Journal of Environmental Management 294 (2021) 113021

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Interacting drivers and their tradeoffs for predicting denitrification potential across a strong urban to rural gradient within heterogeneous landscapes

Emily Stephan [a,*,1], Peter Groffman [b,c], Philippe Vidon [a], John C. Stella [a], Theodore Endreny [a]

[a] SUNY College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, NY, 13210, USA
[b] CUNY Advanced Science Research Center at the Graduate Center, 85 St. Nicholas Terrace, 5th Floor, New York, NY, 10031, USA
[c] Cary Institute of Ecosystem Studies, Box AB, Millbrook, NY, 12545, USA

ARTICLE INFO

Keywords:
Denitrification
Land use management
Urbanization
Nutrient pollution

ABSTRACT

Denitrification is a significant regulator of nitrogen pollution in diverse landscapes but is difficult to quantify. We examined relationships between denitrification potential and soil and landscape properties to develop a model that predicts denitrification potential at a landscape level. Denitrification potential, ancillary soil variables, and physical landscape attributes were measured at study sites within urban, suburban, and forested environments in the Gwynns Falls watershed in Baltimore, Maryland in a series of studies between 1998 and 2014. Data from these studies were used to develop a statistical model for denitrification potential using a subset of the samples ($N = 188$). The remaining measurements ($N = 150$) were used to validate the model. Soil moisture, soil respiration, and total soil nitrogen were the best predictors of denitrification potential ($R^2_{adj} = 0.35$), and the model was validated by regressing observed vs. predicted values. Our results suggest that soil denitrification potential can be modeled successfully using these three parameters, and that this model performs well across a variety of natural and developed land uses. This model provides a framework for predicting nitrogen dynamics in varying land use contexts. We also outline approaches to develop appropriate landscape-scale proxies for the key model inputs, including soil moisture, respiration, and soil nitrogen.

1. Introduction

The acceleration of atmospheric nitrogen (N) fixation to plant-available reactive forms by human activity has motivated studies of regional N fate and transport (Vitousek et al., 1997). There is particular interest in denitrification, an anaerobic microbial process that reverses this process by converting reactive N into N gases; however, this process is difficult to quantify, especially at large scales (Seitzinger et al., 2002). In an analysis of 16 large watersheds in the northeastern United States, denitrification was estimated to be the largest remaining N loss once known input, output and storage terms were considered, accounting for 34% of total storage and loss on average (Van Breemen et al., 2002). While regional mass balances such as these are helpful in quantifying the importance of landscape denitrification, they provide no predictive power or assessment of spatial variation in the process.

Regional-scale denitrification models vary in their predictive goals, with some focused on depicting mechanistic processes of the nitrogen cycle, and others intended for regional landscape management, with large differences in model algorithms and data inputs (Boyer et al., 2006). While mechanistic models focus on how denitrification interacts with microbial processes and soil parameters, regional management models typically focus on quantifying the environmental conditions in which denitrification is expected to occur. Urban ecosystems and landscapes pose a great challenge for these models. The complexity of infrastructure, site disturbance, human behavior, and highly fragmented land ownership in urban areas complicates parameterization of both mechanistic and empirical denitrification models.

Multi-scale studies show that landscape denitrification potential is driven by local-scale site characteristics rather than landscape-scale factors (Russell et al., 2019). Models that quantify these finer-scale

* Corresponding author.
E-mail addresses: eastepha@syr.edu (E. Stephan), pgroffman@gc.cuny.edu (P. Groffman), pgvidon@esf.edu (P. Vidon), stella@esf.edu (J.C. Stella), te@esf.edu (T. Endreny).
[1] Present Address: New York City Department of Parks and Recreation, 1234 5th Avenue, New York, NY 10029, USA.

https://doi.org/10.1016/j.jenvman.2021.113021
Received 23 January 2021; Received in revised form 30 April 2021; Accepted 4 June 2021
Available online 14 June 2021
0301-4797/

geochemical drivers, then, are critical to predicting large-scale net denitrification fluxes that matter at the spatial scale of catchments. A recent study was able to use stream nitrogen and phosphorus concentrations, channel characteristics, catchment land cover, and temperature as linear predictors of denitrification potential at a regional (>100 km) scale (Korol et al., 2019). However, these variables require great effort to obtain, and cannot predict sub-catchment hotspot locations.

Denitrification is a difficult process to measure directly, and methodological challenges have inhibited its estimation at ecosystem and landscape scales (Groffman et al., 2006). *In situ* rates of denitrification are particularly hard to measure and integrate, as they can range greatly based on dynamic driver conditions. As a result, many studies focus instead on potential rate measurements in *ex situ* laboratory assays, where anoxic conditions and carbon and nitrate substrates can be controlled. Denitrification potential assays quantify the maximum biological capacity of soils for denitrification, and have been applied in landscape-scale studies of forested, agricultural and urban landscapes (Bettez and Groffman, 2012; Bruland et al., 2006; Groffman and Crawford, 2003).

Studies of denitrification potential in along rural to urban gradients have demonstrated that urban conditions do not necessarily lead to low denitrification potentials relative to rural settings with more abundant organic matter and soil water precursors for denitrification (Walsh et al., 2005). However, modeling denitrification across rural to urban landscapes is complicated by the spatially patchy distribution of high denitrification rates within small areas, i.e., hotspots, and across short time scales, i.e., hot moments (Groffman et al., 2009, 2012; McClain et al., 2003; Vidon et al., 2010). Integrated across the landscape these discrete hot spots and hot moments cumulatively can account for a high proportion of denitrification activity in many ecosystem types. Compared with rural areas, urban areas can have unique denitrification hotspots associated with concentrated nitrogen sources (e.g., septic systems, leaky sewers) or with engineered structures such as constructed wetlands or stormwater control measures (SCM) that facilitate interaction between nitrogen sources and wet soils with high denitrification potential (Bettez and Groffman, 2012; Groffman and Crawford, 2003; McPhillips and Walter, 2015; Rosenzweig et al., 2011; Zhu et al., 2005).

One approach to addressing the complexity of quantifying denitrification potential across rural to urban gradients within heterogeneous landscapes is to use statistical models to highlight the most influential variables within a phenomenological modeling framework. Proxies can then be developed for estimating the principal drivers in particular ecosystems and landscapes. Studies have shown that denitrification correlates with soil moisture and organic matter (Groffman and Crawford, 2003; McPhillips and Walter, 2015), yet few studies have analyzed the predictive power of these variables (or others) to identify key areas of denitrification potential. Empirical models of denitrification (Anderson et al., 2015; Florinsky et al., 2004) have focused primarily on soil moisture as a driving factor, assuming that high levels of soil moisture and organic matter (SOM) co-occur within particular landscape zones. These assumptions are reinforced by studies that show soils with high moisture content to have high SOM due to the promotion of plant growth and slow rates of organic matter decomposition in wet soils (Pei et al., 2010). Recent studies have used topography to represent the spatial distribution of both soil moisture and SOM, as both correlate significantly with terrain variables (Anderson et al., 2015; Bieger et al., 2019; Florinsky et al., 2004). Human modification of the natural drainage framework and soil properties may make it difficult to identify incidents of high soil moisture and SOM, and this additional complexity should be taken into consideration in modeling efforts.

In this research, we compiled data from multiple studies of denitrification potential in the Baltimore, MD USA metropolitan area to assess the use of soil, hydrologic, and other landscape properties to develop a predictive tool for landscape-scale modeling of denitrification potential. Our objectives were to 1) assess how denitrification potential and associated soil variables vary across soil depths and land uses within a region; (2) quantify controls on denitrification potential and their interactions across urban, suburban, and forested landscapes; (3) assess whether a universal denitrification model is appropriate for this range of land use types; and 4) discuss how these controls could be linked to geographic tools that provide proxies for the distribution of these variables across the landscape.

