

Coastal stormwater wet pond sediment nitrogen dynamics

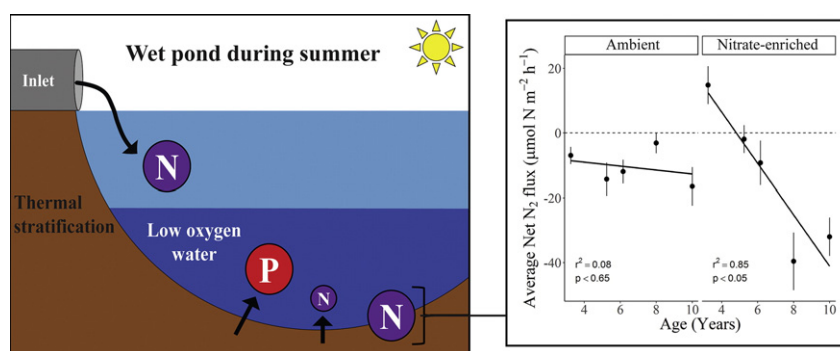
A.C. Gold *, S.P. Thompson, M.F. Piehler

UNC Chapel Hill Institute of Marine Sciences, Curriculum for the Environment and Ecology, 3431 Arendell St, Morehead City, NC 28557, United States

HIGHLIGHTS

- Coastal stormwater ponds are common, but their nitrogen dynamics are understudied.
- Considerable net nitrogen fixation was observed in wet pond sediments during summer.
- Net N_2 fluxes were negatively correlated with pond age after NO_3^- -enrichment.
- Stratification and its effects likely promoted net nitrogen fixation in sediments.
- Wet pond mixing and excavation could increase denitrification during summer.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 June 2017

Received in revised form 21 July 2017

Accepted 21 July 2017

Available online 28 July 2017

Editor: Jay Gan

Keywords:

Coastal stormwater

Denitrification

Nitrogen fixation

Wet pond

Stratification

Water quality

ABSTRACT

Wet ponds are a common type of stormwater control measure (SCM) in coastal areas of the southeastern US, but their internal nitrogen dynamics have not been extensively studied. Using flow-through intact sediment core incubations, net sediment N_2 fluxes before and after a nitrate addition from five wet ponds spanning a range of ages (3.25–10 years old) were quantified through membrane inlet mass spectrometry during early summer. Multiple locations within a single wet pond (6.16 years old) were also sampled during ambient conditions in late summer to determine the combined effects of depth, vegetation, and flow path position on net N_2 fluxes at the sediment-water interface. All pond sediments had considerable rates of net nitrogen fixation during ambient conditions, and net N_2 fluxes during nitrate-enriched conditions were significantly correlated with pond age. Following a nitrate addition to simulate storm conditions, younger pond sediments shifted towards net denitrification, but older ponds exhibited even higher rates of net nitrogen fixation. The pond forebay had significantly higher rates of net nitrogen fixation compared to the main basin, and rates throughout the pond were an order of magnitude higher than the early summer experiment. These results identify less than optimal nitrogen processing in this common SCM, however, data presented here suggest that water column mixing and pond sediment excavation could improve the capacity of wet ponds to enhance water quality by permanently removing nitrogen.

1. Introduction

The coastal plain of the southeastern United States is expected to undergo a steep increase in urbanization over the next 50 years, with

urban area nearly doubling by 2060 (Terando et al., 2014). With the expansion of urban area and the resulting increase in impervious surface area comes the need to manage stormwater to protect coastal water quality, human health, and the ecosystem services provided by coastal systems. Specifically, elevated concentrations of nitrogen in stormwater have been demonstrated to have negative impacts on coastal waters where nitrogen is typically the limiting nutrient for phytoplankton growth (Howarth and Marino, 2006). Coastal stormwater has

* Corresponding author.

E-mail addresses: acgold@live.unc.edu (A.C. Gold), sthompson@email.unc.edu (S.P. Thompson), mpiehler@email.unc.edu (M.F. Piehler).

immediate impacts on sensitive and valuable receiving waters (Sanger et al., 2013), so effective stormwater management must recognize and reduce these impacts.

Stormwater ponds are the most common type of stormwater control measure (SCM) in the US (Collins et al., 2010), and make up the majority (~60%) of SCMs in coastal NC counties (NCDEQ, 2017). Wet ponds, one of the two types of stormwater ponds (i.e., wet ponds and dry ponds), receive water from landscapes and retain a permanent pool of water (Collins et al., 2010). Their main purposes are to extend the storm hydrograph, reduce peak flows downstream, and reduce total suspended solid loads (Hancock et al., 2010; NCDEQ, 2017), but current policy in North Carolina also assumes that they remove nitrogen and other pollutants (NCDEQ, 2017). In the literature, wet ponds are widely considered to be a less effective means of reducing nitrogen loads in stormwater relative to other SCMs (Collins et al., 2010), and wet ponds have been shown to have negative impacts on water quality, including increasing concentrations of phytoplankton (DeLorenzo et al., 2012; Gold et al., 2017; Lewitus et al., 2008; Song et al., 2015) and harmful bacteria (DeLorenzo et al., 2012). Their ability to protect streams from erosion and remove nutrients is highly variable and lower than other types of SCMs (Collins et al., 2010; Hancock et al., 2010; Houle et al., 2013; Koch et al., 2014; Tillinghast et al., 2011).

Denitrification, the microbially-mediated transformation of nitrate into inert N_2 gas through the oxidation of organic matter (Seitzinger et al., 2006), is thought to be an important nitrogen removal process in SCMs (Bettez and Groffman, 2012; Collins et al., 2010; Groffman et al., 2009, 2004; Zhu et al., 2004). Nitrogen fixation, the transformation of N_2 gas into bioavailable nitrogen (Howarth et al., 1988), can be an important part of the sediment nitrogen cycle in low-nutrient water bodies (Newell et al., 2016a; Scott et al., 2008) or water bodies that are nitrogen limited due to large amounts of phosphorus relative to nitrogen (Howarth et al., 1988). Previous SCM studies in coastal areas have used methods that do not directly measure these processes or have used acetylene assays, which significantly alter the microbial community (Fulweiler et al., 2015). Most SCM studies have calculated concentration or load changes between the inflow and outflow of SCMs, but very few studies have gone beyond this approach to directly quantify the processes of denitrification and nitrogen fixation within SCMs (e.g., Scott et al., 2008). No studies, to our knowledge, have directly measured net N_2 gas flux in coastal wet ponds or other coastal SCMs using intact core incubations, but this methodology is important to better understand their impacts on water quality and inform management decisions (Collins et al., 2010), especially in nitrogen-sensitive coastal areas.

Pond and SCM maintenance is believed to be necessary to maintain pollutant removal over time. As they age, ponds fill in with sediments and vegetation, thus decreasing sediment and phosphorus retention in the pond (Hunt and Lord, 2006; Merriman and Hunt, 2014; Sønderup et al., 2016). Because of in-filling, routine pond excavation is recommended to maintain water storage volume and suspended sediment and phosphorus removal (Duan et al., 2016; Merriman et al., 2016; Merriman and Hunt, 2014). While removal of suspended sediments and phosphorus are important for maintaining good water quality and reducing peak flows in some areas, these established practices of wet pond management may not adequately address the removal of nitrogen or the effects of the unique topography, soil type, and hydrology of coastal areas. Additionally, no studies have investigated the variation in nitrogen removal processes inside coastal wet ponds between pond areas with different vegetation, water level (e.g. fringing marsh, shallow water, deep water), and flow path position. Vegetation can increase permanent nitrogen removal by oxygenating soils (Kreiling et al., 2011), thereby fueling coupled nitrification-denitrification in nutrient and organic-rich sediments, but this process remains unstudied in coastal wet ponds. SCM management could be improved by better understanding nitrogen processing in wet ponds to help maximize nitrogen removal and minimize maintenance costs.

