

# “Hotspots” and “Hot Moments” of Denitrification in Urban Brownfield Wetlands

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## ABSTRACT

The influence of hydrology and soil properties on disproportionately high (“hot”) rates of nitrate ( $\text{NO}_3^-$ ) removal via denitrification has been relatively well established. It is poorly understood, however, how the unique soil characteristics of brownfield wetlands contribute to or hinder denitrification. In this study, we examined drivers of “hot” denitrification rates over time (“hot moments”) and space (“hotspots”) in a watershed located on an unrestored brownfield in New Jersey, USA. We carried out measurements of denitrification over 9-day sequences during three seasons in sites with the same vegetation (*Phragmites australis*) but different soils (fill material, remnant marsh soils, flooded organic-rich soils). Denitrification rates above the 3rd quartile value of the data distribution were defined as “hot” and the most important drivers of these rates were determined using mixed models. Porosity and  $\text{NO}_3^-$  availability were the strongest spatial and temporal predictors, respectively, of high denitrification rates, with

coarse-textured, unflooded fill materials unexpectedly supporting the highest rates. These results suggest that pore-scale hydrology is a more complex controller of wetland denitrification than previously thought. Coarse-textured, unflooded soils have high fractions of air-filled pores relative to flooded soils, leading to more endogenous  $\text{NO}_3^-$  production, and less diffusion constraints than fine-textured soils, leading to higher  $\text{NO}_3^-$  availability to denitrifiers in suboxic pores. Laboratory studies confirmed denitrifiers were limited by  $\text{NO}_3^-$  availability. However, denitrification rates in all soils matched or exceeded atmospheric  $\text{NO}_3^-$  deposition and stormwater  $\text{NO}_3^-$  loading at the site, suggesting that brownfields may play an important role in  $\text{NO}_3^-$  removal from urban stormwater.

**Key words:** nitrate removal; spatial heterogeneity; denitrification limitations; soil structure; water-filled pore space; urban wetlands; hot spots and moments; water retention.

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## INTRODUCTION

Due to the many functions of ecological importance provided by wetlands, these environments have become the target of management schemes seeking to improve water and soil quality by using wetland ecosystem services (Stander and Ehrenfeld 2009). Wetland processes are often spatially and temporally heterogeneous, however, and managers lack quantitative, predictive models relating wetland

processes to specific combinations of biological communities, flooding patterns, and soils. Wetlands in urban settings, while having the potential to deliver services of high value (such as nutrient removal) (Bolund and Hunhammar 1999), pose a particular challenge in linking ecosystem processes (such as denitrification) with their environmental drivers, mainly because urban wetlands have been little studied, and each urban wetland system has its own unique set of altered conditions (Ehrenfeld and others 2003).

Geomorphic alterations such as ditching, berms, and waste dumps are common in urban landscapes, and contribute to high variability in both soil surface elevation and water tables in urban wetlands and watersheds (Ehrenfeld 2004). Urban soils are composed of a mixture of materials differing from those of adjacent agricultural or forest areas (that is, natural soils), and/or are heavily modified by human activity (De Kimpe and Morel 2000). Although the areal distribution of natural or undisturbed soil is inversely proportional to the extent of urbanization (Effland and Pouyat 1997), soils in urban landscapes are not uniformly impacted, with patches of undisturbed soil interspersed in the landscape (Effland and Pouyat 1997; Pickett and others 2008). Because urban soils are formed from heterogeneous, often non-soil materials, and have undergone variable times of development, the normal heterogeneity encountered within wetland soils may be greatly magnified in urban wetlands (Ehrenfeld 2004).

Brownfields are areas previously developed and now derelict, vacant, or under-utilized (Lesage and others 2007). Abandoned industrial sites have been estimated to occupy 20,200 km<sup>2</sup> in U.S. cities (U.S. Department of Housing and Urban Development 2013); this positioning within the urban matrix means that brownfields have the potential to both receive and modify materials from surrounding urban areas. Metropolitan development increases the extent of impervious surface and thus the volume of contaminated surface runoff entering urban waterways during storms (Paul and Meyer 2001; Ehrenfeld and others 2003; Walsh and others 2005). In the northeastern U.S., inorganic nitrogen in atmospheric deposition and stormwater is elevated due to fossil fuel combustion, fertilizer application, and leaky sewer infrastructure (Howarth and others 1996; Driscoll and others 2003; Howarth 2004). Excess inorganic nitrogen in surface waters is often transported to estuaries and coastal waters, causing eutrophication and biological perturbations such as dead zones (Mitsch and others 2001) and invasion by exotic species

(Minchinton and Bertness 2003; Silliman and Bertness 2004). There are as many as 425,000 brownfields in the United States (U.S. Department of Housing and Urban Development 2013). Although there has been much attention paid to pollutants, particularly heavy metals, in urban brownfield soils, there has been virtually no study of the function of wetlands that develop on brownfield sites. Denitrification, a microbial process common in wetlands, has been cited widely as a mechanism by which to reduce inorganic nitrogen in urban soils and waterways (Collins and others 2010). However, the denitrification function of urban wetlands is often compromised due to the hydrologic changes caused by urbanization (Groffman and others 2003; Stander and Ehrenfeld 2009). There is particular uncertainty about brownfield wetlands, which have received almost no attention in previous studies.

This study applied the emerging conceptual framework of “hotspots” and “hot moments” (McClain and others 2003; Harms and Grimm 2008; Vidon 2010; Gu and others 2012) for nitrate (NO<sub>3</sub><sup>-</sup>) removal via denitrification in natural wetland soils to wetlands developing on heterogeneous urban soils. “Hot” biogeochemical spots and moments are defined as “show[ing] disproportionately higher reaction rates” relative to “the surrounding matrix” (hotspots) or “longer intervening time periods” (hot moments) (McClain and others 2003). Existing studies lack consensus on how to define rates as “higher” than others, and the definition of a rate as “hot” varies considerably (Johnston and others 2001; Tzoraki and others 2007; Harms and Grimm 2008; Johnson and others 2010; Vidon and others 2010; Darrouzet-Nardi and Bowman 2011; Dai and others 2012; Gu and others 2012; Zhu and others 2012). Many studies simply define “hot” rates as “higher” than other measurements in a particular study, but recent work has emphasized more explicitly using the distribution of measured data to define hotspots and moments in a particular spatial or temporal context (Harms and Grimm 2008; Johnson and others 2010; Darrouzet-Nardi and Bowman 2011). Our study defines the upper quartile of the distribution of denitrification rates as “hot” rates of reaction.

Denitrification is mediated by: (1) the availability of organic carbon substrate (C); (2) the availability of NO<sub>3</sub><sup>-</sup>; and (3) the presence of suboxic (<0.2 mg L<sup>-1</sup> O<sub>2</sub>) conditions (Seitzinger and others 2006). Studies anticipate, therefore, that “hot” rates are created by the intersection of these materials and conditions (Boyer and others 2006). The dimensions and scale at which this intersection

occurs in the environment has proven difficult to model and quantify, however (Groffman and others 2009). Denitrification rates typically display high spatial and temporal variability within a landscape. This phenomenon has led to an extensive body of research exploring the location and environmental drivers of active zones within soil (Groffman and others 2009). A number of studies have demonstrated the influence of soil properties on denitrification rates (Groffman and Tiedje 1991; Pinay and others 2000; Machefert and Dise 2004; Well and others 2005; Koponen and others 2006; Novosad and Kay 2007). Texture influences pore size and water-filled pore space of soil, which in turn influence the volume fraction of water-filled, microbially habitable pores, anaerobic conditions in the soil, and denitrification rate (Groffman and Tiedje 1991; Machefert and Dise 2004; Koponen and others 2006; Novosad and Kay 2007). Many studies linking soil physical qualities to denitrification have taken place on small temporal or spatial scales and in the laboratory (but see Groffman and Tiedje 1991; Pinay and others 2000; Machefert and Dise 2004); the ability to scale up estimations of denitrification rate or potential is therefore often unexplored. Further, measurements of disproportionately high denitrification rates relative to background temporal variability (hot moments) and/or fluctuations in explanatory variables other than moisture and temperature (for example, soil  $\text{NO}_3^-$  and C content) are usually not included in analyses linking soil properties to denitrification. These approaches are thus not suitable for developing models capable of predicting very high or transient denitrification rates (Groffman and others 2009).

