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RESEARCH ARTICLE

10.1029/2021WR029718

Seasonal Variation in Nitrate Removal Mechanisms in Coastal Stormwater Ponds

Adam C. Gold[1], **Suzanne P. Thompson**[2], **and Michael F. Piehler**[1,2]

[1]Institute for the Environment, University of North Carolina at Chapel Hill, Chapel Hill, NC, USA, [2]Institute of Marine Sciences, University of North Carolina at Chapel Hill, Morehead City, NC, USA

Key Points:

- Stormwater pond sediments and water were sampled seven times between spring and fall seasons
- Sediment properties varied among ponds but had minimal impact on N cycling and NO_x fate
- Higher organic nitrogen concentrations, water temperatures, and O_2 uptake corresponded with a shift from denitrification to the retention of NO_3

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

A. C. Gold,
gold@unc.edu

Citation:

Gold, A. C., Thompson, S. P., & Piehler, M. F. (2021). Seasonal variation in nitrate removal mechanisms in coastal stormwater ponds. *Water Resources Research*, *57*, e2021WR029718. https://doi.org/10.1029/2021WR029718

Received 29 JAN 2021
Accepted 15 SEP 2021

Abstract Stormwater wet ponds (SWPs) are engineered structures used to collect and retain stormwater runoff from developed areas. SWPs are generally regarded as important nitrogen (N) sinks, but seasonal variation in SWP N cycling that influences pond nitrogen removal has not been characterized. To inform SWP function across seasons, we sampled the sediments and water columns of three stormwater ponds in the southeastern US coastal plain and measured gas and nutrient fluxes from the sediment-water interface during ambient conditions and nitrate (NO_3)-enriched "simulated storm" conditions. Dissolved organic nitrogen (DON) was the dominant form of dissolved N in the water column, while nitrate + nitrite (NO_x) was typically below detection. SWP sediment organic matter properties varied by study site but had minimal impact on sediment N processes or estimated NO_3 fate. SWP sediments generally functioned as TN sinks during NO_3-enriched conditions, but the estimated fate of NO_3 varied based on water temperature, DON concentrations, and sediment O_2 uptake. These results suggest that permanent N removal (denitrification) by SWPs varies seasonally, with retention of NO_x becoming more important during hotter conditions when NO_x uptake is largest. Low ambient NO_x concentrations and rapid NO_3 uptake suggest that coastal stormwater ponds can host reduced conditions that may promote NO_3 retention over denitrification. Additional research is needed to determine the fate of retained NO_3 in SWP sediments and how variation in NO_3 fate might impact downstream water quality.

1. Introduction

Stormwater runoff from urban areas can have negative ecological consequences for downstream waters such as eutrophication and stream scour (Paul & Meyer, 2001; Walsh et al., 2005), but structural stormwater control measures aim to mitigate these and other negative effects of stormwater runoff (Burns et al., 2012). One of the most common types of stormwater control measures in place today are stormwater wet ponds (SWPs) which collect fast-moving stormwater during storm events, slowly release stormwater over the days following a storm and maintain a permanent water level (National Research Council, 2009). Stormwater runoff from urban areas is often high in nutrient concentrations, such as nitrogen (N) and phosphorus (P) (Hobbie et al., 2017; Kaushal et al., 2011), and SWPs are designed to promote treatment of stormwater runoff through the settling of particulates and extended periods of contact with carbon-rich sediments and plants (Collins et al., 2010; Mallin et al., 2002).

Stormwater wet ponds are often regarded as net N sinks and hotspots for permanent N removal (Bettez & Groffman, 2012; Collins et al., 2010), but recent research shows that this prevailing assumption has been informed mostly by indirect or proxy measurements of stormwater control measure N cycling (Gold et al., 2019). Denitrification is a microbially mediated process that permanently removes bioavailable nitrate (NO_3^-) from aquatic ecosystems by converting it to inert dinitrogen gas (N_2) (Seitzinger et al., 2006). Denitrification requires a suitable carbon source, low-oxygen conditions, and NO_3 (Eyre et al., 2013; Seitzinger et al., 2006), and SWPs can meet all of these requirements—especially during summer storm events when SWPs experience higher temperatures, antecedent low-oxygen conditions, and an influx of NO_3 from the watershed (Bettez & Groffman, 2012; Duan et al., 2016; Moore & Hunt, 2012). Until recently, most studies of SWP N cycling have either utilized a mass-balance loading approach to determine the percent of nitrogen retained by an SWP or used indirect or proxy measurements to characterize certain nitrogen cycling processes (Gold et al., 2019). In the case of mass-balance calculations, a portion of the nitrogen retained by a SWP is often attributed to denitrification whether the process was measured or not (Collins et al., 2010). Indirect or proxy measurements, such as denitrification enzyme assays (DEA) (Groffman et al., 2006), measure potential rates of denitrification after additions of carbon and nitrate but do not account for other relevant processes of N cycling such as coupled nitrification-denitrification or nitrogen fixation (Gold et al., 2019).

NO_3 removal pathways that retain N rather than permanently remove it, such as dissimilatory NO_3 reduction to ammonium (DNRA) and assimilation (Burgin & Hamilton, 2007), could play an important role in SWP nitrogen cycling. SWPs have been found to harbor high levels of algal biomass (DeLorenzo et al., 2012; Lewitus et al., 2008) and DOC derived from autochthonous sources (Kalev et al., 2021; Williams et al., 2016), indicating that some inorganic nutrients retained in SWPs can be transformed to organic forms. Direct measurements of nitrogen cycling show that biotic assimilation of NO_3 and DNRA can be major pathways of nitrate removal or recycling during certain conditions in bioretention cells (Burgis et al., 2020; Norton et al., 2017; Payne et al., 2014) and stormwater wetlands (Messer et al., 2017; Rahman et al., 2019). Additionally, measurements of net N_2 fluxes from SWP sediments showed that sediment nitrogen fixation can exceed rates of sediment denitrification (i.e., sediments functioning as net N source), and both sediment and water column biotic assimilation may play a critical role in SWP nitrate uptake (Gold et al., 2017). Results from this recent research suggest that stormwater control measures can often function as transformers of nitrogen and may alternate between sinks and sources of N to downstream waters.

Mass-balance measurements of SWPs show that N removal changes seasonally with increased removal during warmer weather, but the seasonal variation of nitrogen cycling within SWPs that controls N removal has not been broadly characterized (Gold et al., 2019; Rosenzweig et al., 2011). Though the factors controlling SWP nitrogen cycling have not been characterized, factors that vary seasonally are likely important drivers of SWP nitrogen cycling (Rosenzweig et al., 2011). Temperature strongly influences the fate of nitrate in aquatic environments (Gardner & McCarthy, 2009), and higher temperatures in stormwater wetlands can promote denitrification (Rahman et al., 2019). Seasonal vegetation growth and senescence in stormwater wetlands can alter nutrient cycling (Macek et al., 2019), and sediment microbial community structure and function can change seasonally (Bledsoe et al., 2020). SWPs differ from stormwater wetlands by having less vegetation and much deeper water columns, but temperature and residence time drives seasonal water column stratification within SWPs that can decrease oxygen concentrations at the sediment-water interface (Gao et al., 2016; McEnroe et al., 2013; Song et al., 2013). Despite evidence of seasonal variation in factors relevant to SWP N cycling and N removal, no studies have characterized seasonal variation in SWP nitrogen cycling in any single location (Gold et al., 2019).

To better understand the effectiveness of SWPs at removing stormwater-borne N, this study aimed to characterize rates of sediment nitrogen cycling in SWPs in the southeastern US coastal plain across a range of seasonal conditions (spring—fall). We selected three stormwater ponds and conducted seven sampling events across a seasonal temperature gradient, excluding winter. For each sampling event, we collected intact sediment cores and water from each site and conducted flow-through incubations to measure gas and nutrient fluxes from the sediment-water interface. During each flow-through incubation, we measured fluxes before and after a NO_3 amendment to simulate "ambient" and "storm" conditions. Using N_2 and NO_x fluxes, we aimed to estimate the fate of NO_3 removed from the water column as either permanent removal (via denitrification) or retention (via DNRA or assimilation). We hypothesized that changes in seasonal variables, such as temperature and oxygen demand, would increase denitrification and the overall rate of NO_3 removal during the summer.

2. Materials and Methods

2.1. Site Description

Three SWPs located in Beaufort, NC were selected for sampling (Figure 1). The ponds spanned an age gradient from less than 1–8 years old at the time of initial sampling in June 2017, and the ponds drained similar land uses (i.e., residential & light commercial) (Table 1). Pond size and depth ranged from Pond 1, the newest, largest, and deepest pond, to Pond 3, the oldest, smallest, and shallowest pond, with Pond 2 having an intermediate age and depth (Table 1). Our aim for this sampling design was to capture seasonal patterns across a range of SWP characteristics rather than to focus on how specific physical attributes (e.g., age, size, and depth) affect SWP nitrogen cycling.