This study directly measured summer net N_2 fluxes from the sediments of five coastal wet ponds of different ages during ambient and nitrate-enriched conditions, which simulated nutrient concentrations during baseflow and stormflow, respectively. Net N_2 fluxes from sediments in different locations within a single wet pond were measured to determine the effects of depth, vegetation cover, and flow path position on nitrogen cycling.

The objectives of this study were to:

- Quantify rates of net sediment N_2 flux from coastal stormwater wet ponds spanning a range of ages during ambient and nitrate-enriched conditions.
- Quantify rates of net sediment N_2 flux in different areas of a coastal stormwater wet pond.

2. Methods

2.1. Site description

All data were collected on United States Marine Corps Base Camp Lejeune (MCBCL) in Jacksonville, North Carolina, USA between June 2016 and August 2016. ESRI ArcMap was used to select five stormwater wet ponds spanning a range of ages from 3.25 to 10 years (as of June 2016) with similar land use and soil types (Fig. 1). All ponds sampled are located in Tarawa Terrace, an on-base residential neighborhood. A mid-aged pond (6.16 years old, Fig. 2) was selected for more intensive study, comparing measurements from the forebay and main basin and different locations within each basin (Fig. 2).

2.2. Pond age core flux experiment

2.2.1. Pond conditions

Pond ages as of June 2016 were determined from a base-wide SCM shapefile provided by Environmental Management at MCBCL and were rounded to the nearest month. To calculate the percent cover of vegetation for each sample pond, aerial Google Earth imagery from November 2015 was used to manually delineate marsh vegetation, floating vegetation, and open water area. In late June 2016, sediment cores collected from the deep main basin of each pond were analyzed for percent organic matter by loss-on-ignition. On the same date, surface water samples (depth = 0.1 m) from each pond were collected between 11:00 AM and 3:00 PM and analyzed for nutrient concentrations (NO_3^- -N, NH_4^+ , PO_4^{3-} , total nitrogen, and organic nitrogen) using a Lachat nutrient auto-analyzer, total suspended solids concentrations by weighing particulates on a glass fiber filter after filtering a known amount of water (Clesceri et al., 1998), and chlorophyll-*a* concentrations by analyzing sonicated filters from water samples with a Turner Designs Trilogy fluorometer (Welschmeyer, 1994).

2.2.2. Gas and nutrient fluxes from the sediment-water interface

To measure net sediment N_2 fluxes in ponds of different ages, three replicate sediment cores (6.4 cm diameter \times 30 cm) were collected using an extended sediment corer deployed from a canoe in the middle of the deep main basins of five different wet ponds in Tarawa Terrace in late June 2016 (Fig. 1). Sediment core tubes contained approximately 17 cm of sediment with site-specific water filling the rest of the core tube (~400 ml) (Smyth et al., 2013). Sediment cores with overlying site water were transported immediately to the UNC Institute of Marine Sciences in Morehead City, North Carolina (NC), and allowed to equilibrate for 24 h in site-specific pond water at in situ water temperature. Sediment core tubes were capped, excluding air bubbles, and connected to a flow-through system after the 24-hour equilibration period (Eyre et al., 2002). The flow-through system was located in a climate controlled chamber set to the in situ water temperature at the time of sampling. The flow-through system moved aerated, site-specific pond water into the top of the overlying water of sediment cores and out through a

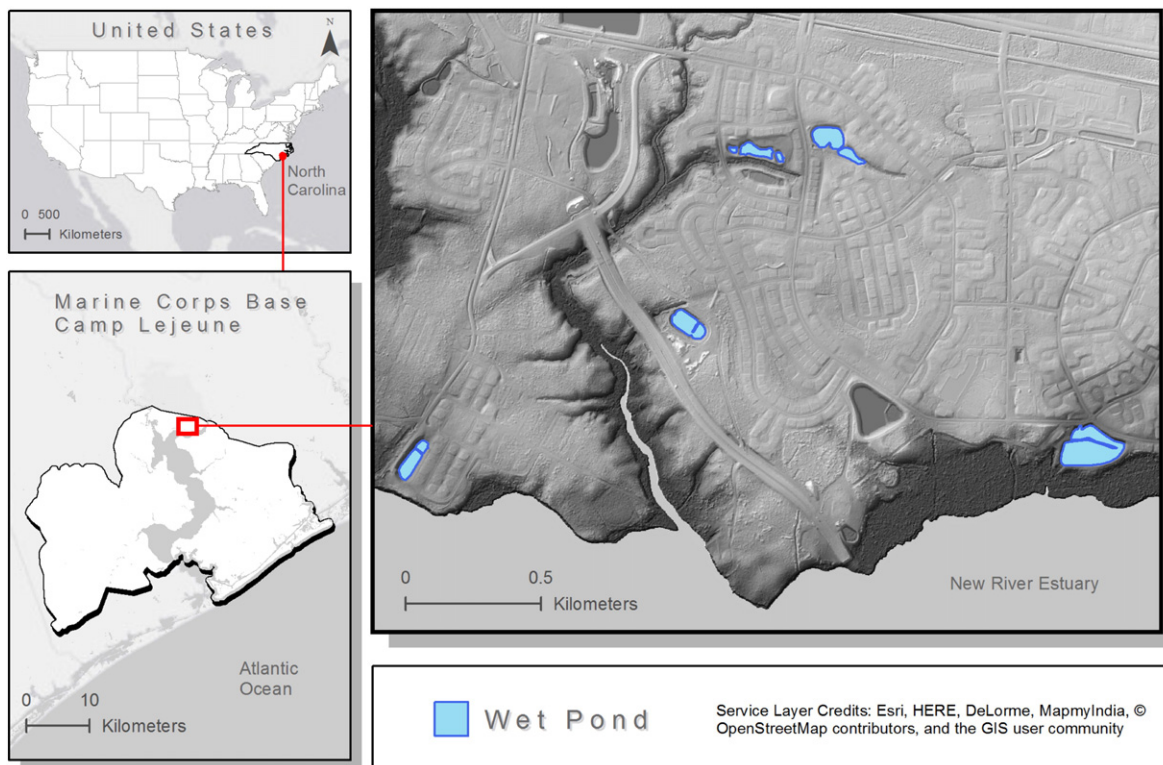


Fig. 1. The five stormwater wet ponds sampled, located on Marine Corps Base Camp Lejeune near Jacksonville, North Carolina, USA.

tube approximately 2 cm above the sediment surface at a rate of 1 ml/min, resulting in an 11 cm difference between inflow and outflow points. Water samples from each core outflow were analyzed for $N_2:Ar$ with a membrane inlet mass spectrometer (MIMS, described by Smyth et al., 2013), and net N_2 fluxes were calculated for each core by difference from dissolved gases in inflow water samples pumped through lines that bypassed cores (Piehler and Smyth, 2011). Standards of de-ionized water were used to determine gas concentrations and to correct for instrument drift. Following the initial incubation, nitrate was added to the feed waters, raising them to a concentration of $30 \mu M NO_3^- - N$ that was similar to nitrate concentrations measured in ponds during storm events (Piehler Lab unpublished data). The incubation equilibrated for

12 h before sampling was reinitiated for analysis of net N_2 fluxes. Water samples from the nitrate-amended feed waters were collected for analysis of nitrate concentrations at the same time as water samples were collected and analyzed for nitrate-enriched net N_2 fluxes.