This study took advantage of a freshwater wetland system (Teaneck Creek Conservancy) in which monospecific stands of *Phragmites australis* are located on adjacent patches of clayey, loamy (construction fill), and organic-rich (according to USDA-NRCS 2010 definition) soils. The presence of these patches enabled isolation of the effects of soil type and soil-generated differences in hydrology on the spatial and temporal distribution of hotspots and hot moments of  $\text{NO}_3^-$  removal. Particulate organic matter in soil is an important source of labile carbon to denitrifiers, and availability of labile organic matter has been linked to both hotspots and hot moments of denitrification in soil (Parkin 1987; Christensen and Tiedje 1990; Hill and Cardaci 2004). Conducting measurements under the same vegetation community allowed us to examine drivers of high denitrification rates under similar carbon inputs. Our goal was to use the temporal

and spatial variability in denitrification within and among each of the three soil types to (1) define the dimensions of hotspots and hot moments in  $\text{NO}_3^-$  removal and (2) examine soil physical properties as a driver of both spatial and temporal variability in such phenomena.

We hypothesized that anaerobic conditions were the primary limiting factor to denitrification in wetlands at the site. Because atmospheric deposition of N is high in the region (Meyers and others 2001; Song and Gao 2009),  $\text{NO}_3^-$  inputs were also expected to be high and thus not a major limiting factor to denitrifiers. We therefore expected to find differences in both spatial and temporal variability of denitrification rates among the three soil types, due to differences in their hydraulic properties and surface water hydrology, that is, in their ability to support anaerobic microsites. Fine-textured soils (that is, high clay and/or silt content) have smaller pores, which tend to remain anaerobic even when a soil is well aerated, due to high water retention capacity under a range of moisture conditions (Groffman and Tiedje 1989a, b, 1991; Pinay and others 2000). Poorly drained soils also tend to more consistently support the anaerobic conditions that promote higher denitrification rates (Aulakh and Rennie 1985; Groffman and Tiedje 1989a, b, 1991; Pinay and others 2007). Further, soils with low aeration tend to accumulate organic matter, and organic matter improves the water holding capacity and water retention of soils (Brady and Weil 2002).

We hypothesized that soils that were more consistently flooded and/or with higher clay and organic matter content (that is, clayey or organic-rich soils) would provide the high volume of suboxic pore space necessary to promote hotspots of denitrification on the landscape. For this reason, we expected that soil mean particle size, percent clay, percent organic matter, and other soil structural characteristics related to hydraulic conductivity (porosity, bulk density) would all be important predictors of denitrification hotspots. We also hypothesized that rain and flooding would (1) create greater volumes of water-filled (and therefore suboxic) pore space, and (2) provide inputs of  $\text{NO}_3^-$  to soils, thereby promoting hot moments of denitrification. We therefore expected that flooding, water-filled pore space, redox potential, and soil  $\text{NO}_3^-$  availability would be important predictors of denitrification hot moments in the landscape.

Temperature influences microbial activity and diffusion rates, and a combination of high temperature and moisture often leads to the highest rates of denitrification (Spieles and Mitsch 2000;

Hernandez and Mitsch 2007). In addition to differences in temperature, seasons vary in organic inputs (for example, litterfall in autumn), nutrient pulsing (for example, soil thaw and snowmelt in spring), and flood pulsing (for example, larger thunderstorms in summer) to soils; these differences can drive when hot moments of denitrification occur (Bechtold and others 2003). We hypothesized that among three seasons (spring, summer, fall) more hot moments of denitrification would occur in the summer, when average monthly temperatures in the study region fall within the optimal range for denitrification (20–25°C) (Spieles and Mitsch 2000).

## METHODS

### Study Site

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

Channelization, downcutting, and berming of the creek and dumping of clay dredge and debris in the floodplain have compacted the upper layers of the soil profile and impeded groundwater and creek connectivity. Precipitation and stormwater are the primary hydrologic inputs for the site's wetlands. Six stormwater outfalls drain directly into Teaneck Creek and its wetlands, and a local hospital is permitted to pump 378,541 L d<sup>-1</sup> of groundwater into Teaneck Creek to keep its basement dry (Arnold 2008).

The numerous geomorphologic, biological, and hydrologic alterations relating to development activities at the site have led to high variation in soil profiles. Broad soil categories examined in this study include clayey soil, loamy fill, and unconsolidated organic-rich soils. The areas characterized by reduced clays likely represent the original wetland soils in the site, when the area was a freshwater marsh/stream system. The loamy fill is from construction of the NJ Turnpike in the 1950s. Fill piles additionally consist of trash deposited on the

site in the 1960s (Arnold 2008). The organic-rich soils are located on what are likely former tidal channels running through the site (before tide gate construction); they are composed of a combination of slowly decomposing litter (due to the nearly constant presence of surface water) and loamy fill that has washed in via surface water flows. Although the site supports a range of vegetation communities, all soil types support large stands of the invasive grass species *P. australis*; these areas were used for this study (Figure 1).

### Identifying “Hotspots” and “Hot Moments”

Seven patches representative of the range of soil types found in the watershed (clayey, loamy fill, organic-rich soil) were identified for sampling, and two 3 × 3 m plots were demarcated in each patch. A total of 14 plots were utilized for the study (Figure 1). The top 20 cm of the soil profile was considered in NO<sub>3</sub><sup>-</sup> removal dynamics. To identify differences in denitrification rates between soils over time, soil cores were collected from each plot every day for 9 days following a rain event (>2.5 cm of precipitation). Cores were collected in 2006 in each of three seasons when temperatures were high enough for high rates of denitrification to occur: spring (May), summer (July), and fall (November).

During each season, one core 10–17 cm long and 2.5 cm wide was collected in each plot every day for 9 days using a 20 × 3 cm corer. These cores were used immediately for static core, acetylene-based measurements of denitrification rate (Groffman and others 1999). Cores were transported back to the lab, sealed with gas-tight rubber stoppers, and brought to ambient air pressure by venting with a needle. Five milliliters of acetylene was injected into the headspace of each core, and the headspace was mixed three times with a 40 ml syringe. Five milliliters of sample was collected from the headspace of each core and injected into an evacuated 9 ml gas vial 2 and 6 h after injecting acetylene. Cores were maintained at room temperature (23°C) throughout analysis, and gas samples were stored in the lab at room temperature until analyzed for N<sub>2</sub>O content on a Shimadzu 14A Gas Chromatograph.

### Contribution of Soil Physical Properties to Denitrification Dynamics

To characterize differences between soil types in hydraulic properties, the mass-based gravimetric water content of all soil cores collected during the