2. Methods

2.1. Data sources

We utilized published (Bettez and Groffman, 2012; Gift et al., 2010; Groffman et al., 2002; Groffman and Crawford, 2003; Hale and Groffman, 2006; Harrison et al., 2012; Waters et al., 2014) and unpublished (sampled in 2014) data from the Baltimore Ecosystem (BES) study, a component of the U.S. National Science Foundation funded long-term ecological research (LTER) network. Most studies were carried out in the Gwynns Falls watershed; a main study site for BES that includes a mix of urban and suburban (~75%) and forested (~20%) land and numerous stormwater control measures (SCM) typical of the mid-Atlantic Piedmont region of the U.S. (Doheny, 1999). These studies included sites with a range of urban development density (urban, suburban, exurban), land cover (forest versus herbaceous), wetland type (forested versus SCM), stream restoration approaches, and other factors. Here, our objective was to search for strong statistical relationships across this diversity of urban sites.

The BES denitrification potential dataset (Groffman, 2016) contains 465 observations of denitrification potential (DEA) and a set of ancillary variables including soil nitrate (NO3), ammonium (NH4), total nitrogen (total N), microbial respiration (respiration), potential net N mineralization (Nmin), potential net nitrification (Nnit), soil organic matter (SOM), and soil moisture (Moisture), along with metadata such as land use context and sampling depth. Data came from 66 urban, 109 suburban, and 77 forested sites (Fig. 1). There were 387 shallow, 58 mid-depth, and 37 deep samples (represented by 0–10 cm, 10–70 cm, and 70+ cm, respectively).

2.2. Data exploration and visualization

The data were first stratified to evaluate the variation in DEA with land use (urban, suburban, and forested) and sampling depth (shallow, mid-depth, and deep), as described above. We tested the differences between land uses and between sampling depths using ANOVA and Tukey pairwise comparisons. We summarized the distributions in terms of mean and standard deviation of variables across the urban, suburban, and forested land uses.

We compiled soil and environmental variables for the shallow depth samples, and excluded observations with missing values for any predictor variables ($n = 312$). We used principal component analysis (PCA) to reduce the dimensionality of the data and visualize salient patterns. Sample points were also plotted across a land use gradient to visualize the relationship between land use context and the principal components.

2.3. Data analysis and modeling

We split the shallow depth (0–10 cm) data into two groups for model development and cross-validation. Sampled data were taken at 35 discrete locations. Since data were taken at some locations at several points in time, we used 25 of these locations for model development ($N = 188$) and 10 for cross-validation ($N = 150$). A correlation table was developed to demonstrate significant relationships between predictor variables and DEA, and to show which predictor variables were highly correlated with each other. Correlations were tested using a significance level of $p < 0.05$. We also checked the distributions of predictor and response variables to assess whether they were normally distributed; if they were not, we chose to log-transform the variables. The variables

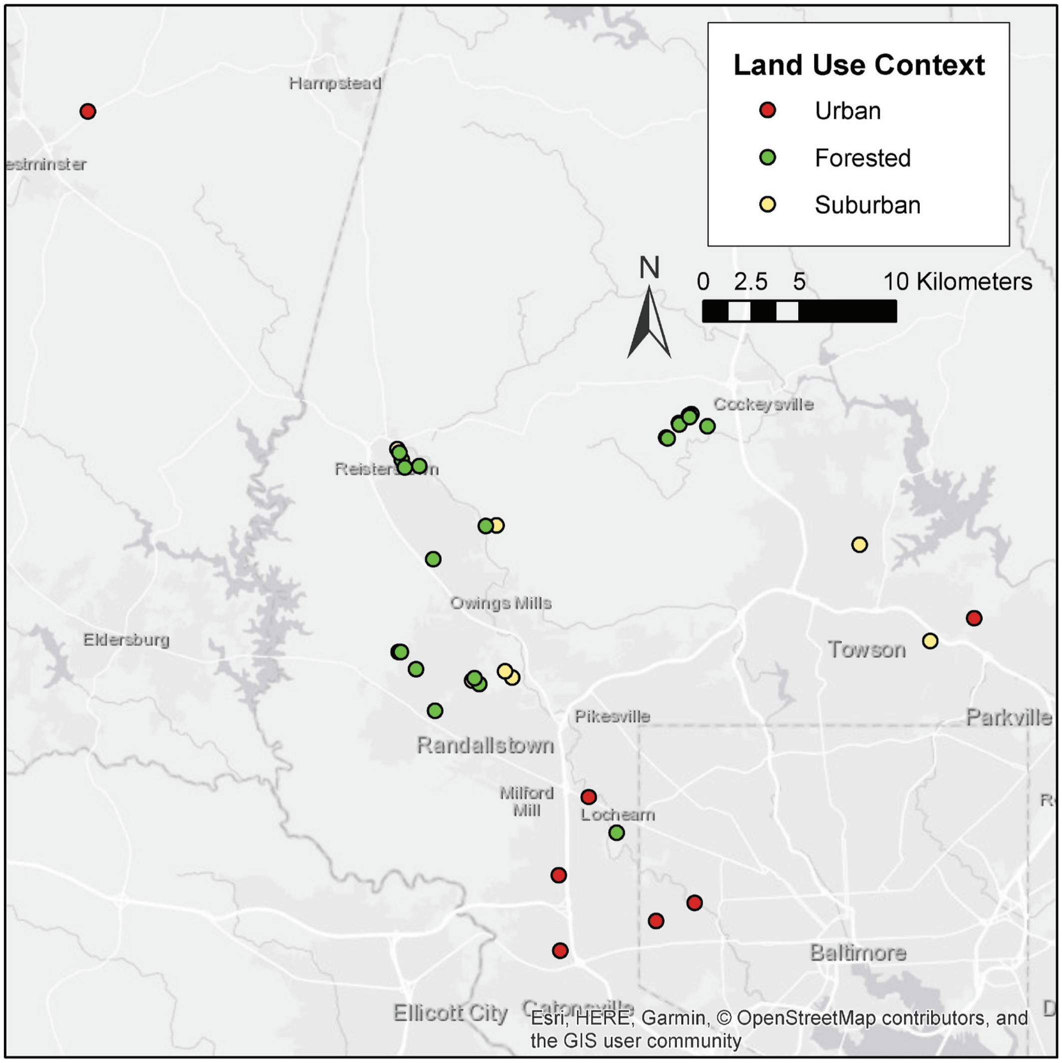

Fig. 1. Map of sampling sites by land use type.

that were log-transformed prior to model selection and validation were DEA, total N, and respiration.

We used this information to select a set of predictor variables with which to model DEA and used linear regression to compare a set of nine candidate models that included different combinations of main effects and their interactions. Model selection used the Akaike information criterion (AIC), with better models having lower AIC scores. The best models (deemed equivalent where $\Delta AIC \leq 2$) were then tested for multicollinearity using the variance inflation factor (VIF). Models with VIFs of above 10 that suggested high collinearity among predictor variables were excluded from the selection process (Kutner et al., 2004), and the best model was chosen. Following the selection of a best-fit model of denitrification potential, we tested its performance using the cross-validation dataset. Evaluation of model predictive capacity was determined based on linear regression between observed vs. predicted values (Piñeiro et al., 2008). Model interaction terms were also included to understand how individual variables drive DEA while holding other variables constant. All analyses were conducted in the statistical software program R (R Core Team, 2017).

3. Results

3.1. Denitrification variation with depth and land use

DEA decreased significantly with depth (Fig. 2) based on an ANOVA test ($F_{2,430} = 16.22$; $p < 0.001$). Pairwise comparisons showed that the differences between shallow (0–10 cm) and mid-depth (10–70 cm) samples were significant ($DEA_{diff} = 951$ ng/g soil/hr; $CI_{95} = (464, 1438)$; $p < 0.001$), and differences between shallow (0–10 cm) and deep (70–100 cm) samples were significant ($DEA_{diff} = 983$ ng/g soil/hr; $CI_{95} = (390, 1577)$; $p < 0.001$); there was no significant difference between mid-depth (10–70 cm) and deep (70–100 cm) samples ($DEA_{diff} = 32$ ng/g soil/hr; $CI_{95} = (-689, 753)$; $p = 0.99$). Noting the observed DEA values were significantly higher in the top 10 cm of soils, we focused model development on this subset of soil depth. Statistical analysis revealed there were no significant differences in denitrification potential between urban, suburban or forested sites (ANOVA $F_{2,249} = 0.882$; $p = 0.42$, Fig. 3).