The same gas flux methodology was used to measure sediment oxygen demand (SOD) ($O_2:Ar$), the flux of oxygen into the sediment. SOD was divided by the dissolved oxygen concentration of the water sample from each core to calculate normalized SOD, or the flux of oxygen into the sediment, normalized by dissolved oxygen available in the water column. This measurement was used to correct for variability in oxygen concentrations among ponds.

Sediment nutrient fluxes were measured using the same flow-through system methodology. Concentrations of $NO_x^- - N$ (NO_x , detection limit = $0.05 \mu M$), NH_4^+ (NH_4 , detection limit = $0.24 \mu M$), PO_4^{3-} (PO_4 , detection limit = $0.02 \mu M$), and organic nitrogen (ON, detection limit = $0.75 \mu M$) were measured using a Lachat Quick-Chem 8000 Nutrient Auto-Analyzer.

Flow-through intact core experiments are a robust way to directly measure processes occurring at the sediment-water interface, but as with many forms of environmental sample analysis, there may be experimental effects that could alter the value of measured variables compared to actual values in situ. This method of analysis has been used extensively to measure net sediment N_2 fluxes and sediment oxygen demand in marine, estuarine, and freshwater ecosystems (Piehler and Smyth, 2011; Poe et al., 2003; Scott et al., 2008; Smyth et al., 2013).

2.3. Within-pond core flux experiment

2.3.1. Pond depth profiles

Temperature, dissolved oxygen, and turbidity were measured from surface and bottom water from both the forebay and main basin of a mid-aged pond (Fig. 2) using a YSI 6600EDS-S water quality sonde. Measurements were taken concurrent with pond sediment core extraction in August 2016. Relative thermal resistance to mixing (RTRM) was calculated using temperature measurements from the top and bottom

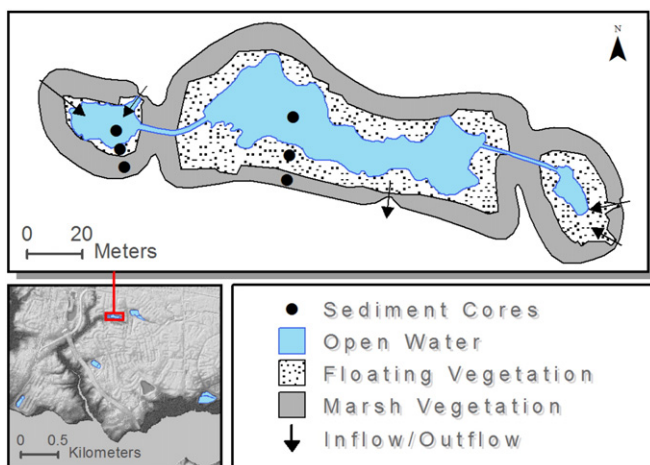


Fig. 2. Intensively sampled pond with vegetation types, location of sediment cores, and inset of study site. Cores from the forebay (left transect) and main pond (right transect) were compared.

of the water column to determine if the ponds were stratified at the time of sampling (Eq. (1), Wetzell, 2001):

$$\varphi = \frac{(\rho_{z2} - \rho_{z1})}{(\rho_4 - \rho_5)} \quad (1)$$

where φ = RTRM (dimensionless), ρ indicates water density (kg/m^3) at the bottom of the pond (z_2), the top of the pond (z_1), at 4 °C, and 5 °C. Water density was calculated from temperature measurements using an equation derived from reference table values from Hornberger et al. (1998) (Eq. (2)):

$$\rho = -0.006t^2 + 0.0383t + 999.92 \quad (2)$$

where ρ = density (kg/m^3) and t = temperature (°C). Consistent with previous studies in stormwater ponds and shallow water bodies, a RTRM >50 indicated pond stratification, and a RTRM <50 indicated mixed conditions (Chimney et al., 2006; Song et al., 2013).

2.3.2. Gas fluxes from the sediment-water interface

The flow-through core incubation method described above for measuring net sediment N_2 and O_2 fluxes, excluding the nitrate addition, was repeated later in the summer (early August 2016) on cores from a mid-aged wet pond (6.16 years old, Fig. 2). Three replicate cores from

six sites within the pond were extracted and analyzed to examine relationships between net N_2 fluxes and depth and vegetation type (marsh, shallow with floating vegetation, and deep) within the pond's forebay and main basin. For this experiment, SOD was not normalized by dissolved oxygen concentration because all samples were collected from the same pond.

3. Results

3.1. Pond age core flux experiment

3.1.1. Pond conditions

All ponds were fringed with marsh vegetation, mainly cattails (*Typha* spp.). Floating vegetation in each pond consisted of alligator weed (*Alternanthera philoxeroides*), which was established at the permanent pond surface and reached into the open water. The percentage of the pond surface covered by vegetation exhibited a positive relationship with pond age (Fig. 3a, $p < 0.2$, $r^2 = 0.5$). Sediment organic matter increased with pond age, but the relationship was not significant (Fig. 3b, $p < 0.22$, $r^2 = 0.45$). Total nitrogen concentrations exhibited a strong and significant ($\alpha = 0.05$) negative correlation with pond age (Fig. 3c, $p < 0.02$, $r^2 = 0.91$), and dissolved inorganic nitrogen:dissolved inorganic phosphorus (DIN:DIP) ratios decreased with age (Fig. 3d, $p < 0.12$, $r^2 = 0.61$). All ponds had a DIN:DIP ratio < 5, indicating that they were