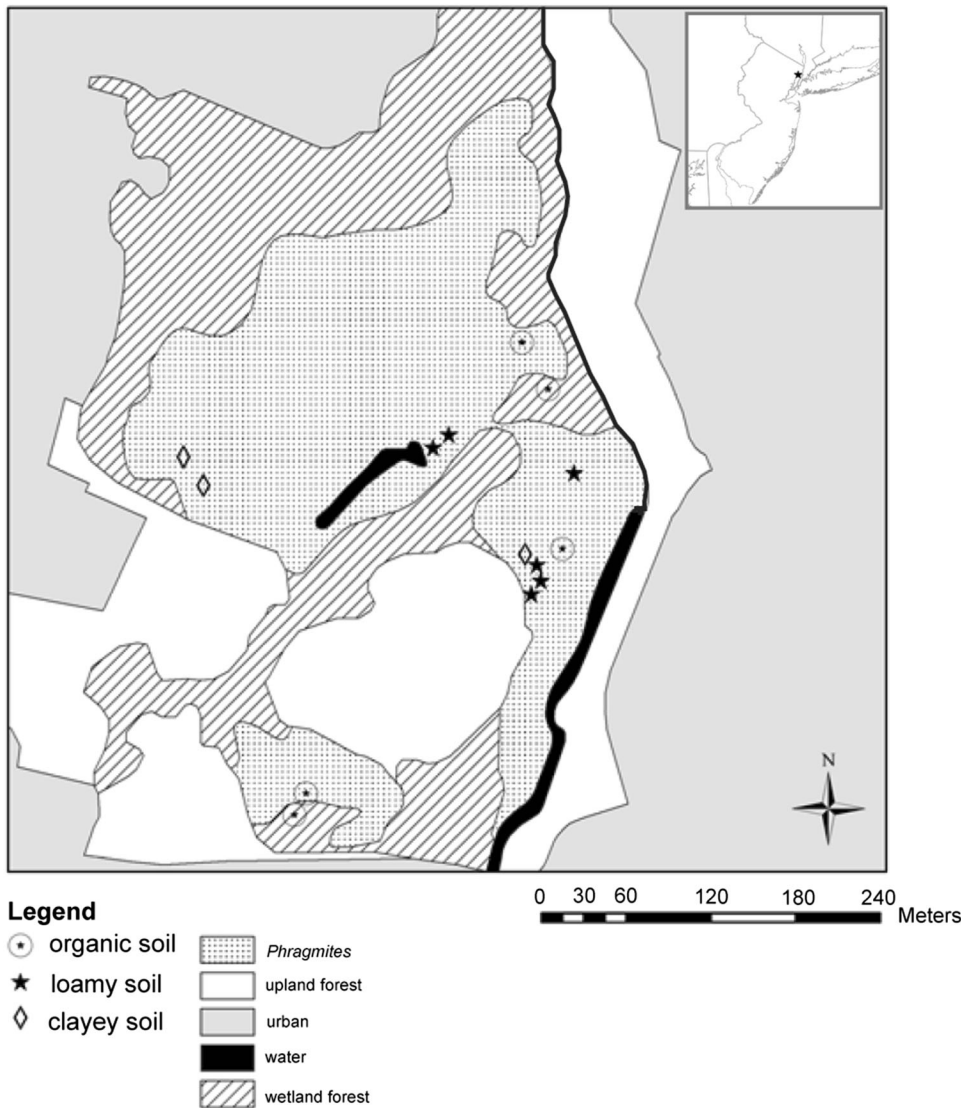


Figure 1. Land uses and sampling points at Teaneck Creek Conservancy. Teaneck Creek is the water body running along the eastern side of the site. Symbols represent the 14 plots used for the study; these plots were characterized by different soil texture, but all supported dense stands of *P. australis*.

study was determined concurrently with N processing. Water level at each plot was measured during sampling; soil was considered “flooded” if water level was 5 cm below the soil surface or higher. Soil texture (percent sand, silt, and clay) and bulk density (Blake and Hartge 1986) were characterized for each plot in the middle of the study, between summer and fall sampling. To determine bulk density, a pit was excavated in each plot, and three cores (5 cm high × 4.7 cm wide) were inserted horizontally into the side of the pit. Cores were dried for 1 week at 105°C and weighed.

Percent organic matter was measured using loss on ignition on a subsample of all soil cores collected during the study (Nelson and Sommers 1996). Soil texture fractions were determined using the hydrometer method (Gee and Bauder 1986). Mean particle size was calculated using soil textural

fractions (Shiozawa and Campbell 1991). Particle density was also determined for all mineral soils using the pycnometer method (Blake and Hartge 1986). Particle density for the organic-rich soils was determined by taking the sum of the particle density of each constituent times its percentage contribution to the whole sample: particle density of organic matter was assumed to be 1.5 kg m<sup>-3</sup>; the particle density of mineral constituents was assumed to be 2.5 kg m<sup>-3</sup> (Blake and Hartge 1986). The porosity of soil in each plot was determined based on the particle density and bulk density (Blake and Hartge 1986).

Water retention curves were simulated for each site to determine “effective air-filled pore space” (AFPS) and the water content at saturation ( $\theta_s$ ). The water retention curve for each site was parameterized using three different models (Rawls

and others 1983; Mayr and Jarvis 1999; Wosten and others 1999). The average water content ( $\theta$ ) predicted by all three models for each plot's soil at  $-33$ ,  $-60$ ,  $-100$ , and  $-1,500$  kPa was then calculated. To fit water retention curves for each site, water content values over the pressure potential sequence were fed into an online program (<http://swrcfit.sourceforge.net>) to calculate parameters for the van Genuchten model, that is, water content at saturation ( $\theta_s$ ), the residual water content ( $\theta_r$ ),  $\alpha$ , and  $n$  (van Genuchten 1980; Seki 2007). Water content at the inflection point of the water retention curve was calculated using an equation from Dexter (2004):

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

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

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

### Contribution of Soil Nitrate to Denitrification Dynamics

To measure soil extractable nitrate and net nitrification concurrently with denitrification measurements,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were extracted with 2 M KCl from all cores used for denitrification measurements within 24 h of collection (Hart and others 1994). KCl extracts were frozen and stored until they could be analyzed for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  using a flow injection analyzer (Hart and others 1994).

Results from the 2006 field study strongly suggested  $\text{NO}_3^-$  limitation to soils and the potential importance of either exogenous or endogenous  $\text{NO}_3^-$  (nitrification) inputs in stimulating high levels of denitrifier activity. To determine the relative importance of endogenous and exogenous  $\text{NO}_3^-$  inputs on denitrification rate, a lab incubation experiment was undertaken in August 2010. To simulate potential denitrification rates under conditions similar to a surface flooding event (that is, an input of exogenous  $\text{NO}_3^-$ ), we selected a concentration at the high end of concentrations found in surface water at Teaneck (*unpublished data*). We hypothesized that all soil types would demonstrate higher and more similar denitrifica-

tion rates under  $\text{NO}_3^-$  additions. An 800-cm<sup>3</sup> volume ( $20 \times 20 \times 20$  cm) of soil was collected from each of the 14 plots, and processed within 24 h. Each sample was thoroughly mixed in a bucket subsampled twice ( $\sim 250$  g each time). Each subsample was assigned to one of two treatments: control or experimental. All subsamples were further subsampled for percent soil moisture and KCl extraction (to determine initial  $\text{NO}_3^-$  and  $\text{NH}_4^+$  content). Two hundred grams soil of the initial 250 g subsample was then placed in a lidded 946-ml Mason Jar with either 500 ml of deionized water (control) or 500 ml of 4 mg L<sup>-1</sup> N- $\text{NO}_3^-$  ( $\text{KNO}_3^-$ ) solution (experimental). The headspace of each sample was evacuated and flushed 5 times using inert  $\text{N}_2$  gas through a septum in each lid to create a sub-aerobic environment, then immediately injected with 25 ml acetylene gas. Ten milliliters of gas was then collected from each Mason jar after 3, 5.5, and 23 h and analyzed for  $\text{N}_2\text{O}$  on a Shimadzu 14A GC. Mason jars were agitated by hand swirling to loosen all gas bubbles from soil pores prior to each gas sampling.

### Statistical Analyses

For the field study, linear comparative models (repeated measures PROC nlmixed) were used to determine the best predictors (soil physical characteristics, soil chemical characteristics, environmental variables) of denitrification rate at each site (SAS 2008). The goodness of fit of various candidate models was compared using Akaike's information criterion with a modification for finite sample sizes (AICC). If the difference between two AICC scores ( $\Delta\text{AICC}$ ) is 6.0, the model with a lower AICC score has a 95% chance of being the correct model, and the model with the higher score has a 5% chance of being the correct model (Motulsky and Christopoulos 2004). If the difference in AICC score is less than 6.0, the two models are more equally likely to be correct. PROC glm and PROC mixed were used to determine whether significant ( $P < 0.05$ ) differences existed between broad soil types (clayey, loamy fill, organic-rich soil) in soil physical and chemical properties over time (SAS 2008).

Denitrification rates across sites and over time within a given site had a highly skewed, non-normal distribution (PROC univariate); natural log transformation of denitrification rates did not result in normally distributed data (SAS 2008). The majority of denitrification measurements were near zero with a long tail to the right caused by a few very high denitrification rate measurements. In

order to identify the variables responsible for the highest denitrification rate measurements, denitrification rate was made into a binomial variable, based on the quartile of the data distribution into which the rate value fell. PROC nlmixed was run with soil variables predicting whether (1) the denitrification rate fell above or below the median (2nd quartile) denitrification rate (0 = below, 1 = above); or (2) the denitrification rate fell above or below the 75th percentile (3rd quartile) value (0 = below, 1 = above).