Predictor variables' means and standard deviations are summarized in Table 2, along with ANOVA test p-values to indicate differences between land use categories for each variable. Variables with significant differences across land uses were NO_3, NH_4, total N, SOM, and soil moisture. Respiration, N mineralization, and N nitrification demonstrated no significant differences between land uses.

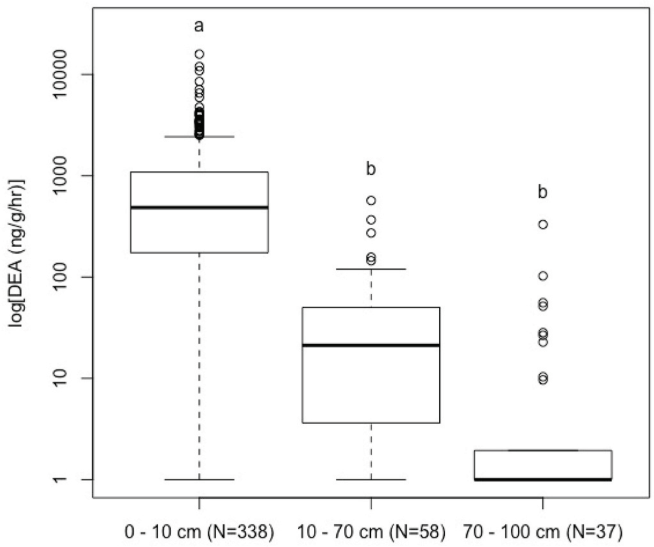

Fig. 2. Variation in DEA (denitrification potential) with depth. Tukey pairwise comparisons show that there is no significant difference between 10-70 cm and 70–100 cm depths ($p = 0.994$), but the differences are statistically significant between 0-10 cm and 10–70 cm and between 0-10 cm and 70–100 cm ($p < 0.001$ for both contrasts).

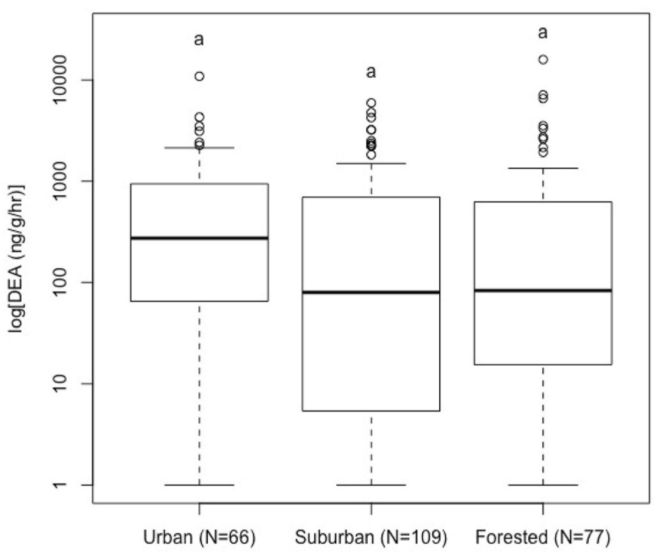

Fig. 3. Variation in DEA (denitrification potential) with land use. There were no significant differences between land use types ($F_{2,249} = 0.882$, $p = 0.42$).

3.2. Principal component analysis (PCA) results

For initial data exploration, we visualized the relationships between predictor variables through PCA (Table 3 and Fig. 4, n = 312); the analysis yielded nine linear combinations (i.e., the principal components). The first two components, PC1 and PC2, together explain 54% of the variation (35% and 19%, respectively) in environmental variables across the samples. Factor scores for the variables included in the PCA indicated that NH_4, total N, and soil moisture were most highly correlated with PCA axis 1. Net nitrification and net N mineralization were the most highly correlated variables with PCA axis 2 (Table 3). Sample points were also plotted along a land use gradient (forested, restored, suburban, urban, and exurban) (Fig. 4). The forested sites were clustered along the PC1 axis, while the suburban sites aligned more closely with the PC2 axis, suggesting the DEA values were driven by different variables for these land use types, even though differences in DEA across land uses were not statistically significant (Fig. 3). This suggests co-limitation of denitrification or that different drivers are prevalent in urban, suburban, and forested land use types.

3.3. Multiple regression models for available shallow denitrification potential data

Correlation analysis of the soil characteristics showed that DEA was positively correlated with soil moisture, soil organic matter, total N, and soil respiration (Table 1). The candidate models were developed using these four variables and their interactions, with the response data comprising the shallow depth (<10 cm) observations designated for model development (n = 188). Of the candidate models, three models had ΔAIC values within 2 (Ranks 1, 2, and 3; Table 4). The top ranked model differed from the Rank 2 and 3 models by one additional term, soil organic matter; the Rank 2 model omitted the interaction term between respiration and total N present in the Rank 1 and 3 models. Since the differences in AIC between the three top ranked models were so small, indicating that retaining the extra term resulted in no substantial improvement in the model, we chose to proceed with the simplest model (ranked #2). The equation for model rank #2 ($F_{4,169} = 22.02$; $p < 0.001$) is below:

$$\log(DEA) = 2.82 + 6.68*Moisture + 0.12*\log(Resp) + 1.14*\log(TotalN) - 1.77*\log(Moisture)*\log(TotalN) \tag{1}$$

Model validation for this selected model was performed using the model validation samples (n = 150). Regression of observed vs. predicted DEA values yielded an R^2 value of 0.36, with the linear model having an intercept of 1.64 and slope of 0.745 (Fig. 5).

3.4. Testing interactions at varying levels of total N

Because the three top-ranked models included the interactions between total N and soil moisture, we explored the parameter space of soil moisture and respiration at varying levels of total N. Although our top model omitted the interaction between total N and respiration, we also wanted to explore the parameter space of soil moisture and total N at varying levels of respiration.

Total N clearly constrains DEA, allowing for the development of high denitrification potential in wet and organic-rich sites (Fig. 6). At low levels of total N, respiration has much less effect on DEA, and soil moisture is the key driver of DEA under low N conditions. However, as total N increases, respiration has an increasing effect, with high respiration rates driving increased DEA for a given soil moisture level at higher levels of N. Compensatory tradeoffs between respiration and soil moisture are amplified at high levels of total N. At low total N and low moisture level, DEA is insensitive to variation in soil respiration, and DEA levels are always low. However, at high total N, moderate DEA can be achieved even at low soil moisture levels. In this case, high respiration values compensate for low soil moisture (and vice versa).

The relationship between soil moisture and total N at varying respiration rates is complex; unlike the plots at varying levels of total N, the relationship between soil moisture and total N remains similar across different levels of respiration, with differences in the magnitude of DEA (higher respiration rates yield higher DEA across all three plots). At low levels of soil moisture, DEA increases substantially with increasing total N. However, at higher levels of soil moisture, this pattern changes, and DEA actually decreases with increased total N, the turning point occurring at around 0.8 soil moisture.

4. Discussion

We demonstrate a novel approach to denitrification modeling using a

Table 1
Correlation matrix (r values) among denitrification potential and select groundwater and soil physiochemical characteristics. Significant correlations ($p < 0.05$) based on Pearson's correlation coefficient are shown in bold. DEA is denitrification potential (ng/g soil/hr), NO_3 is soil nitrate level (μg N/g dry soil), NH4 is soil ammonium (μg N/g dry soil), total N is total soil nitrogen (μg N/g dry soil), Respiration is soil respiration rate (μg C/g/d), Nmin is potential net N mineralization (μg N/g/d), Nnit is potential net N nitrification (μg N/g/d), SOM is soil organic matter (g/g), and Moisture is soil moisture content (g/g). Variables with an asterisk were included as predictors in the DEA model selection process.