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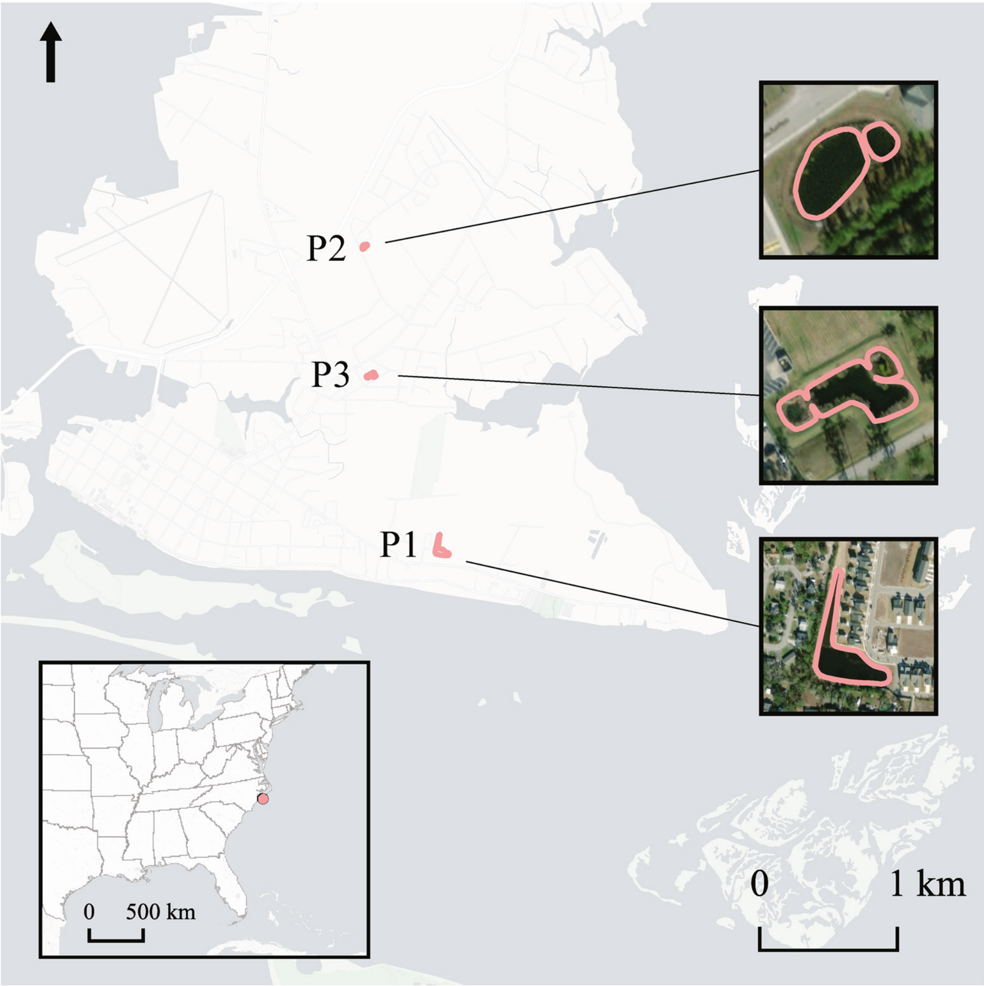

Figure 1. Overview map of the study area.

Study SWPs were sampled seven times, and for each sampling event, three replicate sediment cores were extracted from the middle of each SWP using a PVC coring apparatus deployed from a small boat (see Table 2 for sampling dates). Sediment core tubes were 6.4 cm in diameter and 30 cm long, and the tubes were filled with approximately 17 cm of sediment and site-specific water overlying the sediment (approximately 400 ml). Once collected, cores were sealed on the top and bottom of the core tube using rubber stoppers, briefly stored in a cooler (maximum 3 h), and transported to the UNC Institute of Marine Sciences (IMS) in Morehead City, NC. Water from each study SWP (60 L) was collected adjacent to the sediments using a bilge pump and transported with the sediment cores.

Table 1
Study Stormwater Wet Ponds Information

Name	Surface area (m^2)	Perimeter (m)	Surface area/perimeter	Sample depth range (m)	Date built	Sample n
Pond 1 (P1)	7,258.2	555.2	13.1	2–2.9	4/2017	7
Pond 2 (P2)	1,157.7	169.7	6.8	1.9–2.5	12/2014	6
Pond 3 (P3)	2,235.4	298.6	7.5	1.1–2	1/2010	7

Table 2
Ambient Water Quality and Sediment Characteristics From Sampled Ponds (P1 and P3 n = 7, P2 n = 6)

				Water Characteristics						Sediment Characteristics	
Site	Date	Julian day	Incubation Temp (C)	RTRM	[DON]	[NH_4]	[NO_x]	[PO_4]	[Chl-*a*]	OM (%)	C:N
P1	6/27/2017	178	28	196.5	29.18	1.65	0.05	0.18	–	–	–
	8/1/2017	213	26	36.4	37.94	0.88	0.04	0.35	7.29	24.01	52.92
	10/23/2017	296	22	32.3	27.29	2.14	0	0.18	11.16	34.02	36.35
	5/8/2018	128	19	129.4	17.75	0.4	0	0.04	3.74	18.41	34.15
	7/10/2018	191	28	201.1	28.11	0.96	0	0.2	7.75	26.45	30.47
	7/15/2019	196	31	165.3	27.22	0.57	0	0.2	2.54	23.77	46.35
	10/21/2019	294	20	9.1	20.99	1.67	0.27	0.22	2.28	18.86	42.78
	Total Mean			110	26.92	1.18	0.05	0.2	5.79	24.25	40.50
P2	8/1/2017	213	26	35.6	31.73	0.61	0.16	0.13	12.57	11.66	21.26
	10/23/2017	296	22	34.1	26.16	0.41	0	0.18	7.67	16.28	17.19
	5/8/2018	128	19	2.1	18.73	0.2	0	0.06	8.59	12.76	17.75
	7/10/2018	191	28	11.9	29.21	0.29	0	0.26	15.20	12.85	19.14
	7/15/2019	196	31	90	29.63	0.16	0	0.35	9.34	9.81	20.23
	10/21/2019	294	20	14.3	15.36	0.86	0	0.24	8.30	14.74	20.05
	Total Mean			31.3	25.14	0.42	0.03	0.2	10.28	13.02	19.27
P3	6/27/2017	178	28	4.4	30.98	0.67	0.23	0.13	–	–	–
	8/1/2017	213	26	10.4	39.82	0.6	0.15	0.13	42.11	2.72	11.21
	10/23/2017	296	22	21.6	37.84	0.45	0	0.14	10.53	5.67	10.56
	5/8/2018	128	19	2.8	14.68	0.32	0	0.09	2.82	8.45	12.26
	7/10/2018	191	28	4.1	21.36	0.57	0	0.16	15.21	4.85	11.7
	7/15/2019	196	31	24.2	26.18	0.32	0	0.14	7.98	3.12	11.87
	10/21/2019	294	20	−0.1	9.6	0.33	0	0.55	10.58	4.06	12.93
	Total Mean			9.6	25.78	0.47	0.05	0.19	14.87	4.81	11.75

Note. Concentrations of ON, NH4, NOx, and PO4 are in μM and Chl-*a* is in μg/L.

2.2. Water and Sediment Properties

The temperature and dissolved oxygen content of surface and bottom water were measured at each study pond during sampling events using a YSI 6600EDS-S water quality sonde. The relative thermal resistance to mixing (RTRM) was calculated following established methods (Wetzel, 2001), and values greater than 50 were considered to be indicative of stratification (Chimney et al., 2006; Song et al., 2013). Surface water samples from all SWPs were collected, filtered through Whatman GF/F filters (25 mm diameter, 0.7 μm nominal pore size), and analyzed for nitrate + nitrite (NO_x^-), ammonium (NH_4^+), orthophosphate (PO_4^{3-}), and total nitrogen (TN) with a Lachat Quick-Chem 8000 automated ion analyzer. Bottom water samples were collected during only four sampling trips and analyzed in a similar fashion as surface water samples. Differences between surface and bottom water sample concentrations were minimal (Figure S1), so surface water samples were used for data analysis due to superior temporal data resolution. Dissolved organic nitrogen (DON) was calculated by subtracting inorganic nitrogen concentrations from total nitrogen concentrations. Concentrations of chlorophyll-*a* in surface water samples were measured by filtering water samples (Whatman GF/F), sonicating and extracting frozen filters for 24 hr in a 90% acetone solution, and measuring the fluorescence of the solution with a Turner Designs Trilogy fluorometer (Welschmeyer, 1994).

Sediment cores were subsampled for sediment organic matter content (SOM) and carbon to nitrogen ratios (C:N) immediately after the flow-through core incubation experiment. SOM was measured by loss on ignition. Carbon and nitrogen content was measured in dried sediment samples using a Costech Elemental Combustion System with Elemental Analysis software and used to compute molar carbon to nitrogen ratios.

2.3. Sediment N Fluxes

Dissolved gas (N_2, O_2, and Ar) and nutrient fluxes (NO_x^-, NH_4^+, DON, and PO_4^{3-}) were measured from the sediment-water interface of intact sediment cores for ambient and NO_3-enriched conditions using flow-through incubation experiments (Figure S2; Gold et al., 2017; Piehler & Smyth, 2011). Gas flux measurements can show if the sediment cores are performing net denitrification (positive net N_2 fluxes, permanent removal) or net nitrogen fixation (negative net N_2 fluxes, N addition) and how much oxygen the sediments are using for microbial respiration (O_2 fluxes) (Figure S3). Nutrient fluxes show if the sediments are releasing nutrients into the water column (positive nutrient fluxes) or removing nutrients from the water column (negative nutrient fluxes) (Figure S3). Each SWP core incubation experiment lasted 4 days (from core collection to experiment clean up), and the experiments took place over a period of 2 years (June 2017–October 2019). The incubation experiments were conducted at in situ temperatures (determined as roughly the mean surface water temperature in the field from YSI readings) and in the dark within an environmental chamber (Bally, Inc.). Upon arrival to IMS, sediment cores and water were immediately placed within the environmental chamber at in situ temperature. The top stopper of each sediment core was then removed, and cores were submerged in site-specific water for approximately two hours. Following this short equilibration, cores were capped with gas-tight plexiglass tops containing ports connected to the flow-through system with Tygon tubing. The flow-through system pulled site-specific water into the core at the top of the core tube and out of the core from 2 cm above the sediment-water interface at a rate of 1 ml/min with a peristaltic pump.

Capped cores were left overnight for 17 hr, which was close to three residence times of the overlying water within the sediment core tubes. The following day, 5 ml water samples were collected from the outflow of each core at hours 17 and 22 of the incubation, and dissolved N_2, O_2, and Ar concentrations were measured using a membrane inlet mass spectrometer (Kana et al., 1998). Inflow water samples were obtained for each SWP (i.e., each set of three cores) using two bypass lines that did not flow over cores. Water was also collected for nutrient analysis at 20 hr, filtered, and analyzed using the methods described above. After 24 hr in the flow-through system, the source water for the flow-through system was enriched with $NaNO_3$, raising the concentration of nitrate (NO_3^-) by 30 μM. Water samples were collected from the source water 10 min after NO_x addition and analyzed for nutrient concentrations to verify the nitrate amendment. After 17 h of NO_3-enriched conditions, water samples were again collected and measured for gas and nutrient concentrations.