PROC nlmixed was run with spatial predictors of hotspots (porosity, mean particle size, % clay, % organic matter) using all 14 plots. For the hotspot models, the 2nd and 3rd quartile values for the data distribution of all denitrification measurements from all plots were used to generate the binary variable determining whether a particular variable represented a “hot” value (see Table 1). To predict hot moments, PROC nlmixed was run separately for plots falling into each soil category (clayey:  $n = 3$ ; loamy fill:  $n = 5$ ; organic-rich:  $n = 6$ ) using temporal predictors of denitrification quartile (flooding, effective AFPS, soil extractable  $\text{NO}_3^-$ , season, redox potential, temperature). For the hot moment models, the 2nd and 3rd quartile values for the data distribution of denitrification rates within each soil category were used to generate the binary variable determining whether a particular rate represented a “hot” value (see Table 3). To look for potential nonlinearities in relationships between denitrification quartile and predictor variables due to diffusion or uptake mechanism limitations (Fenchel and others 1998), quadratic models were also run for each variable and compared to linear

models using AICC scores to determine goodness-of-fit.

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

## RESULTS

### Hotspots and Hot Moments

Loamy fill soils supported the highest rates of denitrification during the study, followed by clayey soils; organic-rich soils demonstrated little to no denitrification activity (Figure 2). These differences between soil types (loamy fill > clayey > organic-rich) were significant over the study period according to a repeated measures analysis (PROC mixed;  $P < 0.05$ ). The denitrification rate data distribution was highly non-normal, however, and non-normality violates the assumptions of a repeated measures analysis. Denitrification rates across all soils ranged from  $-1.8$  to  $15.2 \mu\text{g N}_2\text{O-N kg soil}^{-1} \text{ h}^{-1}$ , with 50% of values falling below 0.15 (2nd quartile) and 75% of values falling below  $1.26 \mu\text{g N}_2\text{O-N kg soil}^{-1} \text{ h}^{-1}$  (3rd quartile).

High denitrification activity generally occurred at the same time in clayey and loamy fill soils, although variability in rate on a given sampling day within the two soil categories was high (Figure 2). Soil types had significant differences in how often they demonstrated hot moments of denitrification: among all pooled denitrification rate measurements, loamy fill soils had denitrification rates falling above the 3rd and 2nd quartile values sig-

**Table 1.** PROC nlmixed Results for Soil Spatial Variables

Predictor(s)	2nd quartile (0.15)	3rd quartile (1.26)	Significant predictors
Porosity	AICC = 283.9	AICC = 315.5	2nd: – porosity (<0.0001) 3rd: – porosity (<0.0001)
Porosity (porosity) <sup>2</sup>	AICC = <b>283.8</b>	AICC = <b>304.9</b>	2nd: – porosity <sup>2</sup> (0.15) 3rd: + porosity (0.003), + porosity <sup>2</sup> (0.001)
Mean particle size	AICC = 328.9	AICC = 347.4	
% clay	AICC = 326.8	AICC = 347.5	2nd: + clay (0.07)
% clay, (% clay) <sup>2</sup>	AICC = 319.1	AICC = 338.9	2nd: + clay (0.001), + clay <sup>2</sup> (0.003) 3rd: + clay (0.002), + clay <sup>2</sup> (0.003)
% organic matter	AICC = 320.8	AICC = 331.5	2nd: – organic matter (0.06) 3rd: – organic matter (0.05)

Models predicted whether denitrification rate at a given site exceeded the 2nd quartile value or 3rd quartile value (parenthetically indicated in  $\mu\text{g N}_2\text{O-N kg soil}^{-1} \text{ h}^{-1}$  beside “2nd quartile” or “3rd quartile”). Akaike’s information criterion value (AICC) is reported as relative goodness of fit for each model. Variables with a P value of 0.2 or lower in the model are noted in parentheses in the 4th column. A+ (positive) or – (negative) sign in front of each variable denotes the nature of the relationship between each variable and denitrification quartile. AICC values in bold are the lowest among all models in a given column, indicating the best model among each group of models.

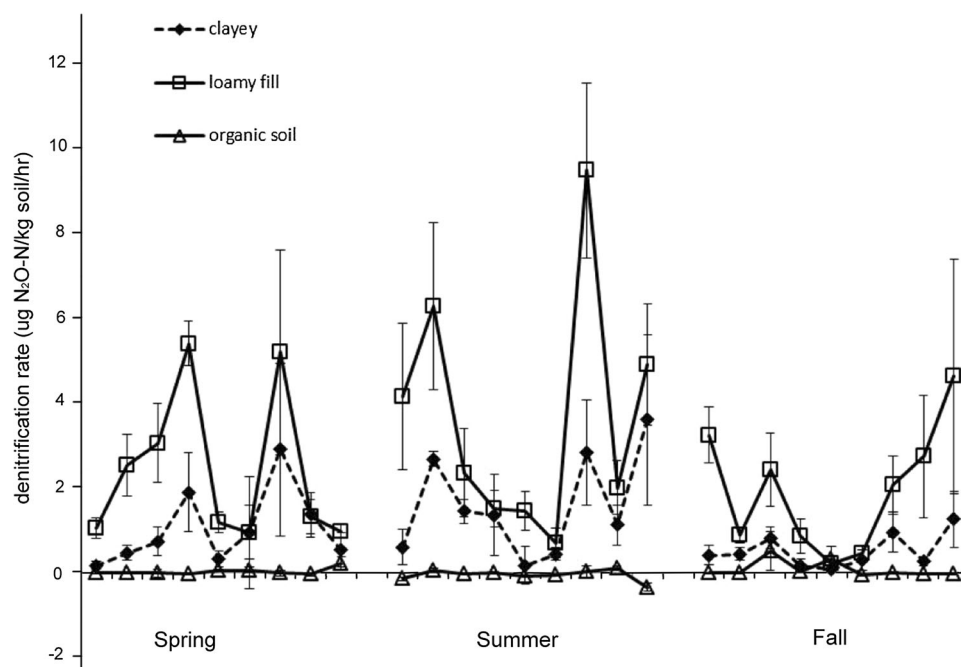


Figure 2. Denitrification rates in clayey, loamy fill, and organic-rich soils during the 2006 field study. Error bars represent one standard deviation from the mean value on a given day.

nificantly more frequently than clayey soils or organic-rich soils, and clayey soils had denitrification rates falling above the 3rd and 2nd quartile values significantly more frequently than organic-rich soils (Figure 3).

### Spatial Variables: Soil Physical Properties

Of all soil properties, porosity was the best predictor of whether a denitrification rate fell into the 2nd, 3rd, or 4th quartile (Table 1). Porosity ranged from 0.45 to 0.55, 0.55 to 0.60, and 0.81 to 0.92 in clayey, loamy fill, and organic-rich soils, respectively (Table 2). Porosity demonstrated a significant negative relationship with denitrification quartile. However, porosity also demonstrated a significant direct quadratic relationship with denitrification quartile (Table 1), indicating that soils with intermediate porosity (that is, loamy fill) had high denitrification rates most frequently (Figure 3). Percent clay also demonstrated a significant direct quadratic relationship with denitrification quartile, but yielded a higher AICC score than the model using porosity and porosity squared as predictors (Table 1). Mean particle size (MPS), which was highest in loamy fill and lowest in clayey soils (Table 2), was not a significant predictor of denitrification rate quartile, and the models utilizing MPS yielded the highest AICC values of any other spatial variable (Table 1). Soil organic matter content was significantly higher in the organic-rich soils

than in the loamy fill or clayey soils (Table 2), and was a significant negative predictor of denitrification quartile among soil types (Table 1).

### Temporal Variables: Fluctuations in Physical Soil Conditions

Although soil  $\text{NO}_3^-$  yielded the best model for predicting denitrification quartile in organic-rich and fill soils, and one of the best models for predicting denitrification quartile in clayey soils, a few physical soil conditions also were significant predictors of denitrification hot moments (Table 3). In clayey soils, a plot being “flooded” was a significant negative predictor of denitrification quartile, and the model with flooding as a predictor of whether a denitrification rate fell above the 3rd quartile value yielded a comparable AICC value to the model with the previous day’s soil  $\text{NO}_3^-$  content as a predictor (Table 3). The presence of flooded conditions did not change much, however, for each plot over the course of the study—organic-rich soils were flooded for the duration of the study, as was one of the three clayey plots; only rarely (1–2 instances) did one of the other clayey plots or the fill plots demonstrate flooded conditions.