	Groundwater				Soil				
	DEA (ng/g soil/hr)	NO_3 (μg N/g dry soil)	NH_4 (μg N/g dry soil)	Initial Total N * (μg N/g dry soil)	Soil Respiration* (μg C/g/d)	Potential Net N Mineralization (μg N/g/d)	Potential Net N Nitrification (μg N/g/d)	Soil organic matter* (g/g)	Soil moisture* (g/g)
DEA	1								
NO_3	0.339	1							
NH_4	**0.352**	−0.072	1						
TotalN*	**0.515**	**0.648**	**0.556**	1					
Respiration*	**0.469**	0.217	**0.459**	**0.445**	1				
Nmin	**−0.134**	0.190	**−0.347**	**−0.154**	**−0.111**	1			
Nnit	−0.017	0.137	0.008	0.090	−0.102	**0.693**	1		
SOM*	**0.189**	0.078	0.195	0.205	0.248	−0.049	−0.132	1	
Moisture*	**0.460**	0.062	**0.434**	**0.318**	**0.419**	**−0.238**	−0.206	**0.467**	1

Table 2
Summary of mean and standard deviation of predictor variables in urban (N = 46), suburban (N = 144), and forested (N = 86) shallow samples. ANOVA p-values are also shown, with statistically significant variables ($p < 0.05$) bold.

Variable[a]	Urban		Suburban		Forested		ANOVA p-value
	Mean	SD	Mean	SD	Mean	SD	
NO_3	3.90	4.71	3.03	5.35	1.80	2.86	**0.031**
NH_4	1.14	1.25	2.14	2.57	7.28	12.84	**<0.001**
TotalN	5.04	5.14	5.18	5.43	9.08	13.05	**0.002**
Respiration	105.72	182.07	61.20	133.23	65.07	163.17	0.212
Nmin	0.27	0.50	0.13	0.92	−0.08	1.46	0.156
Nnit	0.25	0.49	0.18	0.82	0.16	0.36	0.729
SOM	0.06	0.04	0.30	0.21	0.31	0.26	**<0.001**
Moisture	0.25	0.08	0.31	0.11	0.42	0.18	**<0.001**

[a] NO_3 is soil nitrate level (ug N/g dry soil), NH_4 is soil ammonium (ug N/g dry soil), total N is total soil nitrogen (ug N/g dry soil), Respiration is soil respiration rate (ug C/g/d), Nmin is potential net N mineralization (ug N/g/d), Nnit is potential net N nitrification (ug N/g/d), SOM is soil organic matter (g/g), and Moisture is soil moisture content (g/g).

Table 3
Loadings and correlation coefficients for the first two principal components (PC1 and PC2) for all shallow samples (n = 312).

	PC1		PC2	
Variable[a]	Loading	Correlation coefficient	Loading	Correlation coefficient
NO_3	−0.10	−0.17	0.15	0.19
NH_4	−0.53	−0.88	−0.19	−0.23
TotalN	−0.53	−0.88	−0.08	−0.10
Respiration	−0.33	−0.54	−0.08	−0.10
Nmin	0.34	0.57	−0.55	−0.67
Nnit	0.16	0.27	−0.68	−0.84
SOM	−0.12	−0.19	−0.29	−0.36
Moisture	−0.41	−0.69	−0.27	−0.33
Eigenvalue	2.77		1.49	
% Variance explained	34.65%		18.66%	

[a] NO_3 is soil nitrate level (ug N/g dry soil), NH_4 is soil ammonium (ug N/g dry soil), total N is total soil nitrogen (ug N/g dry soil), Respiration is soil respiration rate (ug C/g/d), Nmin is potential net N mineralization (ug N/g/d), Nnit is potential net N nitrification (ug N/g/d), SOM is soil organic matter (g/g), and Moisture is soil moisture content (g/g).

comprehensive dataset across urban, suburban, and rural land uses, and show that DEA is not significantly different across land uses. The drivers of DEA that emerged in our model (moisture, respiration, and total N) differed between land uses, suggesting that different factors limit DEA across the land use types. Strong driver interactions between the predictor variables reveal co-limitation of DEA, and show local variation in soil parameters to be strong drivers which must be considered within land use context.

4.1. *Patterns of denitrification potential*

We expected denitrification potential to be highest in the shallow samples, due to a higher likelihood of microbial activity near the soil surface. The observed trend in DEA with depth matches our expectations and agrees with many previous studies which demonstrate decreasing denitrification capacity with depth (Bettez and Groffman, 2012; Brye et al., 2001; P.M. Groffman and Crawford, 2003; Jefferson et al., 2010; Luo et al., 1998; Parkin and Meisinger, 1989; Saggar et al., 2013). Our focus on surface processes is appropriate for urban landscapes, where there is great interest in capturing and processing stormwater surface runoff. However, it is important to note that activity at depth (more than 10 cm deep) can be significant (Morse et al., 2014) and is especially important for processing of nitrate moving in shallow groundwater (Gold et al., 2001; Vidon and Hill, 2004). This omission in our landscape model should be explored further.

There were no significant differences in DEA between urban, suburban and forested sites. Due to altered urban hydrology (Walsh et al., 2005), changing nutrient export pathways (Kaushal and Belt, 2012), and a "distinct urban biogeochemistry" (Kaye et al., 2006), we expected urban environments to be poorly suited for nutrient uptake and processing. However, denitrification potential has been shown to occur at high rates in urban environments (Grimm et al., 2005; Groffman and Crawford, 2003; Inwood et al., 2005). Groffman and Crawford [2003]

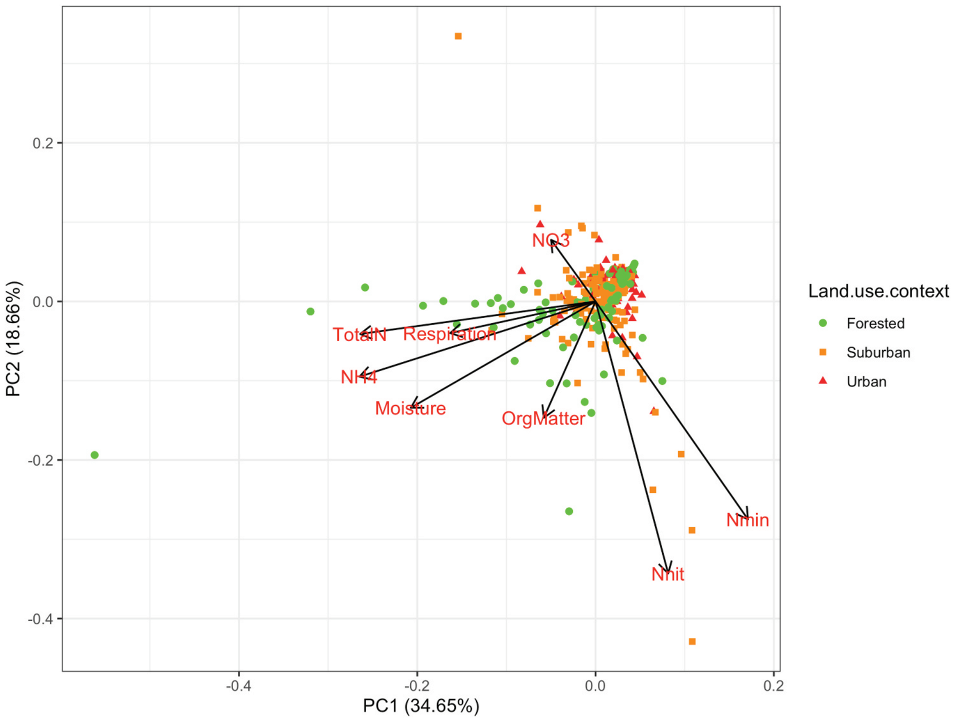

Fig. 4. PCA (principal component analysis) for all denitrification potential samples. Forested sites were clustered along the PC1 axis, while suburban sites aligned more closely with the PC2 axis, suggesting that DEA was controlled by different variables in different areas. DEA is denitrification potential (ng/g/hr), NO_3 is soil nitrate levels (μg N/g dry soil), NH_4 is soil ammonium (μg N/g dry soil), total N is total soil nitrogen (μg N/g dry soil), Respiration is soil respiration rate (μg C/g/d), Nmin is potential net N mineralization (μg N/g/d), Nnit is potential net N nitrification (μg N/g/d), SOM is soil organic matter (g/g), and Moisture is soil moisture content (g/g).