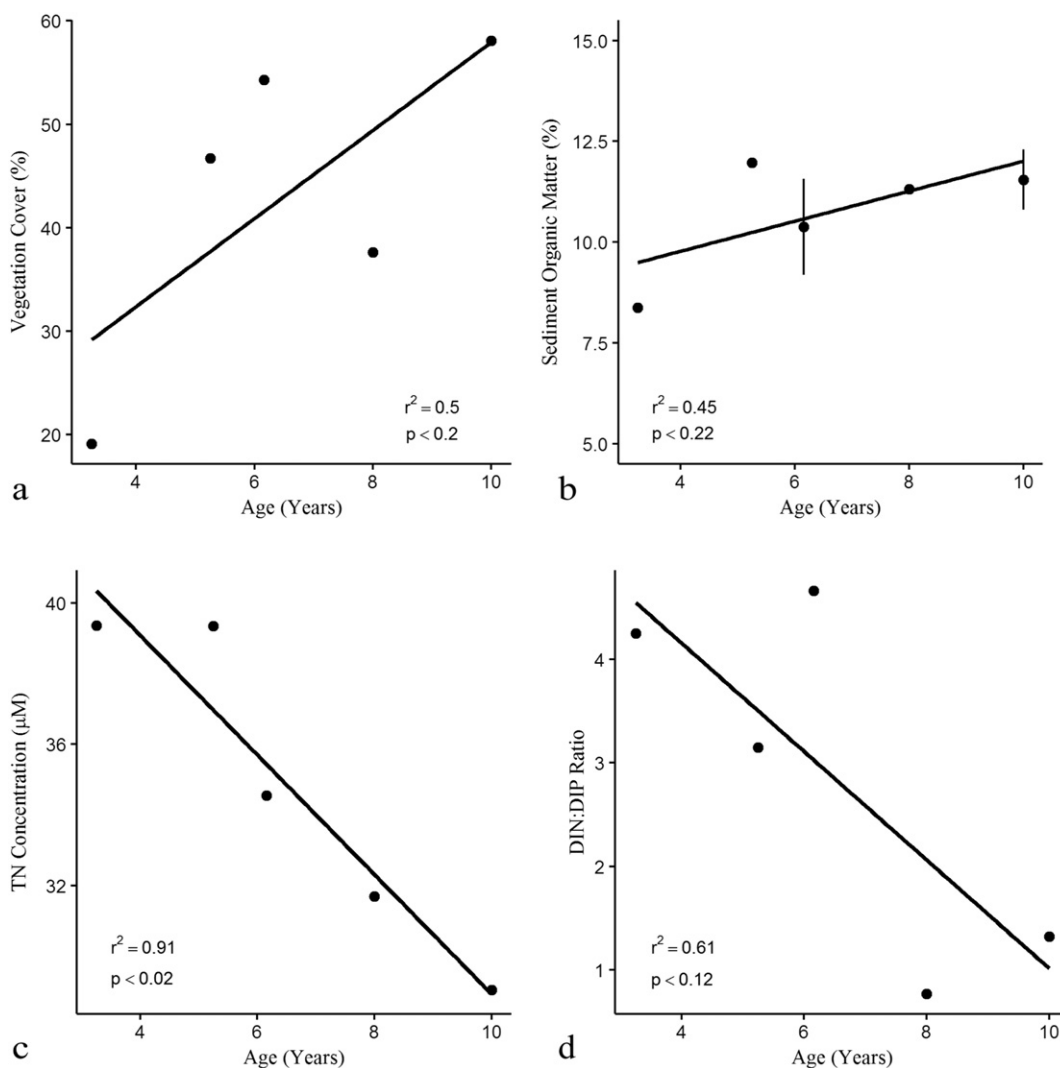


Fig. 3. a) Pond vegetation cover as a function of age b) Mean pond sediment organic matter as a function of pond age c) Mean concentrations of total nitrogen (TN) as a function of pond age d) Pond DIN:DIP ratio as a function of pond age. Error bars indicate standard error for 3b.

nitrogen-limited, assuming that nitrogen limitation consists of a DIN:DIP < 16 (Redfield, 1958, 1934).

3.1.2. Gas and nutrient fluxes from the sediment-water interface

Net sediment N_2 fluxes during ambient conditions exhibited a weak negative relationship with age (Fig. 4, $p < 0.65$, $r^2 = 0.08$). During NO_3 -enriched conditions, net N_2 fluxes showed a strong and significant ($\alpha = 0.05$) negative relationship with pond age (Fig. 4, $p < 0.05$, $r^2 = 0.85$). During ambient conditions, NO_x concentrations were below detection limit. In the NO_3 -enriched conditions, the net N_2 flux of younger pond sediment cores (sediments) increased while the net N_2 flux of older pond sediments decreased relative to ambient conditions. There were slight decreases in dissolved oxygen concentrations of the overlying sediment core water (<1 mg/l) between ambient and NO_3 -enriched net N_2 flux measurements.

Due to the experimental set up, the amount of NO_3 in the inflow of each pond's cores during NO_3 -enriched conditions varied based on the amount of NO_x taken up over the 12-hour period between nutrient enrichment and sampling (Fig. 5). Pond sediments that had higher rates of NO_x removal in their inflow water had net N_2 fluxes that became more negative between ambient and NO_3 -enriched conditions (Fig. 5, $p < 0.001$, $r^2 = 0.99$). Older pond sediments generally had increasingly negative net N_2 fluxes after NO_3 enrichment compared to younger pond sediments (Fig. 5).

Normalized SOD had a significant ($\alpha = 0.05$) positive relationship with age (Fig. 6, Ambient: $p < 0.01$, $r^2 = 0.98$; NO_3 : $p < 0.02$, $r^2 = 0.92$), indicating an increase in microbial activity as ponds age. Net N_2 flux and normalized SOD had a weak negative relationship that was not statistically significant (Ambient: $p < 0.65$, $r^2 = 0.09$; NO_3 : $p < 0.15$, $r^2 = 0.6$).

During the flow-through core incubation with ambient site water, all but one pond had positive NH_4 fluxes from the sediments, all pond sediments had extremely small NO_x fluxes, all but one pond had positive ON fluxes, and all but one pond had positive PO_4 fluxes (Fig. 7). During the NO_3 -enriched phase of the flow-through incubation, the sediments had large negative fluxes of NO_x and all pond sediments had positive PO_4 fluxes (Fig. 7). The eight-year-old pond sediments exhibited

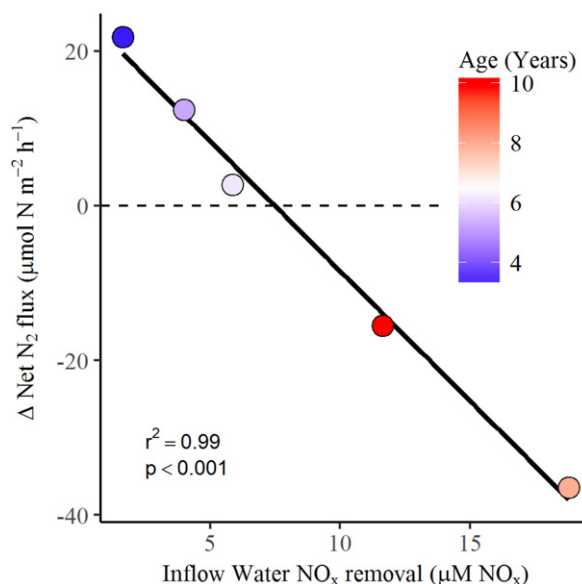


Fig. 5. The change in net N_2 flux between ambient and NO_3 -enriched conditions as a function of the change in inflow water NO_x concentrations during the 12 h between enrichment and sampling.

aberrant fluxes, most notably a smaller negative flux of NO_x compared to the other ponds (Fig. 7).

3.2. Within-pond core flux experiment

3.2.1. Pond depth profiles

During sampling, the main basin had a relative thermal resistance to mixing (RTRM) of 60.82, indicating stratified conditions (Table 1). The forebay was mixed with a RTRM of 26.93 (Table 1). Both the main basin and forebay had higher dissolved oxygen concentrations in the top part of the water column and higher turbidity in the bottom of the water column (Table 1).

