partial^{15}N$ and +11 to +33‰ for $\partial^{18}O$ (Durka et al. 2004). Soil water values ranged from -2 to +2‰ for $\partial^{15}N$ and -2 to +6‰ for $\partial^{18}O$ in unamended agricultural soils, but $\partial^{18}O$ increased to +16‰ in fertilized soils (Mengis et al. 2001). Mayer et al. (2001) found $\partial^{15}N$-NO_3^- to vary from -5 to +15‰ in percolation water from lab incubations of forest floor horizons. Williard et al. (2001) found $\partial^{18}O$ in leachate from lab incubations to vary between +0.2 and +13.7‰. The lack of a 2:1 relationship between $\partial^{15}N$ and $\partial^{18}O$ values of soil water NO_3^- shows no evidence of denitrification as a cause of fractionation, an interesting finding in a set of wetlands with a range of denitrification rates (Chapter 3). It is unclear why there was no denitrification signal in the soil water samples. Most of the soil water samples fell well within the range of $\partial^{15}N$ and $\partial^{18}O$ isotope values ascribed to NO_3^- which has been microbially-processed by nitrifying bacteria (Figure 4.9). This result, combined with the results of the mixing model analysis, strongly suggest that direct contributions of atmospherically-derived NO_3^- to NO_3^- exports are low compared to the contribution of endogenously produced NO_3^-. It is possible that this pattern is so pronounced because soil water was sampled using tension lysimeters which draw soil water out of small pores. These micropores are likely hotspots of aerobic conditions in wetland soils, and thus may support nitrification. As a result, tension lysimeters may disproportionately sample soil water which contains the products of nitrification. This is in contrast to zero tension lysimeters, which are not practical to use in saturated soils, but which sample soil water percolating downward by gravity. This percolating soil water may contain more direct atmospheric NO_3^- than soil water in micropores.

However, the four samples with enriched $\partial^{18}O$ values from EZ and MW in the spring of 2006 suggest that atmospheric NO_3^- inputs did leach directly without microbial processing. Of the studies which have analyzed $\partial^{18}O$-NO_3^- in soil water collected from lysimeters, only Durka et al. (1994) have demonstrated direct leaching to the groundwater of atmospheric NO_3^- from declining forest stands. All other studies have concluded that NO_3^- in soil water samples predominantly originated from nitrification (Williard et al. 2001, Mengis et al. 2001, Mayer et al. 2001), and numerous studies which analyzed stream water samples came to the same conclusion (Williard et al. 2001, Sickman et al. 2003, Pardo et al. 2004, Piatek et al. 2005, Mitchell et al. 2006, Campbell et al. 2006, but see Chang et al. 2002 and Campbell et al. 2002). In some of these studies, though, there is a range of possible atmospheric contributions from 0 to 30% or even 50% (Williard et al. 2001, Spoelstra et al. 2001, Pardo et al. 2005), so perhaps in some cases investigators are underestimating the importance of atmospheric contributions. However, it is true that these studies did not find $\partial^{18}O$ values of stream water higher than +33‰ (Pardo et al. 2004) which is on the lower end of the high $\partial^{18}O$ values I found in soil water. The MW site had very low concentrations of NO_3^- in soil water, just barely above detection (Figures 4.4 and 4.5), and very low rates of net nitrification (Chapter 3). Voss et al. (2006) found $\partial^{18}O$ values greater than +20‰ in stream samples only in rivers with low NO_3^- concentrations. These results suggest that direct atmospheric leaching may be present at all sites at very low rates, and the pattern is only detectable in sites with very low soil water NO_3^- concentrations or low rates of endogenous NO_3^- production. However, the EZ sample from May 2006 with a high $\partial^{18}O$ value did not have a particularly low NO_3^- concentration (17.2 umol L^{-1}), and net nitrification rates are quite high at EZ (Chapter 3). These two sites lie on opposite ends of the urbanization gradient (Table 4.1, Figure 4.2) and have contrasting hydrological patterns: MW is a particularly wet site and EZ is very dry (Chapter 3). It is also important to note that the three high samples from MW represent all of the soil water samples analyzed for this site, while the one high sample from EZ represents only one of 12 soil water samples from EZ. The pattern is thus repeatable in MW (at least over three sampling dates) but not in EZ. Precipitation amounts were high at MW on April 27th (2.7 cm) and EZ on May 12th (2.5 cm) suggesting that perhaps atmospheric NO_3^- is flushed from the soil during a storm event before plant or microbial uptake is able to process it. This would indicate that direct atmospheric NO_3^- leaching occurs on a temporally-limited scale. However, precipitation amount was low for the March 9th MW collection (0.09 cm), and there was no rain in the week prior to the May 12th collection at MW. More sampling is required to make any conclusive statements regarding these four $\partial^{18}O$ enriched samples. A lack of comparable studies in urban systems limits my ability to make inferences and draw conclusions from this unusual and intriguing data. It is also important to note that the two sites which demonstrated an atmospheric signal (EZ and MW) were not the two sites which had greater NO_3^- losses than inputs (OR and GR). This suggests that atmospheric N deposition is not the dominant driver of NO_3^- losses in these urban wetlands.