Table 4
Model selection criteria used in ranking linear regression models predicting the denitrification potential (DEA) of sampled sites (N = 188). The best model (rank = 1) had the lowest AICc value and the highest Akaike weight. There were ten candidate models, including a null model with intercept only (model rank = 10). Models ranked 1, 2, and 3 were deemed equally suitable, given that ΔAICc <2.

DEA model rankings						Coefficient estimates (with standard error)[a]						
Rank	df	AICc	ΔAICc	Akaike weight	Cum. weight	Moisture	Resp.	Total N	SOM	Moisture: Resp	Moisture: TotalN	Resp.: TotalN
1	6	602.57	0	0.36	0.36	9.72 ± 2.36	0.01 ± 0.15	1.19 ± 0.31	−1.2 ± 0.6		−2.59 ± 0.92	0.05 ± 0.09
2	4	603.19	0.62	0.26	0.62	6.68 ± 1.91	0.12 ± 0.09	1.14 ± 0.25			−1.77 ± 0.79	
3	5	604.47	1.9	0.14	0.75	7.45 ± 2.08	0 ± 0.16	1 ± 0.3			−2.19 ± 0.91	0.09 ± 0.09
4	5	605.23	2.66	0.09	0.85	7.77 ± 3.56	0.2 ± 0.24	1.11 ± 0.27		−0.31 ± 0.86	−1.68 ± 0.84	
5	3	606.17	3.6	0.06	0.91	2.96 ± 0.96	0.13 ± 0.09	0.64 ± 0.12				
6	6	606.24	3.67	0.06	0.96	9.61 ± 3.95	0.13 ± 0.25	0.91 ± 0.33		−0.58 ± 0.9	−2.1 ± 0.92	0.1 ± 0.1
7	4	607.17	4.6	0.04	1	6.56 ± 3.54	0.35 ± 0.23	0.62 ± 0.12		−0.87 ± 0.82		
8	3	636.5	33.93	0	1	10.28 ± 3.75	0.62 ± 0.24			−1.35 ± 0.88		
9	2	636.74	34.17	0	1	4.77 ± 0.97	0.28 ± 0.09					
10	0	717.39	114.83	0	1							

[a] Total N is total soil nitrogen (μg N/g dry soil), Resp is soil respiration rate (μg C/g/d), SOM is soil organic matter (g/g), and Moisture is soil moisture content (g/g).

reported higher variability in denitrification potential in urban areas compared to rural areas, which is logical given the heterogeneous nature of urban landscapes. However, for our dataset, variability in denitrification potential was higher in forested and suburban land uses as compared to urban (Fig. 3). Since soil moisture, respiration, and total N emerged as the most important predictors of denitrification potential, we also examined differences in these three variables between the three land use classifications. Soil moisture and total N showed statistically significant differences between land uses (Table 2). These results suggest that while one denitrification model is applicable to all land uses, the mechanisms for modeling soil moisture and total N should vary. We suggest appropriate future modeling directions below.

It should be noted that denitrification potential does not necessarily reflect the actual denitrification rates occurring in the field. Denitrification potential and rate have been shown to correlate well (Groffman and Tiedje, 1989), but a lack of anoxic conditions, carbon source, or available nitrate can lead to locations with high denitrification potential but low actual rate. There is a clear need for analysis of relationships between actual and potential denitrification rates in urban areas and/or demonstration that measurements of denitrification potential are mechanistically predictive in ecosystem and landscape-scale nitrogen mass balances (Groffman et al., 2006).

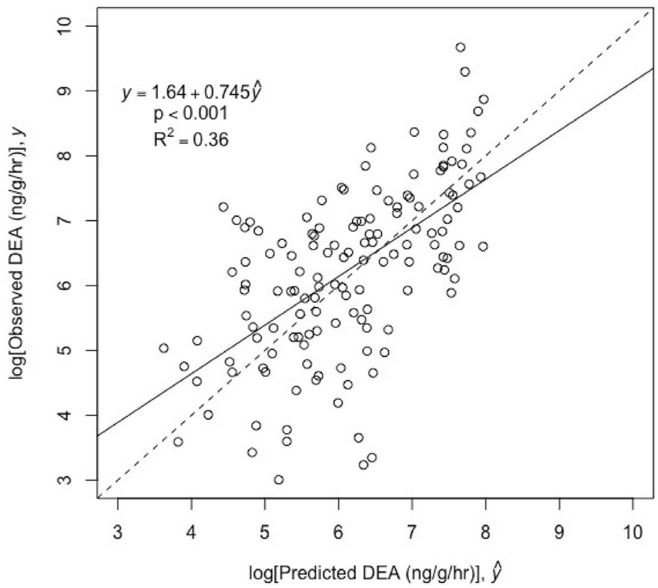

Fig. 5. Observed vs. predicted denitrification for model validation. The solid line represents the fit between observed vs. predicted, and the dashed line shows the 1:1 line.

Although for this study, we looked exclusively at freshwater systems with no tidal influence, recent research suggests higher DEA rates in tidally-influenced systems, likely due to higher soil moisture, organic, and nutrient content (Korol and Noe, 2020). Future research should consider these unique tidal freshwater forested wetlands as hotspots of denitrification potential, and examine how these locations fit into the framework presented in this study.

4.2. Best models predicting denitrification potential

The variables that emerged in the final model (moisture, respiration, and total N) reveal patterns that have not yet emerged from prior modeling efforts. We hypothesized that soil organic matter would be a strong predictor of denitrification potential. Organic matter is a logically strong predictor of denitrification potential as it provides an index of the supply of carbon to support heterotrophic denitrifiers and of the potential for oxygen consumption by overall heterotrophic activity. Bettez and Groffman [2012] demonstrated strong correlations between denitrification potential and soil moisture ($R^2 = 0.66$), soil organic matter ($R^2 = 0.89$), microbial biomass C ($R^2 = 0.79$), and respiration ($R^2 = 0.81$) in an analysis of a subset of the samples in our datasets. Many other studies have also found soil organic matter to be a strong predictor of denitrification potential (Burford and Bremner, 1975). However, our model development and selection process concluded that soil respiration was a stronger predictor than organic matter (Table 1). This is perhaps not a surprising result, as respiration is driven by increased levels of labile carbon and is therefore a more direct controller of heterotrophic activity than total organic matter content. Respiration may be a particularly useful/important predictor of denitrification in urban watersheds, where hydrologic changes have altered relationships between water table depth, stream channel depth, soil moisture and organic matter content (Groffman et al., 2003). It should be noted that a complex microbial process such as respiration is driven by many environmental factors (e.g. soil moisture, organic matter) and other microbial processes; therefore, respiration as a variable may integrate other factors that are difficult to quantify or account for in the model.

Total N also emerged as a strong predictor of DEA in our study. The inclusion of total N is novel, as in many current models, soil moisture (or a topographic proxy) is assumed to be the primary driver of denitrification (Anderson et al., 2015; Florinsky et al., 2004). A recent metagenomic analysis of denitrification gene abundance revealed that both soil moisture and nitrate were critical in selecting for denitrifying microbial communities (Nadeau et al., 2019). Denitrification rates have also been elevated due to increased nitrogen deposition, supporting our inclusion of total N as a key predictor (Palacin-Lizarbe et al., 2020). The emergence of total nitrogen as an important predictor, separate from soil moisture, represents a significant finding. Given the mechanisms governing denitrification, it is not surprising that our selected model (ranked 2 in Table 4) included indicators of all three key drivers with soil moisture, respiration, and total N, as well as interactions between these terms.

The interaction plots (Fig. 6) demonstrate likely co-limitation of DEA by total N, respiration and soil moisture. These co-limitation effects may explain the significant differences in these drivers among urban, suburban and forested sites, even though there were no significant differences in DEA across the land uses. Sites with high respiration rates (urban sites, Table 2) may have also been low in total N and/or soil moisture, whereas forested sites which tended towards higher total N and moisture values may have been limited by lower respiration rates. These complex relationships highlight local variation in soil parameters as a stronger control than landscape patterns, and allow for the denitrification model proposed in this study to be used across different land uses and, thus, across different predictor variable parameter spaces.