All gas and nutrient fluxes were calculated with the following equation:

$$flux = \left(C_{out} - C_{in}\right) \times \frac{flow\left(ml \times \min^{-1}\right)}{area\left(m^2\right)}$$

where C represents a gas or nutrient concentration (N_2:Ar or O_2:Ar in the case of gases), flow is the pumping rate of 1 ml min^{-1}, and the area is the surface area of the sediment-water interface in the sediment core tube (0.0032 m^2). The two measurement events before the NO_3-enrichment were averaged and represent "ambient" or in situ conditions. The two measurement events after the NO_3 enrichment were averaged and represent "NO_3-enriched" conditions that aim to simulate increased nitrate concentrations following a storm event. A nitrate-enriched concentration of 30 μM was chosen because this concentration of nitrate is typical during storms in stormwater ponds (Piehler Lab unpublished data) and urban streams in this region (Mallin et al., 2009).

2.4. Data Analysis

An estimate of the percent of NO_x uptake that was permanently removed via denitrification after NO_3-enrichment was calculated using the following formula:

$$\%\,\mathrm{NO}_x\ denitrified = -100 \cdot \frac{Net\ N_2\ Flux}{NO_x\ Flux}$$

This estimate compares the amount of net denitrification to the amount of NO_x taken up by sediments, where a value of 100% would mean that the amount of NO_x-N taken up by the sediments was equal to the amount of N released from the sediments via denitrification (as N_2-N). A value greater than 100%, where net denitrification exceeds NO_x uptake, would suggest that in addition to denitrification of water column NO_3, coupled nitrification-denitrification was occurring (Von Korff et al., 2014). Cores that had positive NO_x fluxes, indicating that the sediments were releasing NO_x after NO_3 additions were removed for this analysis (core $n = 6$, or 10% of all cores). This metric was used to estimate the fate of NO_3 taken up by sediments, with high values indicating that denitrification was an important mechanism for NO_3 removal and low values indicating that NO_3 uptake was driven by other processes and retained in the sediments during the experiment.

Relationships between variables were analyzed using robust linear mixed effect models via the R package "robustlmm" (Koller, 2016) with centered and scaled predictors. Robust linear mixed effect models were used because of the repeated-measures structure of the data set (i.e., study pond as a random effect) and failure to meet the assumptions of typical parametric testing due to outliers and non-normal residuals of traditional linear mixed-effect models. The robust linear mixed effect models weight outliers so their influence is limited, but the full dataset can still be used without transformation. Individual regressions were performed to determine the relationship between **1)** water temperature & sediment properties (*x*-variables) and ambient water quality (*y*-variables), and **2)** water temperature, ambient water quality, sediment properties (*x*-variables), and sediment gas and nutrient fluxes (*y*-variables). Each regression included only one predictor and had the following structure: $y \sim x + (1|\text{Site})$. Conditional R^2 (full model) and marginal R^2 (fixed effects) were calculated for each regression using the R package "performance" (Lüdecke et al., 2021) that utilizes methods from Nakagawa et al., 2017. To help identify strong relationships, *p*-values were calculated for each regression by simulating model parameters over 10,000 iterations with the R package "parameters" (Lüdecke et al., 2020). The slope was also extracted from each regression to show if the modeled relationship was positive or negative. Measurements that represent each study pond as a whole will be referred to as "pond-level" values, and measurements that represent cores from study ponds (three values for each study pond) will be referred to as "core-level" values.

To aid in exploratory data analysis, repeated measure correlations were calculated using the "rmcorr" package (Bakdash & Marusich, 2017). These correlation coefficients rely on parametric assumptions but were used to help identify potentially important correlations between sediment fluxes (see Table S1). Robust linear mixed effect models were then used to model relationships that were identified by the repeated measures correlation coefficients as important.

Kruskal-Wallis and Dunn's post-hoc tests were used to test for significant differences ($p < 0.05$) of overall fluxes among ponds and between ambient and NO_3-enriched conditions. We utilized the R package "dunn.test" to perform these tests (Dinno, 2017).

All analyses were completed using R version 4.0.2 (R Core Team, 2020)

3. Results

3.1. Water and Sediment Properties

Dissolved organic nitrogen was the dominant form of dissolved nitrogen in the water column of all SWPs during all sampling events (Table 2). Ammonium was the second most prevalent form of dissolved nitrogen, while NO_x concentrations were almost always below the detection limit (Table 2). The sampled SWPs varied in sediment organic matter content and sediment C:N ratios with pond age and depth, with the newest and deepest pond having the highest SOM and C:N (P1) and the oldest and shallowest pond having the lowest SOM and C:N (P3) (Table 2, Figures 5a and 5b).

Regressions between pond water and sediment properties (*x*-variables) and pond water quality (*y*-variables) showed that pond surface temperature at the time of sampling was significantly positively correlated with both ambient DON concentrations and RTRM (Table 3, Figure S4). SOM and C:N ratios were positively correlated with ambient NH_4^+ concentrations, while C:N was also negatively correlated with Chl-a concentrations (Table 3).

Table 3
Conditional R^2 (Total Model) and Marginal R^2 (Fixed Effects) for Robust Linear Mixed-Effect Models Between Each Combination of the Following x (Sediment Characteristics and Water Temperature) and y Variables (Ambient Water Chemistry) Where Sample Pond is the Random Effect (Random Intercepts)

	Y variables				
X variables	RTRM	[DON]	[NH_4^+]	[PO_4^{3-}]	[Chl-*a*]
Surface Temp	**(+) 0.67/0.12***	**(+) 0.26/0.26***	(−) 0.58/0.02	(+) 0.01/0.01	(+) 0.24/0.01
Bottom Temp	(+) 0.54/0	(+) 0.16/0.16	(−) 0.52/0	(+) 0.01/0.01	(+) 0.11/0.11
OM	(+) 0.2/0.2	(+) 0.01/0.01	**(+) 0.58/0.45****	(+) 0.02/0.02	(−) 0.13/0.13
C:N	(−) 0.88/0.11	(+) 0.03/0.03	**(+) 0.28/0.28***	(+) 0.1/0.1	**(−) 0.24/0.24***

Note. The direction of the relationship is indicated by a plus (+, positive relationship) or minus (−, negative relationship) in front of the R^2 values. Bold values indicate a significant ($p < 0.05$) relationship. R^2 values rounded to 2 decimal places. * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$.

3.2. Sediment N Fluxes

Sediment TN fluxes during ambient conditions varied across sampling events and pond-level TN fluxes were positively correlated with ambient DON concentrations in the water column (Figure 2a, Table 4). Core-level data showed that ambient TN fluxes were almost completely comprised of DON fluxes (marginal $R^2 = 0.99$, $p < 0.05$, Table S2, Figure 2c). NH_4 fluxes were small (<10 μmol NH_4-N m^{-2} hr^{-1}) but were negatively correlated with SOM and positively correlated with C:N (Figure 2d and Table 4). NO_x fluxes were often below detection due to a lack of detectable NO_x within the ponds during ambient conditions (Figure 2b). Ambient net N_2 fluxes were generally small (−20 to 20 μmol N_2-N m^{-2} hr^{-1}), fluctuated between net denitrification and net nitrogen fixation, and overall were not significantly different among ponds (Figure 5). Pond-level net N_2 fluxes were negatively correlated with ambient DON and NH_4^+ concentrations, and core-level net N_2 fluxes were negatively correlated with SOM (Figure 3a, Table 4). Ambient O_2 fluxes varied greatly by sampling event, and pond-level O_2 fluxes were negatively correlated with ambient DON and Chl-a concentrations (Figure 3b and Table 4).

Sediments had significantly lower TN fluxes after NO_3-enrichment due to large increases in sediment NO_x uptake (Figures 2 and 5). Net N_2 fluxes were significantly larger (i.e., more net denitrification) after NO_3-enrichment (Figure 5), and pond-level net N_2 fluxes were negatively correlated with pond surface water temperature at the time of sampling (Figures 3a and S4; Table 4). NO_x fluxes were generally the largest sediment nutrient fluxes during NO_3-enriched conditions (Figure 2), and NO_x fluxes were significantly positively correlated with O_2 fluxes (marginal $R^2 = 0.46$, $p < 0.001$, Figure 4a) and negatively correlated with SOM and ambient DON and NH_4^+ concentrations (Table 4). Our estimate of % NO_x denitrified, like most measured sediment fluxes presented here, varied by sampling event, and pond-level values were negatively correlated with pond surface temperature at the time of sampling (Figures 3c and S4; Table 4). There was evidence of coupled nitrification-denitrification (% NO_x denitrified >100%), where the rate of denitrification was higher than the rate of NO_x uptake, and instances of net nitrogen fixation combined with NO_x uptake (% NO_x denitrified <0). Aside from net N_2 and NO_x fluxes which were used to calculate % NO_x denitrified, O_2 flux was the only measured core-level variable that was significantly correlated with % NO_x denitrified (marginal $R^2 = 0.17$, $p < 0.05$ Figure 4b and Table 4).

Differences in sediment fluxes among ponds were fairly small, with no significant differences among ponds for net N_2 fluxes (ambient and NO_3-enriched) and % NO_x denitrified (Figures 5c and 5d). There were small differences in O_2 fluxes and NO_x fluxes among ponds, where P2 exhibited significantly less O_2 uptake (ambient and NO_3-enriched conditions) and NO_x uptake (NO_3-enriched conditions) than the other two ponds (Figures 5e and 5g). P2 also had significantly less TN uptake during NO_3-enriched conditions, while P3 had significantly less TN uptake than the other study ponds during ambient conditions (Figure 5f).