Volume-weighted mean NO_3^- concentrations in soil water at 50 cm depth in eight urban, upland forest stands in Baltimore, MD, ranged from roughly 3 to 15 µmol L^{-1}

(Groffman et al. 2006). Most of my soil water samples were much higher than this range, except at MW where concentrations were even lower than this range (Table 4.2, Figure 4.4). Samples at all sites except MW fell within the range of concentrations reported for soil water in previously agricultural upland soils heavily invaded by earthworms in a sugar maple forest in New York State (Bohlen et al. 2004) and were equal to or greater than soil water in less disturbed northern hardwood forests in New Hampshire (Fitzhugh et al. 2001). Concentrations were particularly high at OR (Figure 4.4), high enough, in fact, that they often exceeded EPA's standard of 10 mg L^{-1} for surface waters. Concentrations from other sites did not exceed EPA standards. Leachate fluxes were low, particularly in comparison to throughfall fluxes, at all sites except OR and GR (Table 4.2, Figure 4.5). These two sites, like EZ and MW, fall on opposite sides of the urbanization gradient (Table 1, Figure 4.2) and have highly contrasting hydrological patterns (Chapter 3). The lack of significant relationships of soil water concentrations, fluxes, and isotope values with indicators of watershed urbanization suggests that local factors control NO_3^- loss. Hydrological patterns and N cycling rates may explain the high rates of leachate at OR, a site which has extremely low water tables on a continual basis, high rates of net nitrification, and low rates of denitrification (Chapter 3). However, GR exhibits classic wetland hydrology for northeastern red maple swamps, namely water tables within 30 cm of the surface for most of the year with a prominent draw down during the summer (Golet et al. 1993) due largely to herbaceous vegetation growth and resulting high rates of evapotranspiration. Rates of net nitrification and denitrification are not especially high or low at GR in comparison to other sites I measured (Chapter 3). The high rates of NO_3^- loss from the GR site are not explainable based on the variables I measured. Again, due to a lack of comparable studies in urban systems, I cannot determine whether these findings represent the idiosyncratic nature of urban wetlands (Ehrenfeld et al. 2003, Chapter 1/Stander and Ehrenfeld submitted) or are indicative of larger trends.

It is very striking that the two sites which demonstrated direct leachate of atmospheric NO_3^- were located on opposite ends of the urbanization gradient. This was also the case for the two sites which had higher NO_3^- losses than inputs. These results may be indicative of the multifaceted nature of urbanization, which is only captured to a certain degree by watershed scale urbanization indicators. Local effects of urbanization appear to be very important drivers of N retention and loss, suggesting we need to utilize a more subtle understanding of urbanization than is encompassed in watershed scale measurements of imperviousness or land use/land cover. We cannot generalize about the effects of urbanization on ecosystem function without characterizing urban effects on a more local scale. However, it is important to remember that considerable variation in N retention is common in both forested and agricultural systems (Chapter 3). It is not clear in this study that urbanization, either on the local or landscape scale, is entirely responsible for the patterns of retention and loss I have documented.