4.3. Implications of results for modeling DEA at the watershed scale

Using the model developed in this study to predict denitrification across unmonitored settings requires identification of landscape scale proxies for our key predictor variables; soil moisture, respiration, and total N. Soil moisture modeling has been active for many decades but is greatly complicated in urban environments by the presence of grey infrastructure which routes water independently of topography, which is a key predictor for many hydrologic models. A promising development is the i-Tree Hydro model (Wang et al., 2008), built upon TOPURBAN model concepts (Valeo and Moin, 2000), which uses a topographic framework to effectively route water from upslope impervious and pervious areas to predict likelihood for soil saturation. This i-Tree Hydro model dynamically models infiltration and may better account for transport of nitrogen using the coupled i-Tree Buffer tool with its weighting of export coefficients (Stephan and Endreny, 2016). Other watershed models have used road network maps to enhance land cover maps to improve runoff quantity estimates (Endreny and Thomas, 2009), but have not explicitly explored the resulting soil moisture regimes. There is a need to better couple natural and human-influenced water routing processes to allow for more accurate and robust estimates of soil moisture across urban landscapes.

Proxies for soil respiration can potentially be derived from estimates of soil temperature, which has been shown to be a strong driver of variation in soil respiration, especially when coupled with precipitation (Raich et al., 2002). In addition, adding leaf area index (LAI) to as an index of carbon supply improved the model's ability to predict soil respiration (Reichstein et al., 2003). The increasing availability of satellite images of LAI and soil temperature and precipitation data suggests that the prospects for modeling soil respiration as a factor driving DEA are promising.

Development of proxies for N supply to denitrifiers could focus on modification of existing export coefficient models. These models can be modified to depict the spatial distribution of both point and nonpoint sources of N across landscapes (Stephan and Endreny, 2016). However, in order to predict DEA, locations of high nitrate concentrations should be identified, which has proven difficult in developed landscapes. While nitrate yield in suburban and urban watersheds has been shown to be more than 10 times higher than that of completely forested watersheds, retention of N in these disturbed watersheds has been found to be surprisingly high (Groffman et al., 2004). These dynamics suggest that sources of N, as well as the flowpaths and removal mechanisms, must be

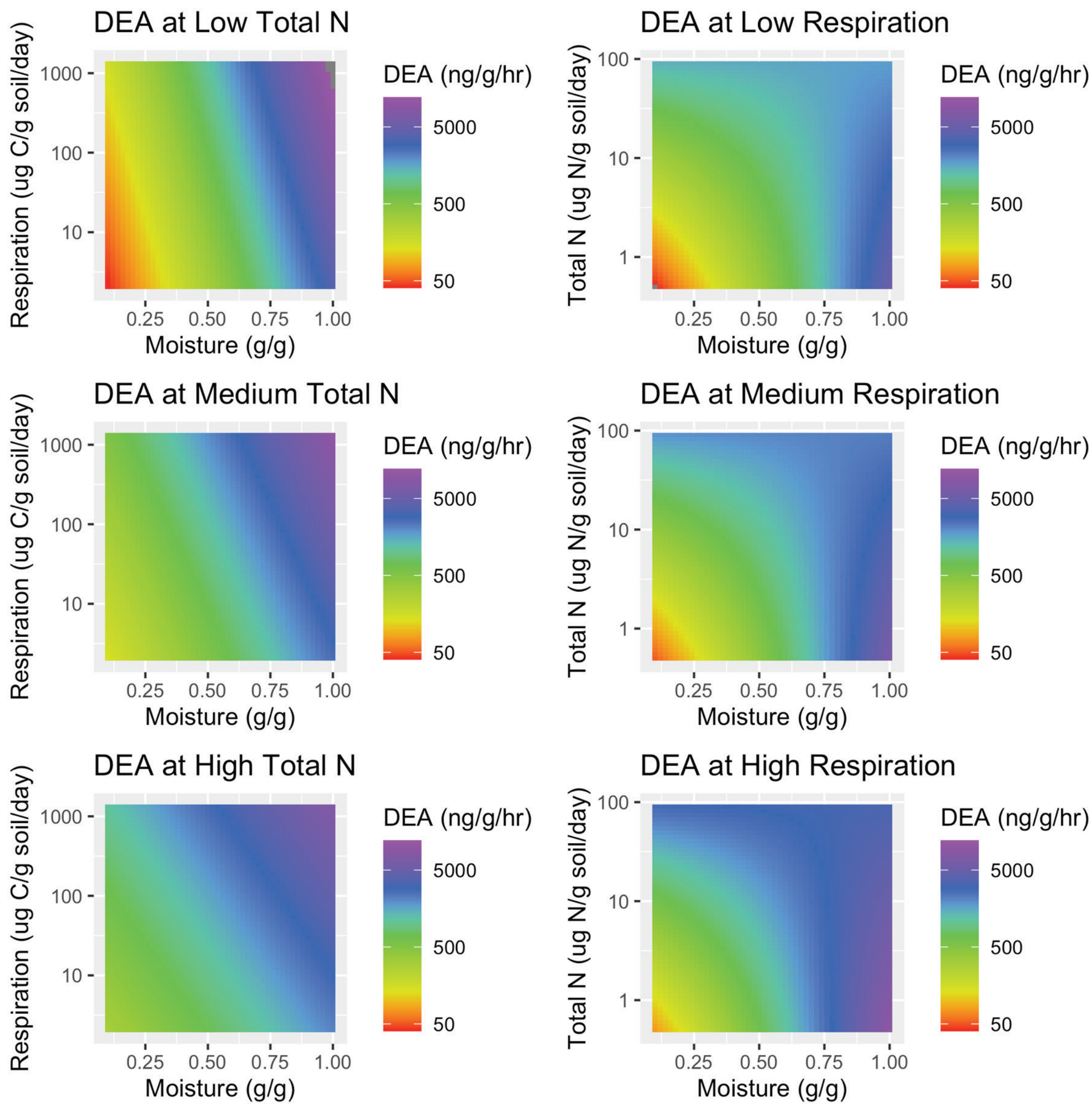

Fig. 6. Interaction plot showing how soil moisture and soil respiration controls on DEA vary with different levels of total nitrogen, and how soil moisture and total nitrogen controls on DEA vary with different rates of respiration. Respiration has no effect on DEA at low levels of total N, but its effect amplifies as total N increases. At high N levels, soil respiration and soil moisture have compensatory effects on DEA. At all rates of respiration, DEA increases with increased total N at low soil moisture, but DEA decreases with increased total N at higher soil moisture (above 0.8).

linked in order to get a full picture of nitrate supply to denitrifiers in these watersheds (Ledford et al., 2017, Sudduth et al., 2013).

5. Conclusion

There is a strong need to model denitrification potential in mixed use landscapes in order to guide resource conservation and management. Using available data from the Baltimore region, we demonstrated that denitrification occurs primarily in the shallow soil depths, and that denitrification potential is not inherently different across land use types. Our data analyses identified soil moisture, respiration, and total N as coherent controls of denitrification potential in the study region; these variables can be represented in statistical models to predict denitrification across rural to urban gradients. A major challenge for future research is to develop models and/or geographic data sources that can depict spatial and temporal variation in the key predictor variables of denitrification potential.

Funding

This research was supported by two agreements with the USDA Forest Service including a Research Joint Venture, 11-JV-11242308-112, and a Challenge Cost Share agreement 11-DG-11132544-340 recommended by the National Urban and Community Forest Advisory Council.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.113021.

Credit author statement

Emily Stephan: Conceptualization, Methodology, Software, Validation, Formal analysis, Data curation, Writing – original draft, Visualization, Peter Groffman: Conceptualization, Methodology, Investigation, Writing – review & editing, Philippe Vidon: Conceptualization, Methodology, Writing – review & editing, John C. Stella: Methodology, Software, Validation, Formal analysis, Writing – review & editing, Theodore Endreny: Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition

References

Anderson, T.R., Groffman, P.M., Walter, M.T., 2015. Using a soil topographic index to distribute denitrification fluxes across a northeastern headwater catchment. J. Hydrol. 522, 123–134. https://doi.org/10.1016/j.jhydrol.2014.12.043.

Bettez, N.D., Groffman, P.M., 2012. Denitrification potential in stormwater control structures and natural riparian zones in an urban landscape. Environ. Sci. Technol. 46 (20), 10909–10917. https://doi.org/10.1021/es301409z.