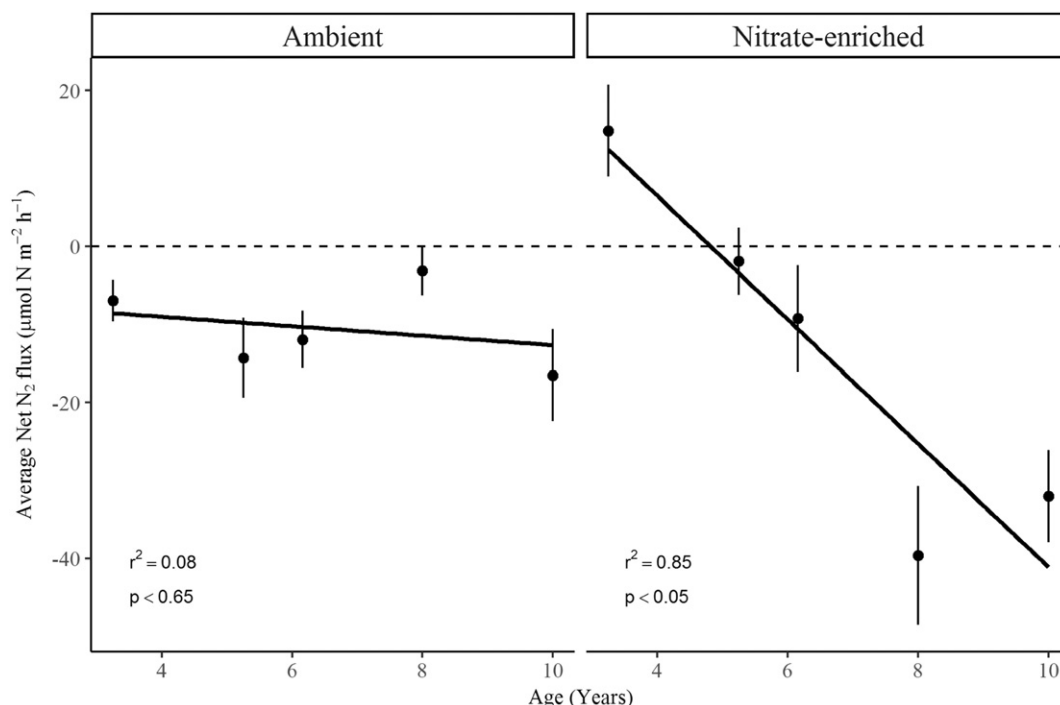


Fig. 4. Net sediment N_2 fluxes as a function of pond age for both ambient and NO_3 -enriched conditions. Error bars indicate standard error between replicate cores.

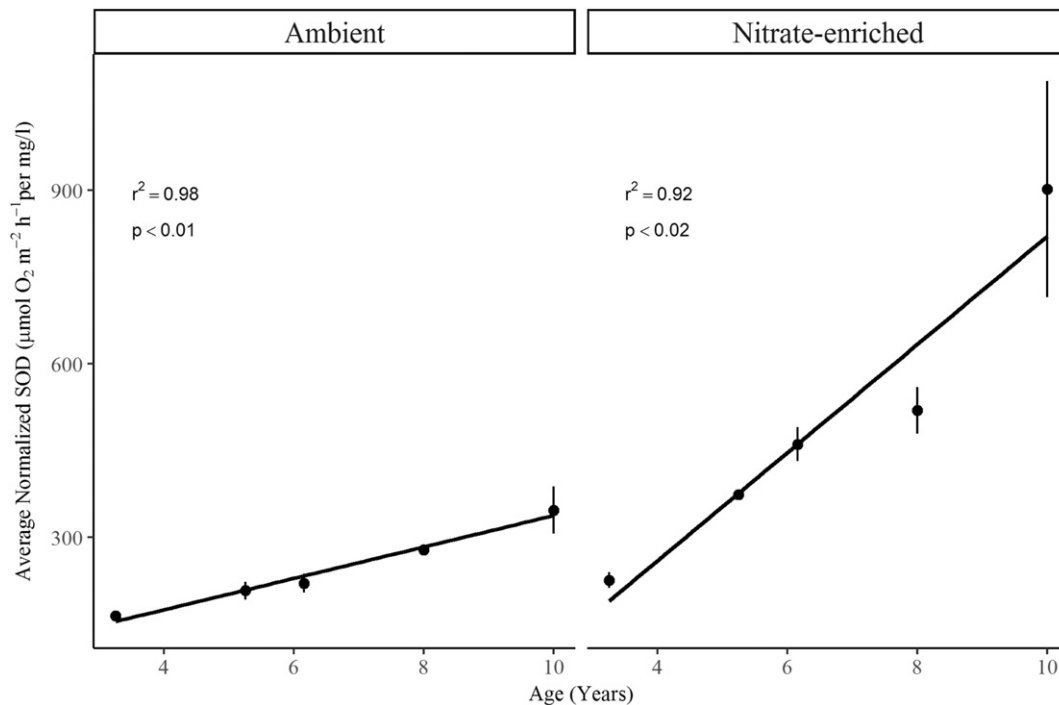


Fig. 6. The relationship between normalized SOD and pond age for ambient and NO₃-enriched conditions. SOD is a proxy for microbial activity. Error bars indicate standard error between replicate cores.

3.2.2. Gas fluxes from the sediment-water interface

In the six-year-old pond sediments, net N₂ fluxes were significantly lower ($\alpha = 0.05$) in the forebay than the main basin based on a two sample *t*-test ($p < 0.001$). There were no significant differences in net N₂ fluxes between zones within the forebay, but the shallow and deep sediments from the main basin had significantly lower ($\alpha = 0.05$) rates of net nitrogen fixation than all other areas sampled (Fig. 8, $p < 0.05$) based on a Tukey HSD post hoc test. Comparing the deep main basin sediment net N₂ fluxes to the same site from almost a month earlier during the pond age core flux experiment, the magnitude of net nitrogen fixation increased five-fold from a net N₂ flux of -11.96 to -60.72 $\mu\text{mol N m}^{-2} \text{h}^{-1}$. Net N₂ flux and SOD showed a strong and significant ($\alpha = 0.05$) negative relationship (Fig. 9, $p < 0.01$, $r^2 = 0.88$).

4. Discussion

4.1. Wet pond chemical and physical conditions

This study examined multiple ponds during summer under conditions of high temperatures and pond stratification that are likely specific to this season. Stormwater ponds and other shallow water bodies experience long periods of thermal stratification between late spring and early fall (Song et al., 2013; Wilhelm and Adrian, 2008) (Table 1). The decomposition of sediment organic matter combined with frequent summer stratification likely fueled the drawdown of dissolved oxygen in the bottom water by microbial activity (Fig. 6) and created extended hypoxic conditions at the sediment-water interface (Diaz and Rosenberg, 2008). These hypoxic conditions likely promoted the release of sediment-sorbed phosphorus, a phenomenon observed in this study (Fig. 7) that has been documented elsewhere (Duan et al., 2016; Song et al., 2013; Wilhelm and Adrian, 2008). Phosphorus accumulates in stormwater pond sediments and bottom water due to loading from the watershed and the remineralization of organic matter within ponds (Song et al., 2015), and this accumulation of phosphorus can contribute to nitrogen limitation by decreasing the ratio of nitrogen to phosphorus if fluxes of nitrogen from the sediments do not greatly

exceed phosphorus fluxes from the sediments. Ammonium is also released from anoxic sediments, and four out of the five sampled ponds had average fluxes of both ammonium and phosphorus out of the sediments during ambient nitrate conditions. These four ponds had average ratios of ammonium fluxes to phosphate fluxes ranging from 2.30–11.77, indicating fluxes that result in nitrogen limitation (i.e. NH₄:PO₄ < 16). Nitrate fluxes out of the sediments during ambient conditions were negligible, so they were excluded from this calculation.

4.2. Sediment/water nitrogen and oxygen dynamics

4.2.1. Influence of wet pond age

The amount of organic matter in stormwater pond sediments increased with pond age in this study, a finding consistent with previous work (Fig. 3b, Moore and Hunt, 2012). This was likely caused by sediment loading from the watershed, increased vegetation in the ponds as they age, as well as phytoplankton production and subsequent deposition of phytoplankton material on the sediments (Fig. 3a). Under conditions of summer stratification (Song et al., 2013) (Table 1), summer nitrogen limitation in wet ponds increased as a function of pond age likely due to increased organic matter accumulation in the sediments, fueling respiration, promoting anoxic conditions, and promoting phosphorus release. This explanation assumes that phosphate fluxes out of the sediments proportionally exceed ammonium fluxes to create nitrogen limitation at the sediment-water interface, and this was supported by observed fluxes. This interpretation was further supported by an observed increase in normalized SOD with pond age (Fig. 6), indicating that older ponds had more microbial activity (e.g., SOD is a proxy for organic matter oxidation by microbial community (Eyre et al., 2013)) that would create more anoxic and nitrogen-limited conditions. Because regressions between pond age and vegetation cover, TN, and DIN:DIP utilized single measurements, further study of these metrics would be beneficial.