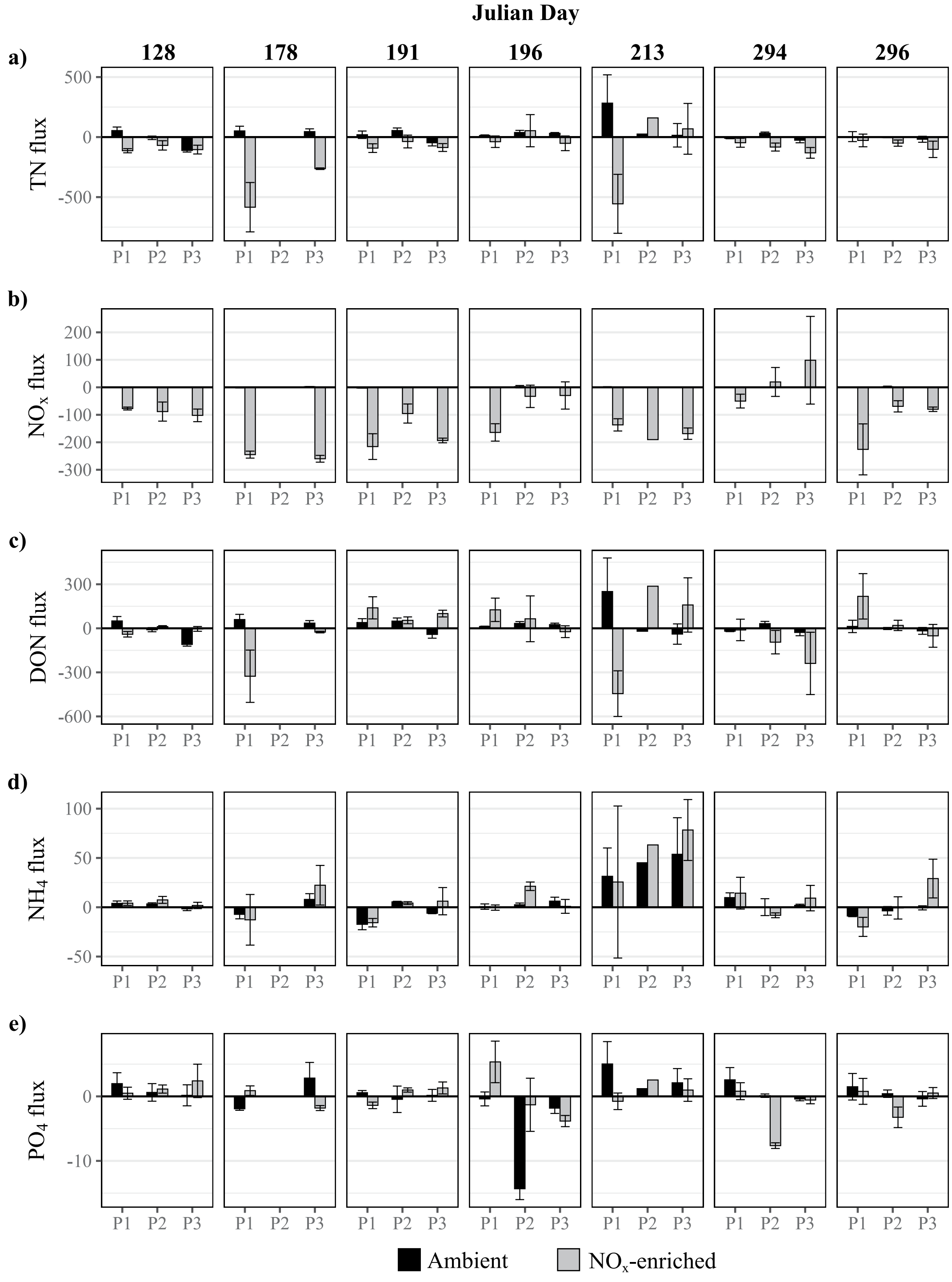

Figure 2. (a–e) Dissolved nutrient fluxes (μmol N or P m^{-2} hr^{-1}) during ambient and NO_3-enriched conditions for each pond and sampling event (by julian day). Error bars indicate standard error. Note the different *y*-axes.

4. Discussion

SWPs are often considered important nutrient sinks and denitrification hotspots in urban areas (Bettez & Groffman, 2012; Collins et al., 2010), but there are few measurements of SWP N cycling processes across seasons (Gold et al., 2019). This study provides measurements of SWP N cycling between spring and fall and suggests that hot summer conditions may promote elevated sediment NO_x uptake driven by retention

Table 4
Conditional R^2 (Total Model) and Marginal R^2 (Fixed Effects) for Robust Linear Mixed-Effect Models Between Each Combination of Sediment Properties and Water Temperature (x Variables) and Sediment Fluxes (y Variables) Where Sample Pond is the Random Effect (Random Intercepts)

		Y variables						
X variables	State	N_2	O_2	TN	DON	NH_4	NO_x	%ND
OM (core)	Amb	**(−) 0.47/0.23****	(−) 0.53/0.09	(−) 0.57/0.03	(−) 0.49/0.01	**(−) 0.29/0.17***	–	–
CHN (core)	Amb	(+) 0.11/0.03	(−) 0.32/0	(+) 0.34/0.13	(+) 0.3/0.1	**(+) 0.84/0.28*****	–	–
Surface Temp	Amb	(−) 0/0	(−) 0.33/0.06	(+) 0.4/0.13	(+) 0.45/0.08	(+) 0.01/0.01	–	–
Bottom Temp	Amb	(−) 0/0	(−) 0.4/0.08	(+) 0.49/0.09	(+) 0.49/0.04	(+) 0.11/0.11	–	–
(ON)	Amb	**(−) 0.19/0.19***	**(−) 0.56/0.16****	**(+) 0.38/0.16***	(+) 0.38/0.07	**(+) 0.17/0.17***	–	–
(NH_4^+)	Amb	**(−) 0.23/0.23***	(−) 0.38/0.03	(−) 0.23/0	(−) 0.38/0	(−) 0.04/0.04	–	–
(PO_4^{3-})	Amb	(+) 0.01/0.01	(+) 0.4/0.08	(+) 0.18/0.01	(+) 0.34/0.02	(+) 0/0	–	–
(Chl-*a*)	Amb	(−) 0.02/0.02	**(−) 0.46/0.19***	(+) 0.57/0.06	(−) 0.39/0	**(+) 0.4/0.4****	–	–
OM (core)	+NO_x	(+) 0.26/0.09	(−) 0.42/0.08	(−) 0.13/0	(+) 0.04/0.04	**(−) 0.23/0.23*****	**(−) 0.3/0.13***	(−) 0.01/0.01
CHN (core)	+NO_x	(−) 0.02/0.02	(+) 0.25/0.04	(−) 0.16/0.01	**(−) 0.62/0.17***	(+) 0.32/0.01	(+) 0.5/0.05	(−) 0.03/0.03
Surface Temp	+NO_x	**(−) 0.22/0.22***	**(−) 0.25/0.25***	(+) 0.19/0.01	(+) 0.04/0.04	(+) 0.09/0.01	**(−) 0.27/0.21***	**(−) 0.32/0.32****
Bottom Temp	+NO_x	(−) 0.12/0.12	(−) 0.19/0.12	(+) 0.21/0.04	(+) 0.02/0.02	(+) 0.13/0.13	(−) 0.28/0.06	(−) 0.09/0.09
(ON)	+NO_x	(−) 0.12/0.12	**(−) 0.32/0.21***	(+) 0.23/0.04	(+) 0.11/0.11	**(+) 0.4/0.2***	**(−) 0.24/0.22***	(+) 0/0
(NH_4^+)	+NO_x	(+) 0/0	(−) 0.27/0.06	(−) 0.13/0.01	(+) 0.01/0.01	(−) 0.12/0.12	**(−) 0.22/0.22***	(−) 0.01/0.01
(PO_4^{3-})	+NO_x	(−) 0.01/0.01	**(+) 0.33/0.18***	(−) 0.18/0.01	(−) 0.15/0.15	(+) 0.09/0	**(+) 0.26/0.18***	(−) 0.09/0.09
(Chl-*a*)	+NO_x	(−) 0.07/0.07	(−) 0.14/0.14	**(+) 0.39/0.25***	(+) 0.09/0.09	**(+) 0.44/0.44*****	(−) 0.34/0.1	(−) 0.05/0.05

Note. The direction of the relationship is indicated by a plus (+, positive relationship) or minus (−, negative relationship) in front of the R^2 values. Bold values indicate a significant ($p < 0.05$) relationship. R^2 values rounded to 2 decimal places. Regression with *X* variables OM and C:N used core-level data ($n = 58$). Regressions with in situ water temperatures and water quality used pond-level fluxes ($n = 20$). When predicting % NOx denitrified (%ND), only NOx flux values < 0 were used (core $n = 52$, pond $n = 18$). Ambient conditions are represented by rows where State is "Amb," and NOx-enriched conditions are represented by rows where State is "+NOx". * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$.

rather than denitrification in SWPs. Results show that when sediment O_2 and NO_x fluxes, surface water DON concentrations, and water temperature were lower, denitrification was the dominant NO_3 fate (Figure 6). When sediment O_2 and NO_x fluxes, surface water DON concentrations, and water temperature were higher, retention was the dominant NO_3 fate. Despite large differences in pond morphology and sediment characteristics, sediment N fluxes were consistent across study ponds. These results indicate that elevated seasonal temperatures and DON concentrations could push stormwater pond sediments from acting as net N sink to N transformers, but more research is needed to track the fate of retained NO_3 in SWPs and evaluate its downstream impacts.