Bieger, K., Arnold, J., Rathjens, H., White, M., Bosch, D., Allen, P., 2019. Representing the connectivity of upland areas to floodplains and streams in SWAT+. JAWRA Journal of the American Water Resources Association 55. https://doi.org/10.1111/1752-1688.12728.

Boyer, E.W., Alexander, R.B., Parton, W.J., Li, C., Butterbach-Bahl, K., Donner, S.D., Skaggs, R.W., Grosso, S.J.D., 2006. Modeling denitrification in terrestrial and aquatic ecosystems at regional scales. Ecol. Appl. 16 (6), 2123–2142. https://doi.org/10.1890/1051-0761(2006)016[2123:MDITAA]2.0.CO;2.

Breemen, N. van, Boyer, E.W., Goodale, C.L., Jaworski, N.A., Paustian, K., Seitzinger, S. P., Lajtha, K., Mayer, B., Dam, D. van, Howarth, R.W., Nadelhoffer, K.J., Eve, M., Billen, G., 2002. Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern U.S.A. *Biogeochemistry*. https://doi.org/10.1023/A:1015775225913, 57–58-1-267-293.

Bruland, G.L., Richardson, C.J., Whalen, S.C., 2006. Spatial variability of denitrification potential and related soil properties in created, restored, and paired natural. Wetlands 26 (4), 1042–1056. https://doi.org/10.1672/0277-5212(2006)26[1042:SVODPA]2.0.CO;2.

Brye, K.R., Norman, J.M., Bundy, L.G., Gower, S.T., 2001. Nitrogen and carbon leaching in agroecosystems and their role in denitrification potential. J. Environ. Qual. 30 (1), 58–70. https://doi.org/10.2134/jeq2001.30158x.

Burford, J.R., Bremner, J.M., 1975. Relationships between the denitrification capacities of soils and total, water-soluble and readily decomposable soil organic matter. Soil Biol. Biochem. 7 (6), 389–394. https://doi.org/10.1016/0038-0717(75)90055-3.

Doheny, E.J., 1999. Index of Hydrologic Characteristics and Data Resources for the Gwynns Falls Watershed, Baltimore County and Baltimore City, Maryland. USGS Report OFR 99-213. U.S. Geological Survey, Denver, CO, p. 24.

Endreny, T., Thomas, K., 2009. Improving estimates of simulated runoff quality and quantity using road-enhanced land cover data. J. Hydrol. Eng. 14 (4), 346–351. https://doi.org/10.1061/(ASCE)1084-0699(2009)14:4(346).

Florinsky, I.V., McMahon, S., Burton, D.L., 2004. Topographic control of soil microbial activity: A case study of denitrifiers. Geoderma 119 (1–2), 33–53. https://doi.org/10.1016/S0016-7061(03)00224-6.

Gift, D.M., Groffman, P.M., Kaushal, S.S., Mayer, P.M., 2010. Denitrification potential, root biomass, and organic matter in degraded and restored urban riparian zones. Restor. Ecol. 18 (1), 113–120. https://doi.org/10.1111/j.1526-100X.2008.00438.x.

Gold, A.J., Groffman, P.M., Addy, K., Kellogg, D.Q., Stolt, M., Rosenblatt, A.E., 2001. Landscape attributes as controls on ground water nitrate removal capacity of riparian zones. JAWRA Journal of the American Water Resources Association 37 (6), 1457–1464. https://doi.org/10.1111/j.1752-1688.2001.tb03652.x.

Grimm, N.B., Sheibley, R.W., Crenshaw, C.L., Dahm, C.N., Roach, W.J., Zeglin, L.H., 2005. N retention and transformation in urban streams. J. North Am. Benthol. Soc. 24 (3), 626–642. https://doi.org/10.1899/04-027.1.

Groffman, Peter M., 2012. Terrestrial denitrification: Challenges and opportunities. Ecological Processes 1 (1), 11. https://doi.org/10.1186/2192-1709-1-11.

Groffman, Peter M., Bain, D.J., Band, L.E., Belt, K.T., Brush, G.S., Grove, J.M., Pouyat, R. V., Yesilonis, I.C., Zipperer, W.C., 2003. Down by the riverside: Urban riparian ecology. Front. Ecol. Environ. 1 (6), 315–321. https://doi.org/10.1890/1540-9295(2003)001[0315:DBTRUR]2.0.CO;2.

Groffman, Peter M., Boulware, N.J., Zipperer, W.C., Pouyat, R.V., Band, L.E., Colosimo, M.F., 2002. Soil nitrogen cycle processes in urban riparian zones. Environ. Sci. Technol. 36 (21), 4547–4552. https://doi.org/10.1021/es020649z.

Groffman, Peter M., Butterbach-Bahl, K., Fulweiler, R.W., Gold, A.J., Morse, J.L., Stander, E.K., Tague, C., Tonitto, C., Vidon, P., 2009. Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models. Biogeochemistry 93 (1–2), 49–77. https://doi.org/10.1007/s10533-008-9277-5.

Groffman, Peter M., Law, N.L., Belt, K.T., Band, L.E., Fisher, G.T., 2004. Nitrogen fluxes and retention in urban watershed ecosystems. Ecosystems 7 (4), 393–403. https://doi.org/10.1007/s10021-003-0039-x.

Groffman, Peter M., Tiedje, J.M., 1989. Denitrification in north temperate forest soils: Relationships between denitrification and environmental factors at the landscape scale. Soil Biol. Biochem. 21 (5), 621–626. https://doi.org/10.1016/0038-0717(89)90054-0.

Groffman, P.M., Altabet, M.A., Böhlke, J.K., Butterbach-Bahl, K., David, M.B., Firestone, M.K., Giblin, A.E., Kana, T.M., Nielsen, L.P., Voytek, M.A., 2006. Methods for measuring denitrification: Diverse approaches to a difficult problem. Ecol. Appl. 16 (6), 2091–2122. https://doi.org/10.1890/1051-0761(2006)016[2091:MFMDDA]2.0.CO;2.

Groffman, P.M., Crawford, M.K., 2003. Denitrification potential in urban riparian zones. J. Environ. Qual. 32 (3), 1144–1149.

Hale, R.L., Groffman, P.M., 2006. Chloride effects on nitrogen dynamics in forested and suburban stream debris dams. J. Environ. Qual. 35 (6), 2425–2432. https://doi.org/10.2134/jeq2006.0164.

Harrison, M.D., Groffman, P.M., Mayer, P.M., Kaushal, S.S., 2012. Microbial biomass and activity in geomorphic features in forested and urban restored and degraded streams. Ecol. Eng. 38 (1), 1–10. https://doi.org/10.1016/j.ecoleng.2011.09.001.

Inwood, S.E., Tank, J.L., Bernot, M.J., 2005. Patterns of denitrification associated with land use in 9 midwestern headwater streams. J. North Am. Benthol. Soc. 24 (2), 227–245. https://doi.org/10.1899/04-032.1.

Jefferson, A., O'Driscoll, M., Manda, A., Clinton, S., Jefferson, A., McMillan, S., 2010. Urbanization effects on watershed hydrology and in-stream processes in the southern United States. Water 2 (3), 605–648.

Kaushal, S.S., Belt, K.T., 2012. The urban watershed continuum: Evolving spatial and temporal dimensions. Urban Ecosyst. 15 (2), 409–435. https://doi.org/10.1007/s11252-012-0226-7.

Kaye, J.P., Groffman, P.M., Grimm, N.B., Baker, L.A., Pouyat, R.V., 2006. A distinct urban biogeochemistry? Trends Ecol. Evol. 21 (4), 192–199. https://doi.org/10.1016/j.tree.2005.12.006.

Korol, A.R., Noe, G.B., 2020. Patterns of denitrification potential in tidal freshwater forested wetlands. Estuar. Coast 43 (2), 329–346. https://doi.org/10.1007/s12237-019-00663-6.

Korol, A.R., Noe, G.B., Ahn, C., 2019. Controls of the spatial variability of denitrification potential in nontidal floodplains of the Chesapeake Bay watershed, USA. Geoderma 338, 1429. https://doi.org/10.1016/j.geoderma.2018.11.015.