Effective AFPS varied more within a given plot than “flooding” and was lowest, on average, in organic-rich soils and highest in clayey soils (Table 2). Water retention curves predicted higher water content in organic-rich soils than in loamy fill or clayey soils over a wide range of matric potentials



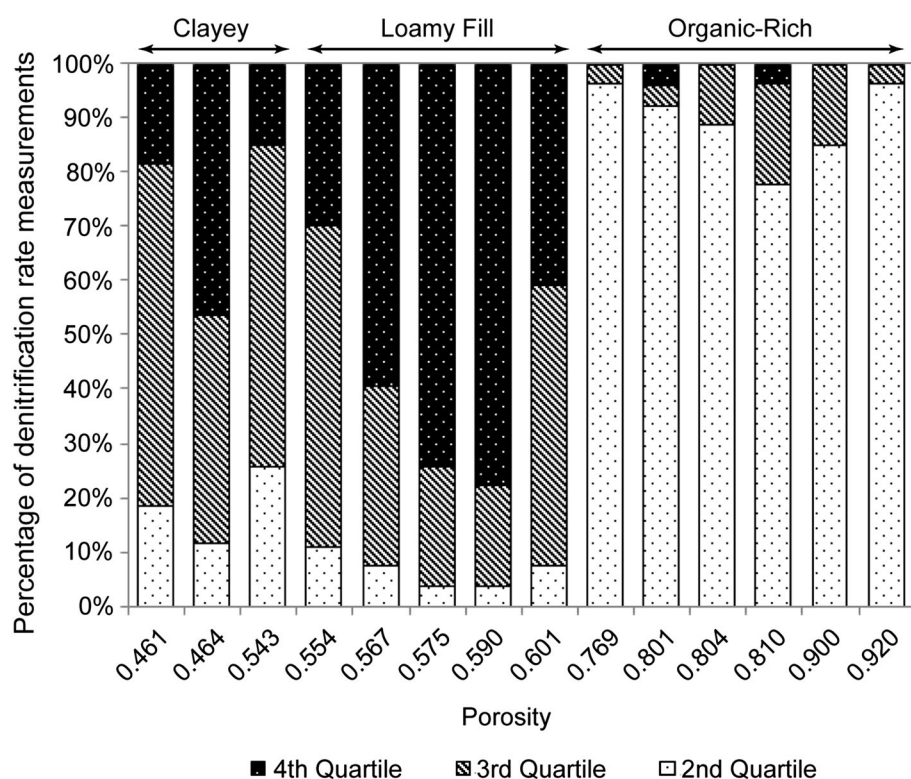


Figure 3. Porosity versus denitrification quartile. “Quartile” refers to the quartile of the entire data distribution (data from all sites pooled) into which a given measurement of denitrification rate falls: below the median value (2nd); between the median and 75th percentile values (3rd); or above the 75th percentile value (4th). The y-axis is the percent of denitrification rate measurements for each soil porosity (x-axis) value falling into either the 2nd, 3rd, or 4th quartile of the data distribution.

Table 2. Characteristics of Soils at Teaneck Creek Conservatory

Soil type	MPS (μm)	Bulk density (g cm <sup>-3</sup> )	% clay	Porosity	% organic matter	Effective AFPS	Soil NO <sub>3</sub> <sup>-</sup> -N (μg N g <sup>-1</sup> soil <sup>-1</sup> )	Soil NH <sub>4</sub> <sup>+</sup> -N (μg N g <sup>-1</sup> soil <sup>-1</sup> )
Clayey	3 ± 1 <sup>A</sup>	1.2 ± 0.07 <sup>A</sup>	48.11 ± 9.87 <sup>A</sup>	0.49 ± 0.03 <sup>A</sup>	7.92 ± 0.29 <sup>A</sup>	2.33 ± 0.16 <sup>A</sup>	0.59 ± 0.18 <sup>A</sup>	2.58 ± 0.27 <sup>A</sup>
Loamy Fill	24 ± 5 <sup>B</sup>	1.1 ± 0.04 <sup>A</sup>	16.80 ± 1.99 <sup>B</sup>	0.58 ± 0.01 <sup>B</sup>	11.76 ± 0.32 <sup>A</sup>	1.97 ± 0.07 <sup>B</sup>	0.18 ± 0.05 <sup>B</sup>	3.77 ± 0.16 <sup>A</sup>
Organic-Rich	26 ± 7 <sup>B</sup>	0.4 ± 0.05 <sup>B</sup>	12.67 ± 1.09 <sup>B</sup>	0.81 ± 0.03 <sup>C</sup>	16.78 ± 0.45 <sup>B</sup>	1.33 ± 0.07 <sup>C</sup>	-0.08 ± 0.03 <sup>B</sup>	7.33 ± 0.53 <sup>B</sup>

Mean values over the entire study period ± 1 standard error of the mean for each parameter are reported. Different letter superscripts in a given column represent a significant ( $P \leq 0.05$ ) difference according to PROC glm (MPS, bulk density, % clay, porosity) or a repeated measures PROC mixed model (% organic matter, effective AFPS, soil NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>).

MPS = mean particle size, AFPS = air-filled pore space.

(Figure 4). Clayey soils were predicted to retain slightly higher water content than loamy fill soils at field capacity (-33 kPa) and drier, but the two soil types retained a similar water content at high levels of saturation (Figure 4). Effective AFPS was a significant negative predictor of denitrification quartile in fill soils, and the models with effective AFPS as a predictor of denitrification quartile in fill soils yielded lower AICC scores than the models with flooding as a predictor (Table 3). In clayey and organic-rich soils, AICC scores of models using effective AFPS as a predictor were comparable to models using flooding as a predictor (Table 3). Unlike the models using porosity as a predictor of denitrification quartile (Table 1), effective AFPS did

not demonstrate a significant quadratic relationship with denitrification quartile in any of the soils, and AICC scores did not differ significantly between models using effective AFPS and both effective AFPS and effective AFPS<sup>2</sup> as predictors.

Temperature and redox potential in organic-rich soils were significantly lower than in clayey or fill soils; these two soil categories were not significantly different from each other in either variable (PROC mixed; data not shown). Unlike redox potentials in organic-rich soils (39–455 mV), redox potentials in clay and loamy fill soils were typically above the optimal range for denitrification (361–719 mV). Temperature and redox potential were marginally significant ( $P < 0.15$ ) positive and

**Table 3.** PROC nlmixed Results for Temporal Variables

Quartile denitrification value	Organic-rich			Clayey			Fill		
	2nd (-0.02)	3rd (0.03)		2nd (0.5)	3rd (1.3)		2nd (1.4)	3rd (3.0)	
Flooding	228.8	186.1		<b>105.2</b> ( <i>P</i> = 0.05)	<b>87.5</b> ( <i>P</i> = 0.07)	-	190.7	153.0	
Eff AFPS	228.8	185.1		107.8 ( <i>P</i> = 0.15)	<b>91.0</b>	+	<b>172.8</b> ( <i>P</i> = 0.005)	145.6 ( <i>P</i> = 0.03)	-
NO <sub>3</sub> <sup>-</sup> (same day)	227.6	183.1		109.2	<b>92.0</b>	-	190.0	151.9	
NO <sub>3</sub> <sup>-</sup> (previous day)	<b>203.4</b> ( <i>P</i> = 0.19)	<b>172.2</b>	-	<b>101.3</b>	<b>87.1</b>	+	<b>168.0</b>	<b>137.6</b>	-
Season	230.9 ( <i>P</i> = 0.03)	189.7	Su < F,Sp (2nd)	112.8	94.5 ( <i>P</i> = 0.05)	F < Su (3rd)	192.8 ( <i>P</i> = 0.05)	155.4 ( <i>P</i> = 0.17)	F < Su
Redox	98.9	80.5		46.8	35.8		80.1 ( <i>P</i> = 0.14)	53.6 ( <i>P</i> = 0.12)	-
Temperature	89.5 ( <i>P</i> = 0.06)	75.1	+	45.1	32.2 ( <i>P</i> = 0.19)	+	75.9 ( <i>P</i> = 0.13)	53.7 ( <i>P</i> = 0.10)	+

Models predicted whether denitrification rate at a given site exceeded the 2nd quartile value or 3rd quartile value (parenthetically indicated in µg N<sub>2</sub>O-N kg soil<sup>-1</sup> h<sup>-1</sup> beside '2nd' or '3rd' for each soil type). Akaike's information criterion value (AICc) is reported as relative goodness of fit for each model. Variables with a *P* value of 0.2 or lower in the model are noted in parentheses. A + (positive) or - (negative) sign in the rightmost column under each soil type denotes the nature of the relationship between each variable and denitrification quartile for that soil type. AICc values in bold are the lowest among all models in a given column, indicating the best model among each group of models. Note temperature and redox status utilize a subset of the data used in all other models, since they were only measured during part of the study.

negative predictors, respectively, of denitrification quartile in fill soils (Table 3). Temperature was a marginally significant positive predictor of whether denitrification rate exceeded the 3rd quartile value in clayey soils (*P* = 0.19) and whether denitrification rate exceeded the median value in organic-rich soils (*P* = 0.06) (Table 3).