In summary, urban wetlands are generally N retentive; however, there were two sites at which NO_3^- outputs were higher than inputs, suggesting overall N loss. I was not able to determine the cause of NO_3^- loss in these two sites based on the variables I quantified. Throughfall NO_3^- concentrations and fluxes did increase with increasing urbanization. Isotopic evidence suggested that the source of NO_3^- was the same at all sites, however, suggesting that local sources are not contributing to NO_3^- deposition increases in more urban locations. Seasonal variations in throughfall isotope values are likely controlled by seasonal changes in atmospheric chemistry in the case of $\partial^{18}O$ and either by seasonal changes in source emissions or seasonal changes in storm tracks in the case of $\partial^{15}N$. There was no evidence of an urban effect in leachate NO_3^- concentrations or fluxes, suggesting that leachate is controlled by local factors. However, none of the local variables I measured, which included throughfall NO_3^- concentrations and fluxes, precipitation amounts, soil and hydrological properties, or rates of N cycling, were correlated with NO_3^- in soil water or outputs. According to isotopic evidence, NO_3^- in soil water and leachate was largely the product of soil nitrification rather than direct export of atmospherically-deposited NO_3^-. However, four soil water samples from two sites during the spring of 2006 showed very high $\partial^{18}O$ values, strongly suggesting a direct atmospheric influence. Although N retention appears to be high in this set of urban wetlands, high fluxes of NO_3^- in leachate at two sites and the direct export of atmospherically-deposited NO_3^- at two other sites indicates that N retention may not be spatially or temporally universal in urban wetlands.

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Conclusions

This dissertation was designed to explore the effects of urbanization on nitrogen (N) cycling dynamics in urban wetlands. In particular, I set out to determine whether urban wetlands, like wetlands in less disturbed systems, serve as N sinks in landscapes or whether, due to the effects of urbanization, they export nitrate (NO_3^-) and thus contribute to water quality concerns in receiving rivers and estuaries. I chose to quantify altered hydrology (Chapters 1-3) and elevated atmospheric N deposition (Chapter 4) as two potentially important effects of urbanization on wetland N cycling functions. The conceptual foundation of the research was the idea that if hydrological alterations cause wetlands to be drier or flashier than they have been historically, this may cause wetland soils to produce more NO_3^- through the aerobic microbial process of nitrification and remove less NO_3^- through the anaerobic microbial process of denitrification. The cascading effect of these changes could be a release of NO_3^- through leaching to the shallow groundwater, where this NO_3^- could then be discharged to streams and contribute to eutrophication of receiving estuaries. An additional consequence of changing N cycling dynamics could also be that wetland assessment frameworks designed to model wetland functions based on natural hydrogeomorphic (HGM) setting may not be valid in urban wetlands if their N functions are driven by altered hydrological patterns caused by their urban context. If functional assessment models used by federal regulatory agencies do not effectively predict critical wetland N functions in urban settings, important management decisions concerning permitting, mitigation, and restoration of urban wetlands could be based on inaccurate information. In addition to the effects of altered hydrology, I also hypothesized that elevated levels of atmospheric N deposition in urban landscapes may cause N saturation in urban wetlands, particularly if these wetlands are also producing more and removing less NO_3^- due to drier conditions. If NO_3^- was found to be leaching from urban wetlands, I wanted to quantify the relative contributions of endogenously-produced NO_3^- due to altered hydrology, versus the direct leaching of exogenous inputs of atmospheric NO_3^-, to NO_3^- export.

To approach these questions, I first quantified patterns of hydrology and N cycling process rates in a population of palustrine, forested wetlands in northeastern New Jersey, the most urban part of the state. Water table levels were monitored continuously over five years in 12 sites, and *in situ* rates of net N mineralization, net nitrification, and denitrification were measured monthly in 14 sites over the course of one year. Replicate wetlands were chosen in three different HGM classes in order to test the assumptions and models of the HGM functional assessment protocol. In Chapter 1 I found that rates of N cycling processes were not effectively described by natural HGM setting. Chapter 1 findings also demonstrate that the *a priori* designation of reference standard sites using a qualitative assessment of alteration was not effective in identifying urban wetlands which had low rates of net nitrification and high rates of denitrification, the prime conditions for NO_3^- retention. Rather, an *a posteriori* designation of urban wetlands as having either normal or altered (dry and/or flashy) hydrology was better able to predict which sites had low nitrification and high denitrification rates. It is thus recommended that HGM functional assessment protocols identify reference standard sites in urban settings using results of water table monitoring over at least one water year.