4.1. Influence of Sediment Characteristics on N Cycling

Differences in morphology and sediment characteristics among ponds did not correspond with notable differences in sediment N cycling, but within each pond, sediment characteristics correlated with NH_4 fluxes and concentrations and ambient net N_2 fluxes (Figures 2, 3 and S2). Overall, the observed influence of sediment characteristics on sediment N cycling appears low and did not have a detectable impact on denitrification or % NO_x denitrified during NO_3-enriched conditions. Although these results do not provide a definitive assessment of SWP morphology, the minimal influence of a fairly broad range of sediment characteristics on sediment N cycling during NO_3-enriched conditions suggests that SWP sediment N removal may be less influenced by morphology than broader environmental variables such as temperature or residence time. A survey of stormwater ponds across the US found that potential denitrification rates were likely controlled by environmental variables that varied by region rather than surrounding land cover or sediment properties (Blaszczak et al., 2018). Our past study showing pond age was negatively related to net

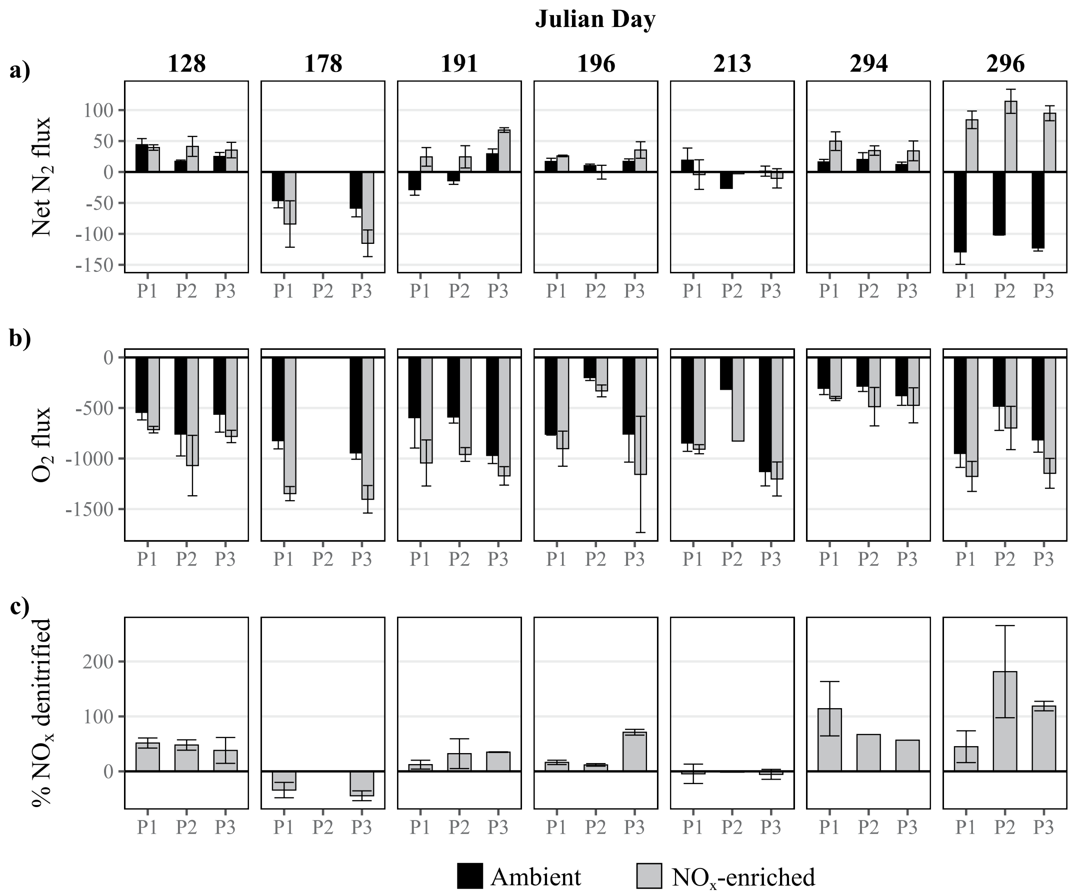

Figure 3. (a) Net N_2 fluxes (μmol N m^{-2} hr^{-1}) and (b) O_2 fluxes (μmol O_2 m^{-2} hr^{-1}) during ambient and NO_3-enriched conditions for each pond and sampling event (arranged by julian day). (c) Percent NO_x denitrified during NO_3-enriched conditions for each pond and sampling event. Note the different *y*-axes.

N_2 fluxes suggests that physical pond properties play a role in controlling N cycling (Gold et al., 2017), but as shown in this study, the seasonal variability in N cycling is likely much greater.

4.2. Variation in NO_3 Fate

Results from this study show that sediment N cycling and NO_3 fate can vary seasonally, but contrary to our hypothesis, retention of NO_3 may be more important than denitrification during hotter conditions. Estimates of NO_3 fate in this study ranged from efficient permanent removal of NO_3 (high % NO_x denitrified) to complete retention of NO_3 (low or negative % NO_x denitrified), and pond surface temperature, DON concentrations, and sediment oxygen uptake were correlated with NO_3 fate across ponds. Also, NO_x uptake was positively correlated with net N_2 fluxes so that NO_x uptake was greatest when retention was highest (low % NO_x denitrified estimates). Though it is known that pond N removal (based on mass-balance) changes seasonally with removal rates increasing during warmer weather (Rosenzweig et al., 2011), the unmeasured mechanism for removal is often attributed to denitrification due to a positive relationship between temperature and denitrification in other aquatic environments (Collins et al., 2010; Gold et al., 2019; Rosenzweig et al., 2011). Results from this study show that this assumption of denitrification as an important fate of stormwater NO_3 may not always hold true, especially during seasonal hot conditions where SWPs may appear to be strong NO_3 sinks based on mass-balance measurements.

The "denitrification-dominant" scenario observed in this study generally matched assumptions often made regarding SWP function: SWPs are N sinks and are important sites for permanent N removal via denitrification (Bettez & Groffman, 2012; Collins et al., 2010) (Figures 3 and 6). In this denitrification-dominant

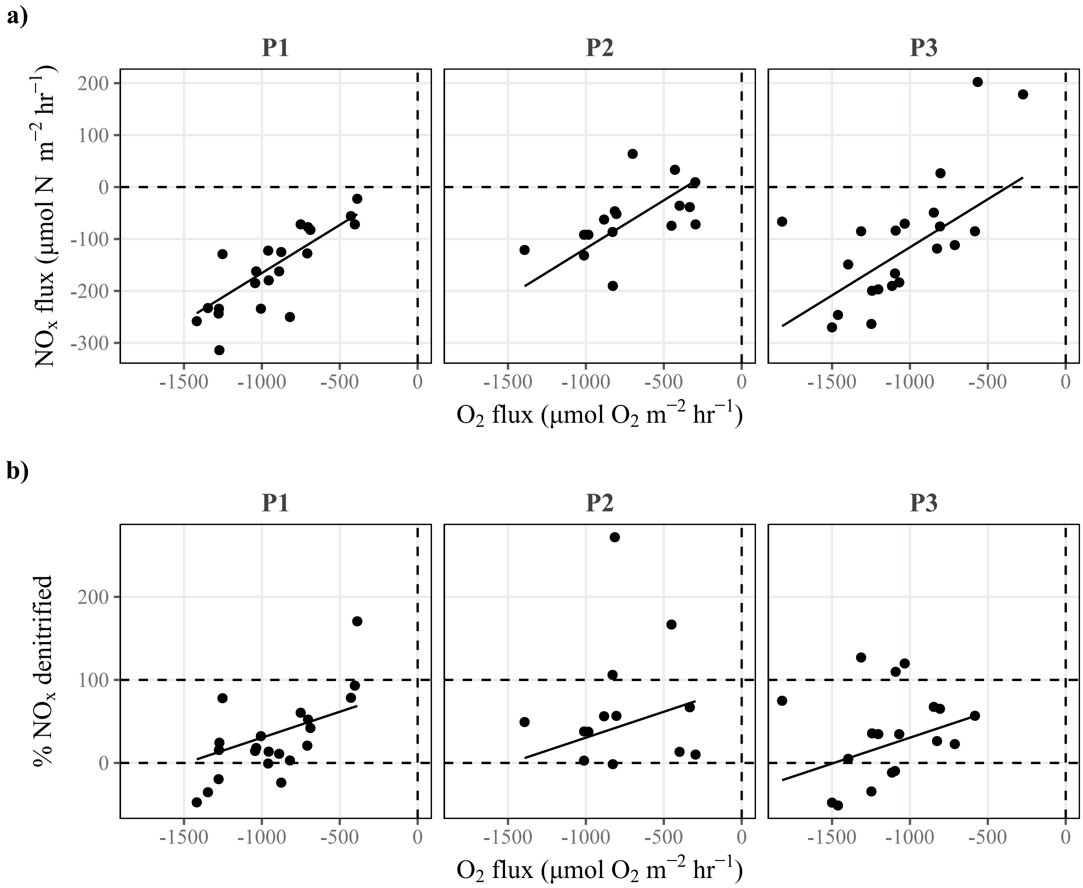

Figure 4. (a) NO_x flux versus O_2 flux for each study pond with regression line from robust linear mixed effect model (conditional $R^2 = 0.60$, marginal $R^2 = 0.46$, $p < 0.001$), and (b) % NO_x denitrified versus O_2 flux for each study pond with regression line from robust linear mixed effect model (conditional $R^2 = 0.17$, marginal $R^2 = 0.17$, $p < 0.01$).

state, the sediment microbial community responsible for N cycling is efficiently taking up NO_3 from the water column and converting it to N_2 gas through denitrification (Figures 2 and 3). This state of N cycling was typified by lower water column DON concentrations, water temperature, NO_x uptake after enrichment, and sediment oxygen demand, which is a proxy for the rate of organic matter oxidation (Eyre et al., 2013) (Figures S1–S3). By contrast, "retention-dominant" conditions were characterized by elevated DON concentrations, water temperature, sediment oxygen demand (i.e., respiration), and NO_x uptake.

Our experimental setup does not pinpoint the mechanism responsible for NO_3 retention observed during retention-dominant conditions, but our measurements constrain the explanation of the observed shift to three possible scenarios. The first possible scenario is that a shift toward retention (i.e., high NO_x removal and low/negative net N_2 flux) is due to elevated assimilative uptake. Several recent studies utilizing tracers in various types of stormwater control measures have found that plant and microbial assimilative NO_3 uptake can dominate over dissimilatory processes during certain conditions such as low-NO_3 concentrations (Burgis et al., 2020; Messer et al., 2017; Payne et al., 2014).