Nitrogen limitation likely explained the pattern of net nitrogen fixation observed during ambient conditions in sediments from ponds spanning different ages. Net N₂ fluxes shifted differentially based on

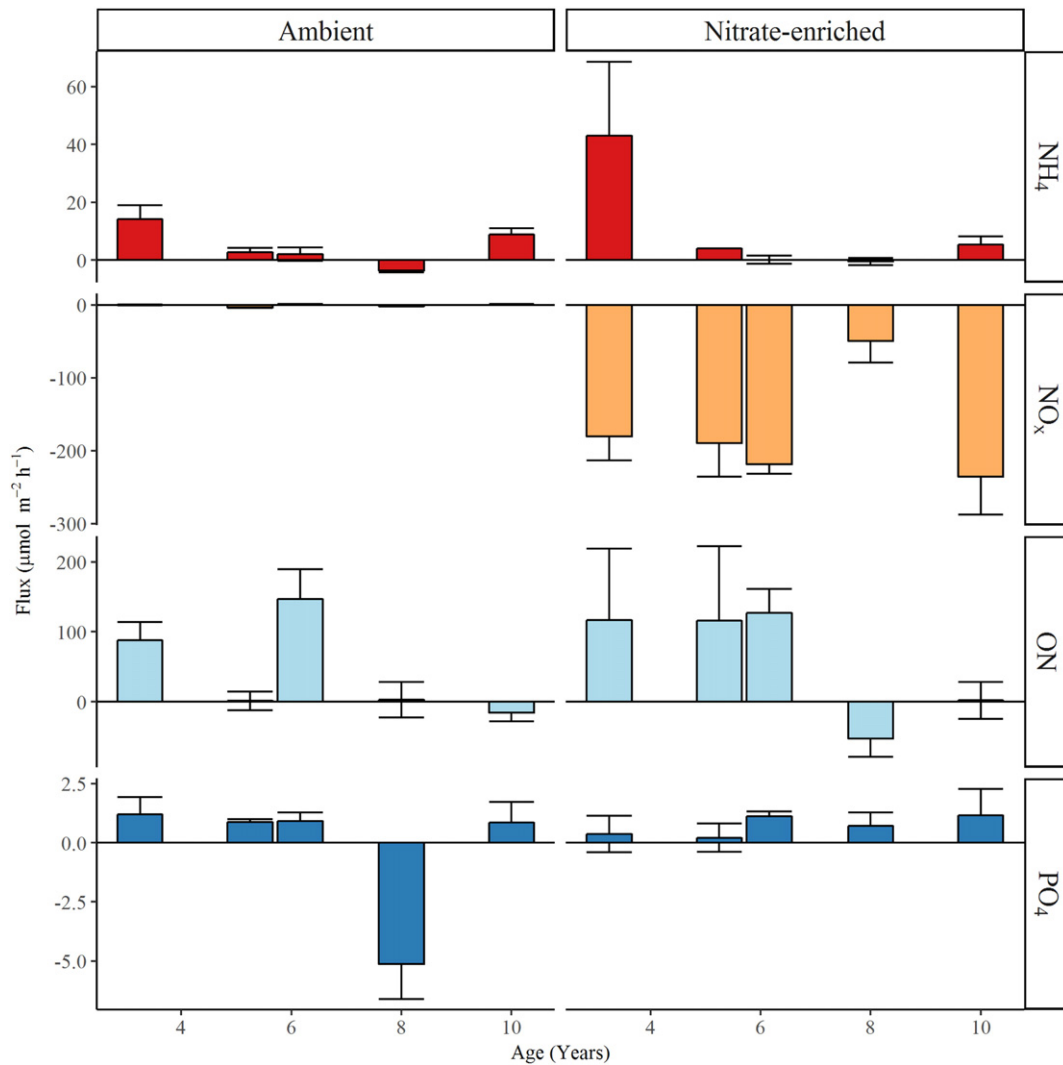


Fig. 7. Mean nutrient fluxes from the sediment surface measured during the flow-through core incubation under both ambient and NO₃-enriched conditions. Error bars indicate standard error between replicate cores.

age in response to nitrate enrichment (Fig. 4). Net nitrogen fixation in aquatic sediments has been measured in low nitrate or low inorganic nitrogen conditions (Fulweiler et al., 2013; Howarth et al., 1988; Newell et al., 2016a, 2016b; Scott et al., 2008), but net sediment nitrogen fixation has not been measured before in stormwater wet ponds. Studies have measured denitrification or hypothesized that denitrification is an important removal mechanism for nitrogen in wet ponds (Bettez and Groffman, 2012; Collins et al., 2010; Groffman et al., 2009, 2004; Zhu et al., 2004), but results from this study suggest that this may not be the case during the summer in coastal wet ponds.

Benthic heterotrophic nitrogen-fixers are less sensitive to levels of inorganic nitrogen than nitrogen-fixers found in the water column (Knapp, 2012), and they can fix substantial amounts of nitrogen at

higher levels of inorganic nitrogen in dark, anoxic waters (Farnelid et al., 2013; Foster and Fulweiler, 2014; Knapp, 2012; Newell et al., 2016b). One explanation for this phenomenon is that extremely low oxygen concentrations and high carbon availability, the conditions found in this study, may reduce the bacterial community's sensitivity to inorganic nitrogen (McGlathery et al., 1998) and allow a select group of nitrogen-fixing benthic heterotrophs to dominate (Newell et al., 2016b). This could explain the increase in net nitrogen fixation between ambient conditions (0 μM NO_x) and nitrate-enriched conditions in older pond sediments (10–20 μM NO_x) that would have been expected to shift towards net denitrification due to the availability of nitrate (Scott et al., 2008). In addition, the decrease in oxygen concentration in the cores' overlying water (caused by an increase in SOD) could explain the increased net nitrogen fixation between ambient and nitrate-enriched conditions (Fig. 9 - within-pond relationship).

In situ, nitrate-rich stormwater flows into the pond and likely takes time to mix with existing water before reaching the sediments. In the summer, pond thermal stratification appears to keep nitrogen delivered in stormwater separated from the sediment-water interface during baseflow conditions (Table 1). If nitrogen from stormflow reaches the sediment-water interface during the summer, results from this study indicate that nitrate would be taken up by the sediments but not permanently removed from the system through denitrification.

Table 1
Depth profile measurements from the top and bottom water of the single pond.