A key characteristic of the HGM functional assessment method is that assessments must be carried out rapidly in order to meet the needs of the regulatory community. In order to test the validity of existing HGM functional assessment models, I carried out rapid assessment protocols in the same 14 wetlands. Soil, vegetation, and hydrological structural indicators were measured using standard rapid techniques. Using these data, I calculated functional capacity index (FCI) scores for each site according to existing rapid assessment models developed for riverine wetlands in less developed landscapes. I then tested the relationships between scores and measures of actual N cycling function. Chapter 2 findings indicate that there was little evidence of significant relationships between FCI scores of three existing models and rates of net N mineralization, net nitrification, and denitrification in urban wetlands.

I developed additional models using both rapid and non-rapid indicators of known controlling factors on specific N cycling process rates. This is in contrast to existing models that are based on indicators of structure, rather than function, of a generalized group of biogeochemical processes. Findings in Chapter 2 demonstrate that models based on rapid indicators were not effective in predicting nitrification or denitrification rates. Models which included non-rapid indicators, such as long-term field measurements of inorganic N concentrations and hydrological patterns or laboratory analyses of soil properties, were successful in predicting net nitrification rates. These non-rapid models were still not able to predict denitrification rates in this set of urban wetlands. The simple structure of these models does not adequately describe denitrification in urban wetlands which display high variability in soil and hydrological patterns. The results of this study strongly suggest that functional assessment models used to make management decisions should be targeted to specific functions. Models should be designed using indicators of known controlling factors of these functions.

Successful models should include non-rapid indicators of soil and hydrological properties.

The remainder of the dissertation focused on understanding the patterns of and processes behind NO_3^- retention and loss in urban wetlands. In Chapter 3 I looked for relationships of landscape urbanization indicators, such as population density, percent impervious cover, and percent urban land cover, with hydrology and N cycling dynamics in the same set of urban wetlands. I also evaluated the strength of relationships between local scale factors, such as soil and vegetation properties, on N cycling process rates. A number of indirect effects, including the effects of landscape urbanization on N cycling as mediated through altered hydrology, the effects of soil texture on hydrology and thus on N cycling, and the effects of water tables on soil moisture and organic matter content and thus on N cycling, were also evaluated.

Chapter 3 findings indicate that rates of net nitrification are controlled by water table levels, particularly as characterized by dryness, and net N mineralization rates. In contrast, denitrification is driven by soil moisture and organic matter content. There was surprisingly no evidence of hydrologic controls on denitrification rates. There was also a surprisingly lack of correlation of hydrological patterns with either landscape level urbanization or soil properties. In a larger context, these findings indicate that N cycling process rates, and denitrification in particular, are controlled by local scale factors. Management efforts aimed at maximizing NO_3^- retention should thus focus on local scale phenomena. Additionally, my dissertation research was not able to identify the root causes of dry and flashy hydrological patterns in this population of urban wetlands. It is possible that local scale disturbances such as ditches and berms, which were not quantified as part of my research, as well as other vagaries of land use history, are important drivers of water table dynamics.