A second possible explanation is that DNRA becomes a more important NO_3 fate as temperatures increase (and perhaps sediment oxygen demand), although a lack of nitrate induced ammonium flux in our sediment cores suggests (Figure 2) that rates of DNRA were low during all flux experiments (Hoffman et al., 2019; Slone et al., 2018). The positive relationship between % NO_x denitrified and sediment O_2 uptake (Figure 4b) suggests that aerobic respiration leading to decreased sediment oxygen availability could be depressing denitrification or increasing DNRA - elevated O_2 sediment uptake is associated with decreased oxygen penetration depth into sediments (Cai & Sayles, 1996; Cornwell et al., 1999) and more reduced conditions that may favor DNRA (Smyth et al., 2013). Also, hot conditions may theoretically increase DNRA

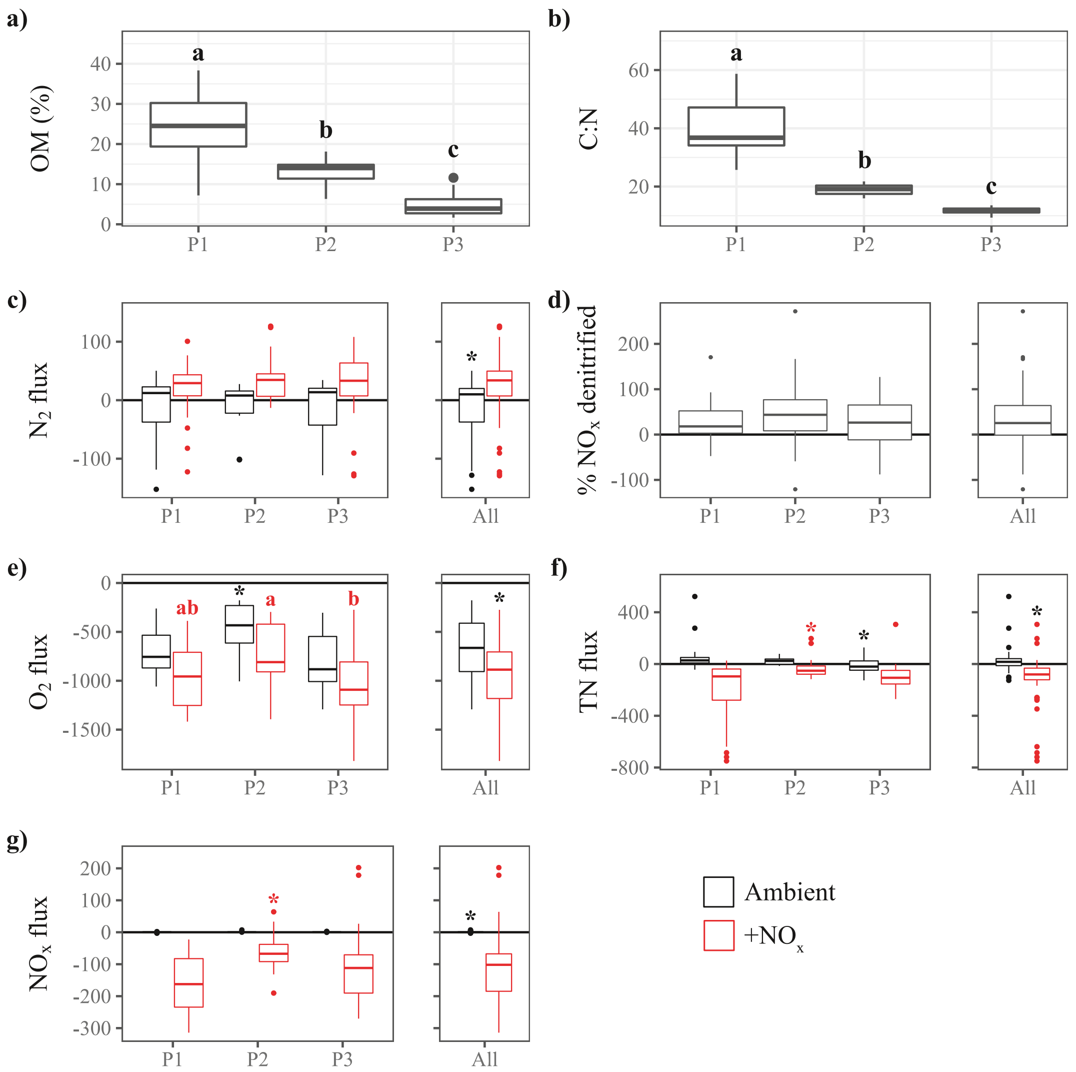

Figure 5. Boxplots of sediment characteristics (panels a and b) and select sediment fluxes (c)–(g). Letters indicate significant differences among study ponds based on Kruskal–Wallis and Dunn's tests ($p < 0.05$), and the color of the letter indicates the group being compared. Asterisks for "All" categories indicate a significant difference ($p < 0.05$) between ambient and NO_x-enriched groups.

relative to denitrification (Burgin & Hamilton, 2007), though one study in stormwater wetlands found that the relative importance of DNRA decreased as temperatures increased (Rahman et al., 2019). Though there are no measurements of DNRA in stormwater ponds, measurements of DNRA in a freshwater wetland or lake sediments have found that they are generally small (<15% of NO_3 reduction) relative to denitrification (Nizzoli et al., 2010; Scott et al., 2008), even though there may be a positive relationship with temperature (Nizzoli et al., 2010).

The third possible scenario is that rates of net N_2 fluxes, and thus the relative importance of denitrification as a sink for NO_3, are lower due to elevated rates of nitrogen fixation. Because denitrification and nitrogen fixation co-occur in aquatic sediments (Fulweiler et al., 2013), elevated rates of nitrogen fixation (with constant denitrification) would decrease net N_2 fluxes and our estimated metric of % NO_x denitrified. Rates of nitrogen fixation from other aquatic environments (both fresh and saline) are known to increase, and sometimes exceed denitrification rates, under low NO_x conditions, highly reduced sediments, or sediments with refractory organic matter (Fulweiler et al., 2013; Grantz et al., 2012; Newell, McCarthy, et al., 2016; Newell, Pritchard, et al., 2016; Scott et al., 2008). Net N_2 fluxes during retention-dominant conditions were

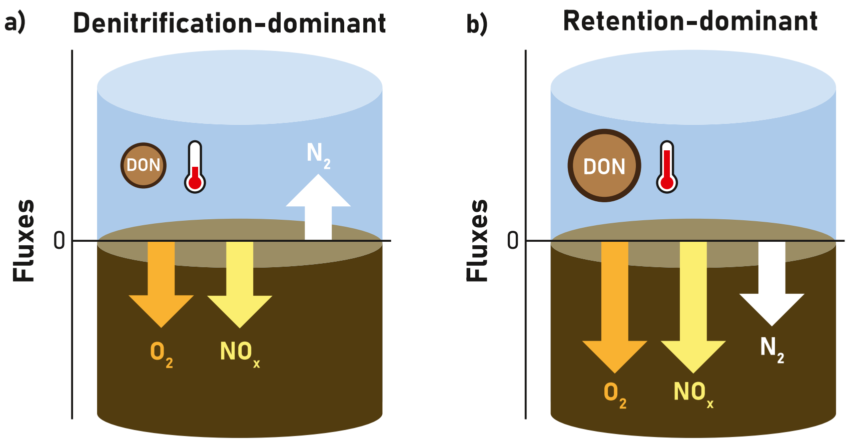

Figure 6. Conceptual diagram showing sediment fluxes and water column conditions during NO_3-enrichment when (a) % NO_x denitrified is high ("denitrification-dominant") and (b) When % NO_x denitrified is low or negative ("retention-dominant").

lower than denitrification-dominant conditions after NO_3 additions, which could be due either to elevated nitrogen fixation, depressed denitrification, or a combination of both effects (Figure 3).

This study provides novel data regarding stormwater pond N cycling across seasons, but some methodological constraints should be considered. First, this study utilized microcosm sediment core flux experiments that attempt to replicate in situ conditions, but conditions for flux experiments in the lab did not encompass diurnal variation (e.g., constant temperature and in the dark). The current study does not incorporate NO_x uptake by actively photosynthesizing organisms (i.e., phytoplankton or plants) that can vary across seasons (Reed et al., 2016), so the importance of denitrification estimated in this study may be overestimated when in situ competition with autotrophs is considered. Second, NO_3 amendments to flux experiment feed water were used to simulate the effects of nutrient-rich stormwater coming into contact with pond sediments, but there are other water quality properties of stormwater and storm events that were not replicated. One example is the quality of dissolved organic matter, which can change within the pond water between storm events based on residence time (Kalev et al., 2021; Lusk & Toor, 2016). Finally, while we estimate the fate of NO_3 by comparing net N_2 fluxes (denitrification) and NO_x uptake, we do not assess NO_3 fate with quantitative methods (i.e., ^{15}N paired isotopes). Also, our gas flux methods would not detect incomplete denitrification that might result in a low % NO_x denitrified value, although a large study of N_2O fluxes in stormwater ponds (indicating incomplete denitrification) showed that they were low relative to N_2 (denitrification) (Blaszczak et al., 2018). The eventual fate of any retained NO_3 observed in this study is unknown and the downstream impacts unclear. NO_3 retained but not denitrified could be denitrified later through remineralization and coupled nitrification-denitrification, buried for longer time scales, or recycled as DON or particulate carbon (i.e., algae) at a later date. Future studies should further assess the fate of NO_3 in SWPs throughout the year to help determine the full impact of ponds on downstream water quality.

4.3. Rapid Processing of NO_3 in SWPs

Results from this study suggest that NO_3 supplied from watersheds was rapidly taken up within the SWPs, as evidenced by consistently low ambient NO_x concentrations. Even when we sampled ponds 1–2 days after rain events, NO_x concentrations were below the detection limit. Although NO_3 concentrations are influenced by the land use of the draining watershed, persistent low NO_3 concentrations have been observed in other coastal stormwater ponds (Gold et al., 2017; Reed et al., 2016) and inland stormwater ponds (Van Meter et al., 2011; Scott & Frost, 2017), suggesting that rapid NO_3 uptake after storms may be common in some areas.

Depending on the watershed nutrient supply and storm frequency, some SWP sediments may go long periods of time without exposure to NO_3 due to rapid NO_3 uptake and low-oxygen conditions at the sediment-water interface. In order to achieve their primary goal of retaining stormwater runoff, SWPs are designed to collect and release water only during storm events and a few days immediately afterward. This sporadic inflow can lead to long residence times between storms ranging from hours to weeks (Jefferson et al., 2015), and long residence times can promote low-oxygen conditions at the sediment-water interface, especially during seasonal hot conditions where thermal stratification may occur (Burgin et al., 2011; Song et al., 2013). After the stormwater-supplied NO_3 is processed within in the sediments or water column, the only source of NO_3 until the next storm is from nitrification within the SWP, which may be inhibited in SWPs with low-oxygen conditions at the sediment-water interface (Nizzoli et al., 2010; Rysgaard et al., 1994; Thompson et al., 2000).