	RTRM	Condition	Depth (m)	Temperature (°C)	DO (mg/l)	DO (%)	Turbidity, (NTU)
Main basin	60.82	Stratified	0.463	28.09	3.61	46.1	3.9
			2.385	25.92	0.71	8.8	22.7
Forebay	26.93	Mixed	0.591	27.26	2.12	26.7	3.3
			1.841	26.29	0.54	6.7	8.2

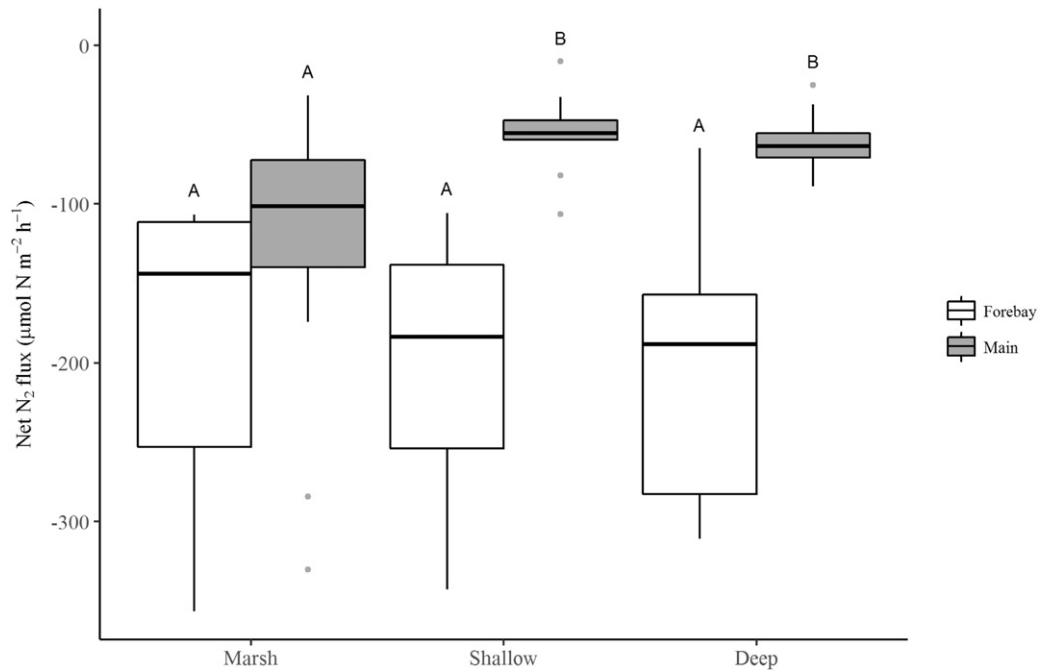


Fig. 8. Rates of net N_2 flux in different areas of the pond (forebay, main) and different vegetation covers (marsh, shallow, deep). Letters indicate significant differences ($\alpha = 0.05$) based on a Tukey HSD post hoc test.

4.2.2. Spatial variability within wet ponds

The net sediment N_2 fluxes from the forebay and main basin sediments of the stormwater pond were significantly different and were significantly correlated with SOD (Fig. 9). This difference in both SOD and net N_2 fluxes is possibly a result of the forebay's position upstream of the main basin, which allows suspended materials to settle out, increasing sediment organic matter (Zhu et al., 2004) and elevating SOD by increasing respiration.

The values of net N_2 flux in both the forebay and main basin sediments were an order of magnitude larger than those observed earlier in the summer (late June compared to early August). This large increase in net nitrogen fixation and the presence of stratification in the main

pond later in the summer supports the idea that pond stratification and associated water quality effects, which can persist through much of the summer (Song et al., 2013), are the root causes of the net sediment nitrogen fixation seen in this study.

4.3. Implications and application to coastal wet pond management

The net nitrogen fixation measured in stormwater wet pond sediments illustrates that the common design of large, deep stormwater wet ponds may not be the most effective solutions for improving the quality of urban stormwater in coastal areas of the southeastern US, especially during the summer. Due to the negative effects on water quality from wet ponds in coastal areas, the authors recommend using alternative kinds of SCMs to manage coastal stormwater. Using SCMs with shallower water or no standing water at all could facilitate net denitrification during the summer by reducing stratification and anoxic conditions in the sediments and bottom water of SCMs. More work is needed on seasonal nitrogen cycling within wet ponds and in alternative SCMs on the coast of the southeastern US. Future work should evaluate alternative SCMs such as stormwater wetlands and bioretention cells that have the potential to control similar volumes of stormwater and possibly produce higher quality water than wet ponds.

A direct solution to pond stratification and its negative effects on water quality is to increase pond mixing to break up the thermocline and reconnect the sediment-water interface with oxygenated water and nitrogen from stormwater inflows. However, exposing sediments to too much oxygenated water could reduce the pond sediments' carbon storage capability and reduce denitrification. A possible compromise for carbon storage, nitrogen removal, and phosphorus removal is to mix the pond periodically to create alternating low and high oxygen conditions, or to design shallower ponds to discourage stratification.

Another management action that could improve pond function is more frequent excavation. Frequent excavation is often associated with greater water storage capacity, suspended sediment removal, and phosphorus removal (Duan et al., 2016; Merriman et al., 2016; Merriman and Hunt, 2014), and this study suggests that frequent excavation could also reduce the amount of net nitrogen fixation during the summer. Excavating organic-rich and phosphorus-rich sediments from

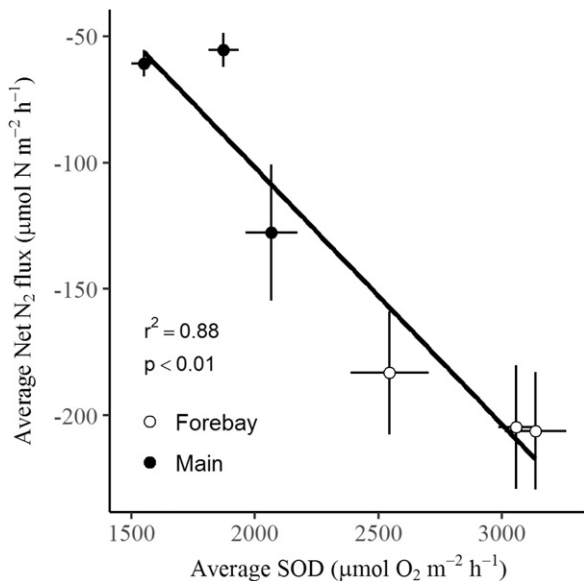


Fig. 9. Average net N_2 flux as a function of Average SOD in the within-pond core flux experiment. Error bars indicate standard error between replicate cores.

ponds, when tenable, could reduce anoxic conditions and phosphorus buildup in bottom water during the summer, which could decrease net nitrogen fixation during summer.

5. Conclusions

Stormwater wet ponds may not be the most effective solutions for improving or maintaining water quality in coastal areas because they did not appear to provide permanent nitrogen removal during the summer. Rather, sediments from ponds of different ages underwent net sediment nitrogen fixation and responded differentially to nitrate enrichment. These pond functions were likely due to thermal stratification, anoxic sediments, phosphorus release from the sediments, and nitrogen limitation. The authors recommend the use of alternative SCMs with shallow water or no standing water instead of wet ponds in coastal areas, increased pond circulation and aeration in existing coastal ponds to decrease stratification and its effects, and frequent pond excavation to reduce anoxic conditions, phosphorus release, and nitrogen limitation in pond sediments.

Acknowledgments

We are extremely thankful to Dr. Susan Cohen of NAVFAC and the Camp Lejeune Environmental Management Division staff, especially Mike Taylor. The authors would also like to acknowledge the three anonymous reviewers, Olivia Torano, Mollie Yacano, Kathleen Onorevole, Dr. Jaye Cable, and Dr. Lawrence Band from UNC Chapel Hill for reviewing drafts and offering helpful comments and advice that significantly enhanced the quality of the manuscript. Funding for this research was provided by the Strategic Environmental Research and Developmental Program—Defense Coastal/Estuarine Research Program [project number RC-2245]. The views expressed are solely those of the authors and do not represent the policies or opinions of the US Department of Defense or associated services.