Finally, in Chapter 4 I characterized weekly NO_3^- inputs in throughfall and outputs in leachate over the course of one year as a means of determining actual NO_3^- retention in urban wetlands. I also analyzed the dual isotope ($\partial^{15}N$ and $\partial^{18}O$) values of NO_3^- in both throughfall and soil water in order to determine the relative contributions of endogenously-produced NO_3^- versus atmospherically-deposited NO_3^- to NO_3^- exports in leachate. Nine sites from the original 14 were chosen for this analysis. The sites were arranged along a gradient of very urban to less urban conditions. Findings from this chapter indicate that NO_3^- retention was high overall, as demonstrated by higher input fluxes than output fluxes of NO_3^-. However, leachate fluxes were higher than throughfall fluxes in two sites which are located on opposite ends of the urbanization gradient. Throughfall inputs did increase with increasing urbanization, but there was no apparent urban effect in leachate outputs. Local scale factors such as hydrology, soil, and N cycling patterns also were not correlated with leachate fluxes. $\partial^{15}N$ values suggested that the same sources of NO_3^- were responsible for atmospherically-deposited NO_3^- at all sites, regardless of urban intensity. $\partial^{18}O$ values indicated that most of the NO_3^- in soil water and leachate was the result of endogenous NO_3^- production. However, high $\partial^{18}O$ values in four samples from two sites in the spring of 2006 were strongly suggestive of a direct atmospheric influence, demonstrating that atmospherically-derived NO_3^- had leached directly without being first processed by soil microbes. This is an unusual finding which has been documented only very rarely in the ecological literature. These two sites again represented opposite ends of the urbanization. Evidence of high leaching fluxes from two sites and direct export of atmospherically-derived NO_3^- at two other sites indicates that N retention may not be spatially or temporally universal in urban wetlands.

This dissertation research represents one of the first attempts to document hydrological and N cycling changes in wetlands as a result of urbanization. It is also one of the first studies characterizing NO_3^- inputs and outputs along a gradient of urban intensity in a highly developed region. To my knowledge, there have been no previous attempts to use dual isotope techniques to partition the sources of NO_3^- export in urban wetlands. Thus this research represents what I hope to be an important contribution to the emerging field of urban ecology as well as the broader wetland community. There are clear management implications of this research that in the best of worlds may spark debate and contribute to improved methodologies in the regulatory context. My dissertation research also demonstrates that urban wetlands represent a special case of wetland ecology, and thus the urban setting needs to be specifically accounted for in designing future research and in making management decisions.

Appendix A. Description of study site locations.

Site	***Municipality***	***Location***	***Latitude, Longitude***
YK	Norwood	End of West Railroad Ave, across the railroad tracks	40°59'N -73°57'W
OR	Cedar Grove	Grove Ave between Bradford Rd and Pompton Ave	40°51'N -74°13'W
EZ	Union Township	Faitoute Ave, across ballfield and stream	40°41'N -74°14'W
RL	Springfield	End of Lawrence Rd	40°40'N -74°18'W
CH	Scotch Plains	End of Knollwood Ct	40°37'N -74°23'W
PA	Scotch Plains	Behind Ashbrook Nursing Home off Raritan Rd	40°36'N -74°21'W
PL	Edison	Behind Durham Woods development across railroad tracks	40°33'N -74°23'W
M5f, fr	Parsippany-Troy Hills	End of Troy Meadows Rd	40°50'N -74°22'W
M6	East Hanover	Behind townhouse development off Park St	40°47'N -74°23'W
MW	Hanover	Behind Hanover Hills townhouse development off	40°48'N -74°27'W

		Ridgedale Ave	
BB	Long Hill	Across from Raptor Trust on Whitebridge Rd	40°41’N -74°29’W
ML	Millstone (Franklin)	Off D&R towpath off Amwell Rd	40°30’N -74°34’W
GR	Griggstown (Franklin)	Off Griggstown Causeway	40°26’W -74°36’W

Curriculum Vitae

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Education

1995-1999	Sc.B. Environmental Science Brown University
2001-2007	Ph.D. Ecology & Evolution Rutgers University

Research Experience

2001-2003	Graduate Assistant Department of Ecology, Evolution & Natural Resources
2004-2007	EPA STAR Graduate Fellowship Graduate Program in Ecology & Evolution
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Teaching Experience

Spring 2004	Teaching Assistant Principles of Applied Ecology
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Publications

Ehrenfeld, J. G., H. Bowman Cutway, R. Hamilton IV, and E. Stander. 2003. Hydrological description of forested wetlands in northeastern New Jersey, USA – an urban/suburban region. Wetlands 24(3): 685-700.

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