Because temperature and redox potential were only measured for a subset of the study (days 5–9 in the summer and days 1–6 in the fall), AICc scores of models utilizing these parameters cannot be compared to the AICc scores of other models in Table 3. Of the two models utilizing either temperature or redox potential as a predictor, the one utilizing temperature had a lower AICc score only in the case of predicting whether denitrification rate exceeded the median value in organic-rich soils (Table 3).

The models utilizing season as a predictor of denitrification quartile did not have high relative AICc scores (Table 3). However, season was a significant or marginally significant predictor of whether denitrification rate exceeded the 3rd quartile value in all soil types (Table 3). In clayey and fill soils, denitrification rates fell into the 3rd quartile significantly fewer times in fall than in summer (Table 3). In organic-rich soils, summer had significantly fewer values exceeding the median value than in any other season (Table 3).

### Temporal Variables: Fluctuations in Soil Chemistry

Among all temporal variables, the amount of soil extractable NO<sub>3</sub><sup>-</sup> available the day prior to denitrification rate measurement (NO<sub>3</sub><sup>-</sup><sub>t-1</sub>) yielded the best model for predicting whether denitrification rate fell into the 2nd, 3rd, or 4th quartile for organic-rich soils (Table 3). NO<sub>3</sub><sup>-</sup><sub>t-1</sub> and flooding both yielded the best models for predicting denitrification quartile for clayey soils (Table 3). In fill soils, NO<sub>3</sub><sup>-</sup><sub>t-1</sub> yielded the best model for predicting whether denitrification rate fell above the 3rd quartile value. Both NO<sub>3</sub><sup>-</sup><sub>t-1</sub> and effective AFPS yielded the best models predicting whether a fill soil's denitrification rate fell above the 2nd quartile value (Table 3). NO<sub>3</sub><sup>-</sup><sub>t-1</sub> was a marginally significant (*P* < 0.20) negative predictor of denitrification quartile in organic-rich soils (Table 3). NO<sub>3</sub><sup>-</sup> content of the soil was significantly higher in clayey soils than in loamy fill or organic-rich soils, and organic-rich soils had significantly higher NH<sub>4</sub><sup>+</sup> than loamy fill or clayey soils (Table 2).

NO<sub>3</sub><sup>-</sup> additions significantly increased denitrification rate in the loamy fill soils, but not in organic or clayey soils (Figure 5). Potential denitrification

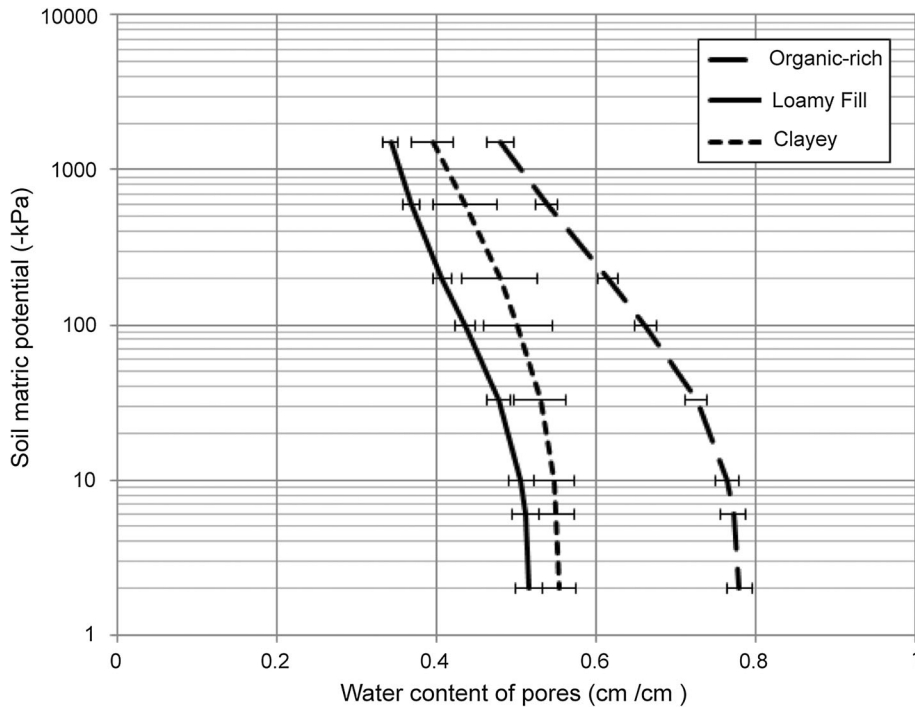


Figure 4. Average calculated water content contained in soil pores at various pressure potentials for organic-rich, loamy fill, and clayey soils. Values were calculated using the van Genuchten (1980) equation. Error bars represent one standard error for the mean value for each soil type at each pressure potential. Note that y-axis values are negative.

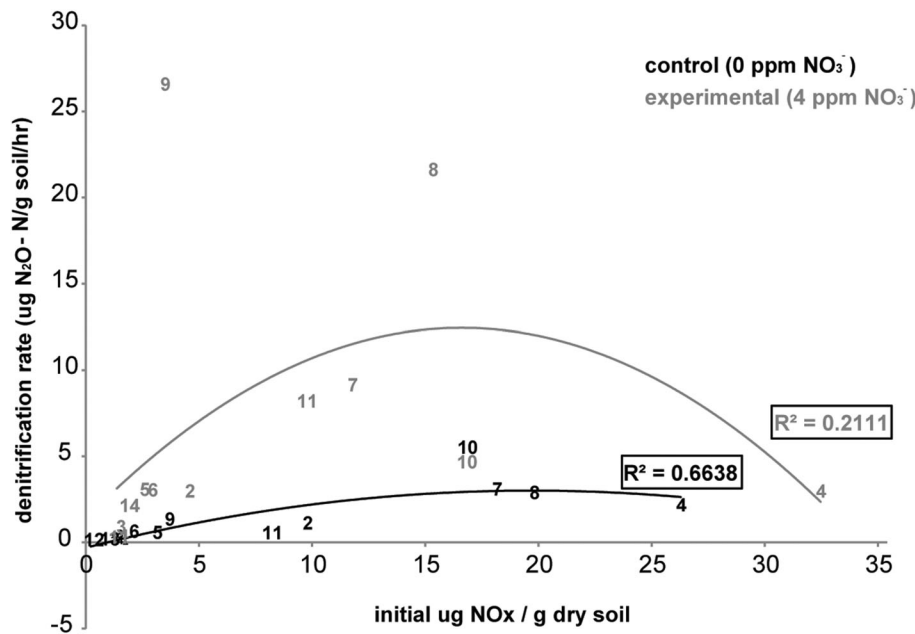


Figure 5. Potential denitrification rate versus soil  $\text{NO}_x$  with (experimental, gray color) or without (control, black color) 4 ppm  $\text{NO}_3^-$  added to the soil. Sites 1–6 are organic-rich soils, sites 7–11 are loamy fill soils, and sites 12–14 are clayey soils.  $R^2$  and  $P$  values apply to analyses performed using  $\ln(\text{denitrification rate})$ , because denitrification rate was non-normally distributed.

rates (that is, under  $\text{NO}_3^-$  additions) were non-normally distributed; the natural log of denitrification rate was therefore used for all subsequent statistical analyses of potential denitrification rates. Initial soil  $\text{NO}_3^-$  was not significantly different between control and experimental treatments (paired  $t$  test:  $t = -0.65$ ,  $P \gg 0.05$ ). Initial soil  $\text{NO}_3^-$  demonstrated a significant direct quadratic relationship with  $\ln(\text{denitrification rate})$  in control treatments

(Figure 5). In experimental treatments,  $\ln(\text{denitrification rate})$  demonstrated a weaker, but still significant, quadratic relationship with initial soil  $\text{NO}_3^-$ ; several loamy fill sites had denitrification rates much higher than would be predicted by initial soil  $\text{NO}_3^-$  content, however (Figure 5).  $\text{NO}_3^-$  and  $\text{NO}_3^-$ -squared generated the best model (that is, highest  $R^2$ ) predicting  $\ln$  experimental – control denitrification (results not shown).