Kutner, M., Nachtsheim, C., Neter, J., 2004. Applied Linear Regression Models, fourth ed. McGraw-Hill Education.

Ledford, S.H., Lautz, L.K., Vidon, P.G., Stella, J.C., 2017. Impact of seasonal changes in stream metabolism on nitrate concentrations in an urban stream. Biogeochemistry 133 (3), 317–331. https://doi.org/10.1007/s10533-017-0336-7.

Luo, J., Tillman, R.W., White, R.E., Ball, P.R., 1998. Variation in denitrification activity with soil depth under pasture. Soil Biol. Biochem. 30 (7), 897–903. https://doi.org/10.1016/S0038-0717(97)00206-X.

McClain, M.E., Boyer, E.W., Dent, C.L., Gergel, S.E., Grimm, N.B., Groffman, P.M., Hart, S.C., Harvey, J.W., Johnston, C.A., Mayorga, E., McDowell, W.H., Pinay, G., 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems 6 (4), 301–312. https://doi.org/10.1007/s10021-003-0161-9.

McPhillips, L., Walter, M.T., 2015. Hydrologic conditions drive denitrification and greenhouse gas emissions in stormwater detention basins. Ecol. Eng. 85, 67–75. https://doi.org/10.1016/j.ecoleng.2015.10.018.

Morse, J.L., Werner, S.F., Gillin, C.P., Goodale, C.L., Bailey, S.W., McGuire, K.J., Groffman, P.M., 2014. Searching for biogeochemical hot spots in three dimensions: Soil C and N cycling in hydropedologic settings in a northern hardwood forest. J. Geophys. Res.: Biogeosciences 119 (8), 2013JG002589. https://doi.org/10.1002/2013JG002589.

Nadeau, S.A., Roco, C.A., Debenport, S.J., Anderson, T.R., Hofmeister, K.L., Walter, M.T., Shapleigh, J.P., 2019. Metagenomic analysis reveals distinct patterns of denitrification gene abundance across soil moisture, nitrate gradients. Environ. Microbiol. 21 (4), 1255–1266. https://doi.org/10.1111/1462-2920.14587.

Palacin-Lizarbe, C., Camarero, L., Hallin, S., Jones, C.M., Catalan, J., 2020. Denitrification rates in lake sediments of mountains affected by high atmospheric nitrogen deposition. Sci. Rep. 10 (3003) https://doi.org/10.1038/s41598-020-59759-w.

Parkin, T.B., Meisinger, J.J., 1989. Denitrification below the crop rooting zone as influenced by surface tillage. J. Environ. Qual. 18 (1), 12–16. https://doi.org/10.2134/jeq1989.00472425001800010002x.

Pei, T., Qin, C.-Z., Zhu, A.-X., Yang, L., Luo, M., Li, B., Zhou, C., 2010. Mapping soil organic matter using the topographic wetness index: A comparative study based on different flow-direction algorithms and kriging methods. Ecol. Indicat. 10 (3), 610–619. https://doi.org/10.1016/j.ecolind.2009.10.005.

Piñeiro, G., Perelman, S., Guerschman, J.P., Paruelo, J.M., 2008. How to evaluate models: Observed vs. predicted or predicted vs. observed? Ecol. Model. 216 (3), 316–322. https://doi.org/10.1016/j.ecolmodel.2008.05.006.

R Core Team, 2017. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. https://www.R-project.org.

Raich, J.W., Potter, C.S., Bhagawati, D., 2002. Interannual variability in global soil respiration, 1980–94. Global Change Biol. 8 (8), 800–812. https://doi.org/10.1046/j.1365-2486.2002.00511.x.

Reichstein, M., Rey, A., Freibauer, A., Tenhunen, J., Valentini, R., Banza, J., Casals, P., Cheng, Y., Grünzweig, J.M., Irvine, J., Joffre, R., Law, B.E., Loustau, D., Miglietta, F., Oechel, W., Ourcival, J.-M., Pereira, J.S., Peressotti, A., Ponti, F., Yakir, D., 2003. Modeling temporal and large-scale spatial variability of soil respiration from soil water availability, temperature and vegetation productivity indices. Global Biogeochem. Cycles 17 (4), 1104. https://doi.org/10.1029/2003GB002035.

Rosenzweig, B.R., Smith, J.A., Baeck, M.L., Jaffé, P.R., 2011. Monitoring nitrogen loading and retention in an urban stormwater detention pond. J. Environ. Qual. 40 (2), 598–609. https://doi.org/10.2134/jeq2010.0300.

Russell, M., Fulford, R., Murphy, K., Lane, C., Harvey, J., Dantin, D., Alvarez, F., Nestlerode, J., Teague, A., Harwell, M., Almario, A., 2019. Relative importance of landscape versus local wetland characteristics for estimating wetland denitrification potential. Wetlands 39 (1), 127–137. https://doi.org/10.1007/s13157-018-1078-6.
Saggar, S., Jha, N., Deslippe, J., Bolan, N.S., Luo, J., Giltrap, D.L., Kim, D.-G., Zaman, M., Tillman, R.W., 2013. Denitrification and N2O:N2 production in temperate grasslands: Processes, measurements, modelling and mitigating negative impacts. Sci. Total Environ. 465, 173–195. https://doi.org/10.1016/j.scitotenv.2012.11.050.
Seitzinger, S.P., Styles, R.V., Boyer, E.W., Alexander, R.B., Billen, G., Howarth, R.W., Mayer, B., Breemen, N. van, 2002. Nitrogen retention in rivers: Model development and application to watersheds in the northeastern. U.S.A. *Biogeochemistry* 57–58 (1), 199–237. https://doi.org/10.1023/A:1015745629794.
Stephan, E.A., Endreny, T.A., 2016. Weighting nitrogen and phosphorus pixel pollutant loads to represent runoff and buffering likelihoods. JAWRA Journal of the American Water Resources Association 52 (2), 336–349. https://doi.org/10.1111/1752-1688.12390.
Valeo, C., Moin, S.M.A., 2000. Variable source area modelling in urbanizing watersheds. J. Hydrol. 228 (1–2), 68–81. https://doi.org/10.1016/S0022-1694(00)00153-0.
Vidon, P., Allan, C., Burns, D., Duval, T.P., Gurwick, N., Inamdar, S., Lowrance, R., Okay, J., Scott, D., Sebestyen, S., 2010. Hot spots and hot moments in riparian zones: Potential for improved water quality management. JAWRA Journal of the American Water Resources Association 46 (2), 278–298. https://doi.org/10.1111/j.1752-1688.2010.00420.x.
Vidon, P.G.F., Hill, A.R., 2004. Landscape controls on nitrate removal in stream riparian zones. Water Resour. Res. 40 (3), W03201. https://doi.org/10.1029/2003WR002473.
Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: Sources and consequences. Ecol. Appl. 7 (3), 737–750. https://doi.org/10.1890/1051-0761(1997)007[0737:HAOTGN]2.0.CO;2.
Walsh, C.J., Roy, A.H., Feminella, J.W., Cottingham, P.D., Groffman, P.M., Morgan, R.P., 2005. The urban stream syndrome: Current knowledge and the search for a cure. J. North Am. Benthol. Soc. 24 (3), 706–723. https://doi.org/10.1899/04-028.1.
Wang, J., Endreny, T.A., Nowak, D.J., 2008. Mechanistic simulation of tree effects in an urban water balance model. JAWRA Journal of the American Water Resources Association 44 (1), 75–85. https://doi.org/10.1111/j.1752-1688.2007.00139.x.
Waters, E., Morse, J., Bettez, N., Groffman, P., 2014. Differential carbon and nitrogen controls of denitrification in riparian zones and streams along an urban to exurban gradient. J. Environ. Qual. 43 (3) https://doi.org/10.2134/jeq2013.12.0504.
Zhu, W.-X., Dillard, N.D., Grimm, N.B., 2005. Urban nitrogen biogeochemistry: Status and processes in green retention basins. Biogeochemistry 71 (2), 177–196. https://doi.org/10.1007/s10533-005-0683-7.