While the mechanistic explanation for the variation in estimated NO_3 fate is unclear, we suggest that rapid NO_3 uptake in some SWPs may correspond with highly reduced conditions at the sediment-water interface that favor retention over denitrification of stormwater-borne NO_3. To test this hypothesis, future research that measures SWP sediment N processes should incorporate water quality monitoring between sampling events to investigate the impacts of residence time and NO_3 availability.

5. Conclusions

Results from this study suggest that NO_3 removal by SWP sediments can change seasonally, with the estimated fate of NO_3 shifting from denitrification toward retention during hot summer conditions. Differences in sediment characteristics between ponds had minimal impact on N cycling, suggesting that seasonal variation was a stronger control on pond N cycling than individual pond characteristics. Low ambient NO_3 concentrations suggest that coastal stormwater ponds rapidly remove NO_3 but may lead to reduced conditions that promote NO_3 retention over denitrification. Additional research is needed to determine the fate of retained NO_3 in SWP sediments and how variation in NO_3 fate might impact downstream water quality.

Data Availability Statement

The data presented here are freely available at Zenodo.org, http://doi.org/10.5281/zenodo.4479508.

Acknowledgments
The authors would like to thank three anonymous reviewers as well as Drs. Ariane Peralta, Scott Ensign, Jaye Cable, and Rachel Noble for reviewing previous drafts of the manuscript.

References

Bakdash, J. Z., & Marusich, L. R. (2017). Repeated measures correlation. *Frontiers in Psychology*, *8*. https://doi.org/10.3389/fpsyg.2017.00456

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

Blaszczak, J. R., Steele, M. K., Badgley, B. D., Heffernan, J. B., Hobbie, S. E., Morse, J. L., et al. (2018). Sediment chemistry of urban stormwater ponds and controls on denitrification. *Ecosphere*, *9*(6). https://doi.org/10.1002/ecs2.2318

Bledsoe, R., Austin, S., Bean, E., & Peralta, A. (2020). A microbial perspective on balancing trade-offs in ecosystem functions in a constructed stormwater wetland. *Ecological Engineering*, *158*, 106000. https://doi.org/10.1016/j.ecoleng.2020.106000

Burgin, A. J., & Hamilton, S. K. (2007). Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. *Frontiers in Ecology and the Environment*, *5*(2), 89–96. https://doi.org/10.1890/1540-9295(2007)5[89:HWOTRO]2.0.CO;2

Burgin, A. J., Yang, W. H., Hamilton, S. K., & Silver, W. L. (2011). Beyond carbon and nitrogen: How the microbial energy economy couples elemental cycles in diverse ecosystems. *Frontiers in Ecology and the Environment*, *9*, 44–52. https://doi.org/10.1890/090227

Burgis, C. R., Hayes, G. M., Zhang, W., Henderson, D. A., Macko, S. A., & Smith, J. A. (2020). Tracking denitrification in green stormwater infrastructure with dual nitrate stable isotopes. *The Science of the Total Environment*, *747*, 141281. https://doi.org/10.1016/j.scitotenv.2020.141281

Burns, M. J., Fletcher, T. D., Walsh, C. J., Ladson, A. R., & Hatt, B. E. (2012). Hydrologic shortcomings of conventional urban stormwater management and opportunities for reform. *Landscape and Urban Planning*, *105*(3), 230–240. https://doi.org/10.1016/j.landurbplan.2011.12.012

Cai, W. J., & Sayles, F. L. (1996). Oxygen penetration depths and fluxes in marine sediments. *Marine Chemistry*, *52*(2), 123–131. https://doi.org/10.1016/0304-4203(95)00081-X

Chimney, M. J., Wenkert, L., & Pietro, K. C. (2006). Patterns of vertical stratification in a subtropical constructed wetland in south Florida (USA). *Ecological Engineering*, *27*(4), 322–330. https://doi.org/10.1016/j.ecoleng.2006.05.017

Collins, K. A., Lawrence, T. J., Stander, E. K., Jontos, R. J., Kaushal, S. S., Newcomer, T. A., et al. (2010). Opportunities and challenges for managing nitrogen in urban stormwater: A review and synthesis. *Ecological Engineering*, *36*(11), 1507–1519. https://doi.org/10.1016/j.ecoleng.2010.03.015

Cornwell, J. C., Kemp, W. M., & Kana, T. M. (1999). Denitrification in coastal ecosystems: Methods, environmental controls, and ecosystem level controls, a review. *Aquatic Ecology*, *33*(1), 41–54. https://doi.org/10.1023/A:1009921414151

DeLorenzo, M. E., Thompson, B., Cooper, E., Moore, J., & Fulton, M. H. (2012). A long-term monitoring study of chlorophyll, microbial contaminants, and pesticides in a coastal residential stormwater pond and its adjacent tidal creek. *Environmental Monitoring and Assessment*, *184*(1), 343–359. https://doi.org/10.1007/s10661-011-1972-3

Dinno, A. (2017). *dunn.test: Dunn's test of multiple comparisons using rank sums*.

Duan, S., Newcomer-Johnson, T., Mayer, P., & Kaushal, S. (2016). Phosphorus retention in stormwater control structures across streamflow in urban and suburban watersheds. *Water*, *8*(9), 390. https://doi.org/10.3390/w8090390

Eyre, B. D., Maher, D. T., & Squire, P. (2013). Quantity and quality of organic matter (detritus) drives N_2 effluxes (net denitrification) across seasons, benthic habitats, and estuaries. *Global Biogeochemical Cycles*, *27*(4), 1083–1095. https://doi.org/10.1002/2013GB004631

Fulweiler, R. W., Brown, S. M., Nixon, S. W., & Jenkins, B. D. (2013). Evidence and a conceptual model for the co-occurrence of nitrogen fixation and denitrification in heterotrophic marine sediments. *Marine Ecology Progress Series*, *482*, 57–68. https://doi.org/10.3354/meps10240

Gao, Y., Zhang, Z., Liu, X., Yi, N., Zhang, L., Song, W., et al. (2016). Seasonal and diurnal dynamics of physicochemical parameters and gas production in vertical water column of a eutrophic pond. *Ecological Engineering*, *87*, 313–323. https://doi.org/10.1016/j.ecoleng.2015.12.007

Gardner, W. S., & McCarthy, M. J. (2009). Nitrogen dynamics at the sediment-water interface in shallow, sub-tropical Florida Bay: Why denitrification efficiency may decrease with increased eutrophication. *Biogeochemistry*, *95*(2), 185–198. https://doi.org/10.1007/s10533-009-9329-5

Gold, A. C., Thompson, S. P., & Piehler, M. F. (2017). Coastal stormwater wet pond sediment nitrogen dynamics. *The Science of the Total Environment*, *609*, 672–681. https://doi.org/10.1016/j.scitotenv.2017.07.213

Gold, A. C., Thompson, S. P., & Piehler, M. F. (2019). Nitrogen cycling processes within stormwater control measures: A review and call for research. *Water Research*, *149*, 578–587. https://doi.org/10.1016/j.watres.2018.10.036

Grantz, E. M., Kogo, A., & Thad Scott, J. (2012). Partitioning whole-lake denitrification using in situ dinitrogen gas accumulation and intact sediment core experiments. *Limnology & Oceanography*, *57*(4), 925–935. https://doi.org/10.4319/lo.2012.57.4.0925

Groffman, P. M., Altabet, M. A., Böhlke, J. K., Butterbach-Bahl, K., David, M. B., Firestone, M. K., et al. (2006). Methods for measuring denitrification: Diverse approaches to a difficult problem. *Ecological Applications*, *16*(6), 2091–2122. https://doi.org/10.1890/1051-0761(2006)16[2091MFMDDA]2.0.CO;2

Hobbie, S. E., Finlay, J. C., Janke, B. D., Nidzgorski, D. A., Millet, D. B., & Baker, L. A. (2017). Contrasting nitrogen and phosphorus budgets in urban watersheds and implications for managing urban water pollution. *Proceedings of the National Academy of Sciences*, *114*(16), 4177–4182. https://doi.org/10.1073/pnas.1618536114

Hoffman, D. K., McCarthy, M. J., Newell, S. E., Gardner, W. S., Niewinski, D. N., Gao, J., & Mutchler, T. R. (2019). Relative Contributions of DNRA and denitrification to nitrate reduction in Thalassia testudinum seagrass beds in Coastal Florida (USA). *Estuaries and Coasts*, *42*(4), 1001–1014. https://doi.org/10.1007/s12237-019-00540-2

Jefferson, A. J., Bell, C. D., Clinton, S. M., & Mcmillan, S. K. (2015). Application of isotope hydrograph separation to understand contributions of stormwater control measures to urban headwater streams. *Hydrological Processes*, *29*(25), 5290–5306. https://doi.org/10.1002/hyp.10680

Kalev, S., Duan, S., & Toor, G. S. (2021). Enriched dissolved organic carbon export from a residential stormwater pond. *The Science of the Total Environment*, *751*, 141773. https://doi.org/10.1016/j.scitotenv.2020.141773

Kana, T. M., Sullivan, M. B., Cornwell, J. C., & Groszkowski, K. M. (1998). Denitrification in estuarine sediments determined by membrane inlet mass spectrometry. *Limnology & Oceanography*, *43*(2), 334–339. https://doi.org/10.4319/lo.1998.43.2.0334

Kaushal, S. S., Groffman, P. M., Band, L. E., Elliott, E. M., Shields, C. A., & Kendall, C. (2011). Tracking nonpoint source nitrogen pollution in human-impacted watersheds. *Environmental Science and Technology*, *45*(19), 8225–8232. https://doi.org/10.1021/es200779e

Koller, M. (2016). robustlmm : An R package for robust estimation of linear mixed-effects models. *Journal of Statistical Software*, *75*(6). https://doi.org/10.18637/jss.v075.i06