## DISCUSSION

This study found large differences in denitrification dynamics between brownfield soil types, and provides important evidence that differences in variables associated with soil texture are a source of patchiness in denitrification within urban wetlands. Rather than identify the drivers of average denitrification rates in a given location, we utilized a novel statistical analysis to isolate the most important drivers of only the highest measured denitrification rates, defining any rate above the 3rd quartile value as “hot.” Contrary to our expectation that exogenous  $\text{NO}_3^-$  would be abundantly available to soils, and anaerobic conditions limiting to denitrification, the highest soil denitrification rates appeared to be associated with paired nitrification–denitrification activity. We hypothesized that more consistently flooded soils with high clay and organic matter content would promote denitrification hotspots in the landscape. Instead, the highest denitrification rates consistently occurred in relatively well-drained loamy soils with high porosity. Organic-rich flooded soils and periodically flooded patches of clayey soil, located between fill piles, appear to remain too anaerobic to support  $\text{NO}_3^-$  production and therefore demonstrate lower denitrification rates. In natural wetlands, hydrogeomorphic setting can be a key determinant of denitrification hotspots (Nelson and others 1995; Clement and others 2002). Our findings identify a useful new approach for predicting where high denitrification occurs in an urban brownfield wetland context, since this type of wetland does not exhibit classically predictable patterns in hydrogeomorphic settings, but instead reflects a pattern of anthropogenic deposition of materials. These results suggest that brownfield restoration projects aiming for higher levels of denitrification within wetlands must carefully consider texture and flooding of wetland soils and placement of fill materials in their design.

As predicted, denitrification hot moments were constrained by  $\text{NO}_3^-$  availability, soil water content, and temperature. However,  $\text{NO}_3^-$  available to denitrifiers appeared to be derived largely from endogenous production rather than exogenous inputs, and soil water content did not exhibit a uniformly positive relationship with denitrification rate. In general, high temperatures and soil characteristics facilitating nitrification promoted the highest levels of denitrification, and flooding and high water-filled pore space was associated with low denitrification rates. Minor decreases in daily soil water content were found to significantly

inhibit denitrification hot moments in fill soils, but flooding (that is, standing water) had a more significant relationship with whether denitrification activity was inhibited in clayey soils than fluctuations in soil water content. Organic-rich soils, which were permanently saturated and almost always flooded, exhibited the fewest hot moments of any soil type.

## Key Factors Controlling Hotspots and Moments of Denitrification: Nitrate Limitation

Contrary to our prediction that  $\text{NO}_3^-$  would not be limiting, hotspots of denitrification at the study site were most common where conditions were optimized for simultaneous denitrification (anaerobic) and  $\text{NO}_3^-$  production (aerobic). This was surprising, given the relatively high levels of wet and dry  $\text{NO}_3^-$  deposition in the region (Meyers and others 2001; Song and Gao 2009). As expected, soils with higher percent clay and organic matter retained more water over a range of simulated soil matric potentials relative to soils with lower clay and organic matter content. However, lower clay and organic matter content and higher porosity meant more denitrification rates falling in the upper quartiles of the data distribution. The plots with high percent organic matter also had standing water for most of the study, and denitrification rates were uniformly low. These findings suggest that a higher percent of aerated pores at a given soil moisture content means higher denitrification activity.

Results of the analysis examining hot moments of denitrification also indicated that coupled nitrification–denitrification drives the highest rates of denitrification in brownfield wetland soils. Available  $\text{NO}_3^-$  the day before denitrification rate measurement generated one of or the best model for predicting hot moments, and effective AFPS generated one of the best models for predicting hot moments (clayey soils) or high denitrification rates (fill soils) in non-flooded areas. “Hot moments” in this wetland system appear therefore to be tied to the degree of small scale (microsite) variability and/or discontinuity in required denitrification reactants (namely, low  $\text{O}_2$  and  $\text{NO}_3^-$ ) within a particular soil type (Parkin 1987). The coincidence of these reactants is likely facilitated by a combination of high  $\text{NO}_3^-$  production in aerated pores; a sufficient amount of anaerobic (water-filled) pore space; an active denitrifier community within the anaerobic pore space; and connectivity between the aerated and anaerobic pores. The structure of

fill soils appears to be the most optimized for this coincidence of conditions. Porosity of clayey soils was significantly lower than that of fill soils; this is unusual for soils of this texture. Low porosity may imply a higher tortuosity value for the medium (Adams 2005) and slower diffusion of  $\text{NO}_3^-$  from aerobic to anaerobic pores. In the lab experiment,  $\text{NO}_3^-$  additions at concentrations comparable to that of stormwater entering the wetland ( $4 \text{ mg L}^{-1}$ ) did not substantially increase denitrification rates in organic fill or clayey soils after 23 h, despite the fact that the soils were made into slurries, lessening the influence of diffusion in the soil pore matrix (Myrold and Tiedje 1985). Soil available  $\text{NO}_3^-$  demonstrated a positive relationship with denitrification rate potential in the control group. It appears therefore that endogenous soil  $\text{NO}_3^-$  production is needed to support active denitrifier populations that can quickly respond to  $\text{NO}_3^-$  loading events.

### Influence of Soil Water Dynamics on Denitrification

Past research has found that denitrification is negligible or on the low end of a range of measurements below a threshold of 60% water-filled pore space (WFPS). Above this threshold, denitrification is positively correlated with soil water content (Aulakh and Rennie 1985; Grundmann and Rolston 1987; Groffman and Tiedje 1991; Parsons and others 1991; Pinay and others 2000) and percent clay (Groffman and Tiedje 1991) or clay + silt (Pinay and others 2000), among other variables. In our study, WFPS (calculated using the formula utilized by Pinay and others 2000, data not shown) exceeded 60% over half the time in all plots over the course of the study, but denitrification rate quartile was only positively associated with soil water content in fill soils (Table 3). Organic and clayey soils, which exceeded 60% WFPS for around 87% of the study exhibited lower denitrification rates than loamy fill soils, which exceeded 60% WFPS roughly 65% of the time. Percent clay in this study demonstrated a significant quadratic relationship with denitrification “hotspots,” because it had a negative relationship with denitrification rate quartile in unflooded soils.

Our results, seemingly inconsistent with the results of past studies, may be due to the fact that in the aforementioned studies, ambient soil  $\text{NO}_3^-$  was in abundant supply due to deliberate soil fertilization (Aulakh and Rennie 1985; Grundmann and Rolston 1987; Parsons and others 1991) or endog-

enous net  $\text{NO}_3^-$  production rates 10–100 times higher than those found in this study (Groffman and Tiedje 1989a, b, 1991; Pinay and others 2000). Therefore, denitrifier communities in these studies may not have been as limited by  $\text{NO}_3^-$ , and aerobic soil pore space (which is negatively related to soil water and clay content) was not as crucial for maintaining high denitrification rates. Further, none of the studies above utilized soils that were classified as pure clay; they typically had low percent clay and were classified as loam or silt soils. Diffusion of  $\text{NO}_3^-$  to denitrifiers can be limited in well-aggregated soils, even if  $\text{NO}_3^-$  concentrations are high (Myrold and Tiedje 1985). This phenomenon was likely occurring in several of the clayey plots, where soil  $\text{NO}_3^-$  was on average high relative to the other soils (Table 2) but denitrification rate was low.

Our study results are similar to those of Hefting and others (2004), who found that average water table levels were a primary determinant of nitrogen dynamics, and that high silt + clay percentages had a significant positive correlation with denitrification rates only when groundwater table levels were below  $-30 \text{ cm}$ . Water table levels between  $-10$  and  $-30 \text{ cm}$  from the soil surface were the conditions under which the highest denitrification rates occurred due to the co-existence of aerobic (nitrifying) and anaerobic (denitrifying) hotspots within the soil profile (Hefting and others 2004). In our study, percent clay had a negative relationship with denitrification quartile in unflooded soils. Although we did not record water levels higher than  $-20 \text{ cm}$  at any loamy fill plots save for a few instances, the soil water content was likely high enough there to create a similar co-existence of aerobic and anaerobic hotspots within the soil profile. In clayey soils, both aerobic and anaerobic pores likely exist (since high  $\text{NO}_3^-$  and denitrification did occur in these soils), but are not well-connected enough to consistently facilitate high denitrification. Water table level (“flooding”) generated the second best predictive model of denitrification quartile in clayey soils after soil  $\text{NO}_3^-$ . Flooding was considered a temporal variable, but most sites were either flooded or unflooded for the entirety of the study. In sites with standing water, denitrification rates were uniformly low, and clayey soils exhibited a negative relationship with flooding. Flooded sites (which in nearly all cases were organic-rich soil sites) had significantly higher levels of  $\text{NH}_4^+$  than other sites (Table 2), low levels of  $\text{NO}_3^-$  (Table 2), and very low rates of denitrification. Hefting and others (2004) found very similar results for sites

with water tables above  $-10$  cm. Excepting a site with high allochthonous  $\text{NO}_3^-$  input, they surmised that the major end-product of N mineralization under water tables above  $-10$  cm was  $\text{NH}_4^+$ , and the rate-limiting step for denitrification was nitrification (Hefting and others 2004).

### Effect of Season and Temperature on Denitrification

As expected, denitrification hot moments occurred more frequently during summer than in fall for fill and clayey soils. Temperature was also a marginally significant positive predictor of hot moments within seasons for fill and clayey soils. Interestingly, in organic-rich soils hot moments occurred less frequently in summer than any other season, and the only hot moments recorded in these soils occurred in fall. Although none of the predictor variables appeared to be substantially different during or immediately prior to these "moments," the fall sampling was preceded by a rain event at least twice as large as those preceding the spring and summer samplings. It is possible that exogenous  $\text{NO}_3^-$  in stormwater accelerated denitrification rates in organic-rich soils after 3–4 days, when denitrifier communities had a chance to grow.

Soil temperatures during our study fell within the optimal range for denitrification ( $20$ – $25^\circ\text{C}$ ) (Speies and Mitsch 2000) almost exclusively during the summer. Distinct seasonal patterns in denitrification have been found by other studies in comparable climatic regions, with pulses of activity in the spring and fall (Hanson and others 1994; Nelson and others 1995) and in the summer (Hanson and others 1994; Hernandez and Mitsch 2007), due in part to substrate loading patterns. All studies cite hydrologic events (flooding, precipitation) as an important controlling seasonal factor on denitrification rates, and soil temperature is also identified as playing an important role, but the relative importance of the two variables in combination has not been elucidated. It has been suggested that a combination of high temperature and moisture can lead to the highest rates of denitrification (Hernandez and Mitsch 2007) and that below a certain temperature, denitrification will not occur even under very high soil moisture conditions (Pinay and others 2007). Our study found a different trend, where under very high moisture conditions (that is, in organic fill soils) temperature increases did not make a difference, but at intermediate moisture levels temperature had a strong positive effect on the creation of denitrification hot moments.

### Brownfield Soils are Likely Serving as a Sink for Atmospheric and Stormwater $\text{NO}_3^-$

Intact core denitrification rate ranges in the Teaneck soils ( $-1.8$  to  $15 \mu\text{g N}_2\text{O-N kg soil}^{-1} \text{ h}^{-1}$ , or  $-80$  to  $490 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ ) were higher than measurements made during the same time frame in railroad fill soils under comparable vegetation (grassy, *P. australis* present) at a site 19.5 km south of Teaneck Creek Conservancy ( $-40$  to  $130 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ ) (Palta and others 2013). Teaneck soils also demonstrated higher denitrification rates than native soils in both urbanized forested wetlands in New Jersey ( $-1.0$  to  $3.0 \mu\text{g N}_2\text{O-N kg}^{-1} \text{ h}^{-1}$ ) (Stander and Ehrenfeld 2009) and cedar swamps in the Pinelands of southern New Jersey ( $1.4$ – $140 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ ) (Watts and Seitzinger 2000). Clayey soils supported denitrification rates comparable to forested wetland soils in northern New Jersey (Stander and Ehrenfeld 2009), but hot moments of denitrification in fill soils at Teaneck were comparable to or exceeded the highest denitrification rates found in these other studies, indicating that Teaneck Creek Conservancy may constitute a hotspot of  $\text{NO}_3^-$  removal in the New Jersey landscape.

Potential denitrification rates of soils ( $0.1$ – $27 \mu\text{g N}_2\text{O-N kg}^{-1} \text{ h}^{-1}$ ) were orders of magnitude lower than average potential rates measured in native tidal freshwater marsh soils under the same vegetation type (*P. australis*) in the same region ( $19,199 \mu\text{g N}_2\text{O-N kg}^{-1} \text{ h}^{-1}$ ) (Otto and others 1999). Potential denitrification rates for loamy fill and clayey soils in this study were also lower than those found for urban riparian soils in Baltimore, Maryland ( $230$ – $759 \mu\text{g N}_2\text{O-N kg}^{-1} \text{ h}^{-1}$ ) (Groffman and others 2002; Groffman and Crawford 2003), but more comparable to those found for a constructed freshwater marsh and unrestored wetlands on railroad fill soils in northern New Jersey ( $0$ – $37 \mu\text{g N}_2\text{O-N kg}^{-1} \text{ h}^{-1}$ ) (Palta and others 2013). The lower potential rates in our study are likely due to the lower concentrations of  $\text{NO}_3^-$  used for our lab incubation ( $4 \text{ mg L}^{-1}$  instead of  $100 \text{ mg L}^{-1}$ ), but may also have to do with differences between the study sites in ambient soil N mineralization or environmental inputs of exogenous  $\text{NO}_3^-$ . However, our study likely more closely captured soil denitrification rates at Teaneck under flooding, because we selected a concentration at the high end of what might be found in surface water there. Despite the low potential denitrification rates relative to other studies of urban wetlands, the significant response of Teaneck soils to  $\text{NO}_3^-$  additions

did demonstrate that denitrifiers at the site are capable of increasing their rates of activity to process  $\text{NO}_3^-$ . Further, denitrification rates in all soils, but especially in clayey and loamy fill soils, matched or exceeded estimated  $\text{NO}_3^-$  wet and dry deposition (roughly  $0.03 \text{ mg m}^{-2} \text{ h}^{-1}$ ) (Turpin and others 2006) and stormwater  $\text{NO}_3^-$  loading (*unpublished data*), indicating that soils at the site may be an important sink for  $\text{NO}_3^-$ .

## CONCLUSION

This study is one of the first to examine denitrification rates in unmitigated fill materials on a brownfield site. Soil physical properties were highly heterogeneous over the extent of the site, and these properties influenced which soils supported the highest rates of denitrification. Soils in the Teaneck wetland site as a whole generally have adequate carbon and anaerobic pore space, but their denitrification capacity is limited primarily by  $\text{NO}_3^-$  availability. Loamy fill soils appear to have optimal structure for supporting simultaneous nitrification and denitrification, and therefore supported the highest rates of denitrification. Our results increase our understanding of the factors regulating denitrification in wetland ecosystems, and suggest that denitrifiers in fill materials are active and capable of high  $\text{NO}_3^-$  removal. This brownfield site and brownfield sites as a whole may therefore serve an important role in  $\text{NO}_3^-$  removal from urban stormwater, potentially performing better than native soils. Further research should determine just how fill materials can be chosen and/or managed to maximize their denitrification potential.

## ACKNOWLEDGMENTS

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