Lüdecke, D., Ben-Shachar, M., Patil, I., & Makowski, D. (2020). Extracting, computing and exploring the parameters of statistical models using R. *Journal of Open Source Software*, *5*(53), 2445. https://doi.org/10.21105/joss.02445

Lüdecke, D., Ben-Shachar, M., Patil, I., Waggoner, P., & Makowski, D. (2021). Performance: An R package for assessment, comparison and testing of statistical models. *Journal of Open Source Software*, *6*(60), 3139. https://doi.org/10.21105/joss.03139

Lewitus, A. J., Brock, L. M., Burke, M. K., DeMattio, K. A., & Wilde, S. B. (2008). Lagoonal stormwater detention ponds as promoters of harmful algal blooms and eutrophication along the South Carolina coast. *Harmful Algae*, *8*(1), 60–65. https://doi.org/10.1016/j.hal.2008.08.012

Lusk, M. G., & Toor, G. S. (2016). Biodegradability and molecular composition of dissolved organic nitrogen in urban stormwater runoff and outflow water from a stormwater retention pond. *Environmental Science and Technology*, *50*(7), 3391–3398. https://doi.org/10.1021/acs.est.5b05714

Macek, C. L., Hale, R. L., & Baxter, C. V. (2019). Dry wetlands: Nutrient dynamics in ephemeral constructed stormwater wetlands. *Environmental Management*, *65*, 32–45. https://doi.org/10.1007/s00267-019-01227-x

Mallin, M., Ensign, S., Wheeler, T., & Mayes, D. (2002). Pollutant removal efficacy of three wet detention ponds. *Journal of Environmental Quality*, *31*(2), 654–660. https://doi.org/10.2134/jeq2002.6540

Mallin, M. A., Johnson, V. L., & Ensign, S. H. (2009). Comparative impacts of stormwater runoff on water quality of an urban, a suburban, and a rural stream. *Environmental Monitoring and Assessment*, *159*(1–4), 475–491. https://doi.org/10.1007/s10661-008-0644-4

McEnroe, N. A., Buttle, J. M., Marsalek, J., Pick, F. R., Xenopoulos, M. A., & Frost, P. C. (2013). Thermal and chemical stratification of urban ponds: Are they "completely mixed reactors"? *Urban Ecosystems*, *16*(2). https://doi.org/10.1007/s11252-012-0258-z

Messer, T. L., Burchell, M. R., Böhlke, J. K., & Tobias, C. R. (2017). Tracking the fate of nitrate through pulse-flow wetlands: A mesocosm scale ^{15}N enrichment tracer study. *Ecological Engineering*, *106*, 597–608. https://doi.org/10.1016/j.ecoleng.2017.06.016

Moore, T. L. C., & Hunt, W. F. (2012). Ecosystem service provision by stormwater wetlands and ponds—A means for evaluation? *Water Research*, *46*(20), 6811–6823. https://doi.org/10.1016/j.watres.2011.11.026

Nakagawa, S., Johnson, P. C. D., & Schielzeth, H. (2017). The coefficient of determination R^2 and intra-class correlation coefficient from generalized linear mixed-effects models revisited and expanded. *Journal of The Royal Society Interface*, *14*(134), 20170213. https://doi.org/10.1098/rsif.2017.0213

National Research Council. (2009). *Urban stormwater management in the United States*. National Academies Press. https://doi.org/10.17226/12465

Newell, S. E., McCarthy, M. J., Gardner, W. S., & Fulweiler, R. W. (2016). Sediment nitrogen fixation: A call for re-evaluating coastal N budgets. *Estuaries and Coasts*, *39*, 1626, 1638. https://doi.org/10.1007/s12237-016-0116-y

Newell, S. E., Pritchard, K., Foster, S., & Fulweiler, R. (2016). Molecular evidence for sediment nitrogen fixation in a temperate New England estuary. *PeerJ*, *4*, e1615. https://doi.org/10.7717/peerj.1615

Nizzoli, D., Carraro, E., Nigro, V., & Viaroli, P. (2010). Effect of organic enrichment and thermal regime on denitrification and dissimilatory nitrate reduction to ammonium (DNRA) in hypolimnetic sediments of two lowland lakes. *Water Research*, *44*(9), 2715–2724. https://doi.org/10.1016/j.watres.2010.02.002

Norton, R. A., Harrison, J. A., Kent Keller, C., & Moffett, K. B. (2017). Effects of storm size and frequency on nitrogen retention, denitrification, and N_2O production in bioretention swale mesocosms. *Biogeochemistry*, *134*(3), 353–370. https://doi.org/10.1007/s10533-017-0365-2

Paul, M. J., & Meyer, J. L. (2001). Streams in the urban landscape. *Annual Review of Ecology and Systematics*, *32*(1), 333–365. https://doi.org/10.1146/annurev.ecolsys.32.081501.114040

Payne, E. G. I., Fletcher, T. D., Russell, D. G., Grace, M. R., Cavagnaro, T. R., Evrard, V., et al. (2014). Temporary storage or permanent removal? The division of nitrogen between biotic assimilation and denitrification in stormwater biofiltration systems. *PloS One*, *9*(3), e90890. https://doi.org/10.1371/journal.pone.0090890

Piehler, M. F., & Smyth, A. R. (2011). Habitat-specific distinctions in estuarine denitrification affect both ecosystem function and services. *Ecosphere*, *2*(1), art12. https://doi.org/10.1890/ES10-00082.1

R Core Team. (2020). *R: A Language and environment for Statistical computing*: R Foundation for Statistical Computing.

Rahman, M. M., Roberts, K. L., Warry, F., Grace, M. R., & Cook, P. L. M. (2019). Factors controlling dissimilatory nitrate reduction processes in constructed stormwater urban wetlands. *Biogeochemistry*, *142*, 375, 393. https://doi.org/10.1007/s10533-019-00541-0

Reed, M. L., Pinckney, J. L., Keppler, C. J., Brock, L. M., Hogan, S. B., & Greenfield, D. I. (2016). The influence of nitrogen and phosphorus on phytoplankton growth and assemblage composition in four coastal, southeastern USA systems. *Estuarine, Coastal and Shelf Science*, *177*, 71–82. https://doi.org/10.1016/j.ecss.2016.05.002

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

Rysgaard, S., Risgaard-Petersen, N., Niels Peter, S., Kim, J., & Lars Peter, N. (1994). Oxygen regulation of nitrification and denitrification in sediments. *Limnology & Oceanography*, *39*(7), 1643–1652. https://doi.org/10.4319/lo.1994.39.7.1643

Scott, A. B., & Frost, P. C. (2017). Monitoring water quality in Toronto's urban stormwater ponds: Assessing participation rates and data quality of water sampling by citizen scientists in the FreshWater Watch. *The Science of the Total Environment*, *592*, 738–744. https://doi.org/10.1016/j.scitotenv.2017.01.201

Scott, J. T., McCarthy, M. J., Gardner, W. S., & Doyle, R. D. (2008). Denitrification, dissimilatory nitrate reduction to ammonium, and nitrogen fixation along a nitrate concentration gradient in a created freshwater wetland. *Biogeochemistry*, *87*(1), 99–111. https://doi.org/10.1007/s10533-007-9171-6

Seitzinger, S., Harrison, J. A., Böhlke, J. K., Bouwman, A. F., Lowrance, R., Peterson, B., et al. (2006). Denitrification across landscapes and waterscapes: A synthesis. *Ecological Applications*, *16*(6), 2064–2090. https://doi.org/10.1890/1051-0761(2006)16[2064:DALAWA]2.0.CO;2

Slone, L. A., McCarthy, M. J., Myers, J. A., Hammerschmidt, C. R., & Newell, S. E. (2018). River sediment nitrogen removal and recycling within an agricultural Midwestern USA watershed. *Freshwater Science*, *37*(1), 1–12. https://doi.org/10.1086/696610

Smyth, A. R., Thompson, S. P., Siporin, K. N., Gardner, W. S., McCarthy, M. J., & Piehler, M. F. (2013). Assessing nitrogen dynamics throughout the estuarine landscape. *Estuaries and Coasts*, *36*(1), 44–55. https://doi.org/10.1007/s12237-012-9554-3

Song, K., Xenopoulos, M. A., Buttle, J. M., Marsalek, J., Wagner, N. D., Pick, F. R., & Frost, P. C. (2013). Thermal stratification patterns in urban ponds and their relationships with vertical nutrient gradients. *Journal of Environmental Management*, *127*, 317–323. https://doi.org/10.1016/j.jenvman.2013.05.052

Thompson, S., Piehler, M., & Paerl, H. (2000). Denitrification in an estuarine headwater creek within an agricultural watershed. *Journal of Environmental Quality*, *29*(6), 1914–1923. https://doi.org/10.2134/jeq2000.00472425002900060026x

Van Meter, R. J., Swan, C. M., & Snodgrass, J. W. (2011). Salinization alters ecosystem structure in urban stormwater detention ponds. *Urban Ecosystems*, *14*(4), 723–736. https://doi.org/10.1007/s11252-011-0180-9

Von Korff, B. H., Piehler, M. F., & Ensign, S. H. (2014). Comparison of denitrification between river channels and their adjoining tidal freshwater wetlands. *Wetlands*, *34*(6), 1047–1060. https://doi.org/10.1007/s13157-014-0545-y

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. *Journal of the North American Benthological Society*, *24*(3), 706–723. https://doi.org/10.1899/0887-3593

Welschmeyer, N. A. (1994). Fluorometric analysis of chlorophyll a in the presence of chlorophyll b and pheopigments. *Limnology & Oceanography*, *39*(8), 1985–1992. https://doi.org/10.4319/lo.1994.39.8.1985

Wetzel, R. G. (2001). *Limnology: Lake and river ecosystems* (3rd ed.). Academic Press.

Williams, C. J., Frost, P. C., Morales-Williams, A. M., Larson, J. H., Richardson, W. B., Chiandet, A. S., & Xenopoulos, M. A. (2016). Human activities cause distinct dissolved organic matter composition across freshwater ecosystems. *Global Change Biology*, *22*(2), 613–626. https://doi.org/10.1111/gcb.13094