References

- 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: 10909–10917. <http://dx.doi.org/10.1021/es301409z>.
- Chimney, M.J., Wenkert, L., Pietro, K.C., 2006. Patterns of vertical stratification in a subtropical constructed wetland in south Florida (USA). *Ecol. Eng.* 27:322–330. <http://dx.doi.org/10.1016/j.ecoleng.2006.05.017>.
- Clesceri, L.S., Greenberg, A.E., Eaton, A.D., 1998. *Standard Methods for the Examination of Water and Wastewater*. 20th ed. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC.
- Collins, K.A., Lawrence, T.J., Stander, E.K., Jontos, R.J., Kaushal, S.S., Newcomer, T.A., Grimm, N.B., Cole Ekberg, M.L., 2010. Opportunities and challenges for managing nitrogen in urban stormwater: a review and synthesis. *Ecol. Eng.* 36:1507–1519. <http://dx.doi.org/10.1016/j.ecoleng.2010.03.015>.
- 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. *Environ. Monit. Assess.* 184: 343–359. <http://dx.doi.org/10.1007/s10661-011-1972-3>.
- Diaz, R.J., Rosenberg, R., 2008. Spreading dead zones and consequences for marine ecosystems. *Science* 321:926–929. <http://dx.doi.org/10.1126/science.1156401>.
- Duan, S., Newcomer-Johnson, T., Mayer, P., Kaushal, S., 2016. Phosphorus retention in stormwater control structures across streamflow in urban and suburban watersheds. *Water* 8:390. <http://dx.doi.org/10.3390/w8090390>.
- Eyre, B.D., Rysgaard, S., Dalsgaard, T., Christensen, P.B., 2002. Comparison of isotope pairing and $N_2:Ar$ methods for measuring sediment denitrification—assumption, modifications, and implications. *Estuaries* 25:1077–1087. <http://dx.doi.org/10.1007/BF02692205>.
- 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. *Glob. Biogeochem. Cycles* 27:1083–1095. <http://dx.doi.org/10.1002/2013GB004631>.
- Farnelid, H., Bentzon-Tilia, M., Andersson, A.F., Bertilsson, S., Jost, G., Labrenz, M., Jürgens, K., Riemann, L., 2013. Active nitrogen-fixing heterotrophic bacteria at and below the chemocline of the central Baltic Sea. *ISME J.* 7:1413–1423. <http://dx.doi.org/10.1038/ismej.2013.26>.
- Foster, S.Q., Fulweiler, R.W., 2014. Spatial and historic variability of benthic nitrogen cycling in an anthropogenically impacted estuary. *Front. Mar. Sci.* 1:1–16. <http://dx.doi.org/10.3389/fmars.2014.00056>.
- 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. *Mar. Ecol. Prog. Ser.* 482:57–68. <http://dx.doi.org/10.3354/meps10240>.
- Fulweiler, R.W., Heiss, E.M., Rogener, M.K., Newell, S.E., LeClerc, G.R., Kortebein, S.M., Wilhelm, S.W., 2015. Examining the impact of acetylene on N-fixation and the active sediment microbial community. *Front. Microbiol.* 6:418. <http://dx.doi.org/10.3389/fmicb.2015.00418>.
- Gold, A.C., Thompson, S.P., Piehler, M.F., 2017. Water quality before and after watershed-scale implementation of stormwater wet ponds in the coastal plain. *Ecol. Eng.* 105: 240–251. <http://dx.doi.org/10.1016/j.ecoleng.2017.05.003>.
- Groffman, P.M., Law, N.L., Belt, K.T., Band, L.E., Fisher, G.T., 2004. Nitrogen fluxes and retention in urban watershed ecosystems. *Ecosystems* 7:393–403. <http://dx.doi.org/10.1007/s10021-003-0039-x>.
- Groffman, P.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* 93:49–77. <http://dx.doi.org/10.1007/s10533-008-9277-5>.
- Hancock, G.S., Holley, J.W., Chambers, R.M., 2010. A field-based evaluation of wet retention ponds: how effective are ponds at water quantity control? *JAWRA J. Am. Water Resour. Assoc.* 46:1145–1158. <http://dx.doi.org/10.1111/j.1752-1688.2010.00481.x>.
- Hornberger, G.M., Raffensperger, J.P., Wiberg, P.L., Eshleman, K.N., 1998. *Elements of Physical Hydrology*. The Johns Hopkins University Press, Baltimore, MD.
- Houle, J.J., Roseen, R.M., Ballester, T.P., Puls, T.A., Sherrard, J., 2013. Comparison of maintenance cost, labor demands, and system performance for LID and conventional stormwater management. *J. Environ. Eng.* 139:932–938. [http://dx.doi.org/10.1061/\(ASCE\)EE.1943-7870.0000698](http://dx.doi.org/10.1061/(ASCE)EE.1943-7870.0000698).
- Howarth, R.W., Marino, R., 2006. Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: evolving views of three decades. *Limnol. Oceanogr.* 51: 364–376.
- Howarth, R.W., Marino, R., Lane, J., Cole, J.J., 1988. Nitrogen fixation in freshwater, estuarine, and marine ecosystems. 1. Rates and importance. *Limnol. Oceanogr.* 33: 669–687. http://dx.doi.org/10.4319/lo.1988.33.4_part_2.0669.
- Hunt, W.F., Lord, B., 2006. *Maintenance of Stormwater Wetlands and Wet Ponds*. NC State and NC A&T State University Cooperative Extension.
- Knapp, A.N., 2012. The sensitivity of marine N_2 fixation to dissolved inorganic nitrogen. *Front. Microbiol.* 3:1–14. <http://dx.doi.org/10.3389/fmicb.2012.00374>.
- Koch, B.J., Febria, C.M., Gevrey, M., Wainger, L.A., Palmer, M.A., 2014. Nitrogen removal by stormwater management structures: a data synthesis. *JAWRA J. Am. Water Resour. Assoc.* 50:1594–1607. <http://dx.doi.org/10.1111/jawr.12223>.
- Kreiling, R.M., Richardson, W.B., Cavanaugh, J.C., Bartsch, L.A., 2011. Summer nitrate uptake and denitrification in an upper Mississippi River backwater lake: the role of rooted aquatic vegetation. *Biogeochemistry* 104:309–324. <http://dx.doi.org/10.1007/s10533-010-9503-9>.
- 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* 8:60–65. <http://dx.doi.org/10.1016/j.hal.2008.08.012>.
- McGlathery, K.J., Risgaard-Petersen, N., Christensen, P., 1998. Temporal and spatial variation in nitrogen fixation activity in the eelgrass *Zostera marina* rhizosphere. *Mar. Ecol. Prog. Ser.* 168, 245–258.
- Merriman, L.S., Hunt, W.F., 2014. Maintenance versus maturation: constructed stormwater wetland's fifth-year water quality and hydrologic assessment. *J. Environ. Eng.* 140:5014003. [http://dx.doi.org/10.1061/\(ASCE\)EE.1943-7870.0000861](http://dx.doi.org/10.1061/(ASCE)EE.1943-7870.0000861).
- Merriman, L.S., Hunt, W., Bass, K., 2016. Development/ripening of ecosystems services in the first two growing seasons of a regional-scale constructed stormwater wetland on the coast of North Carolina. *Ecol. Eng.* 94:393–405. <http://dx.doi.org/10.1016/j.ecoleng.2016.05.065>.
- Moore, T.L.C., Hunt, W.F., 2012. Ecosystem service provision by stormwater wetlands and ponds — a means for evaluation? *Water Res.* 46:6811–6823. <http://dx.doi.org/10.1016/j.watres.2011.11.026>.
- NCDEQ, 2017. *Stormwater Control Measure Credit Document*.
- Newell, S.E., McCarthy, M.J., Gardner, W.S., Fulweiler, R.W., 2016a. Sediment nitrogen fixation: a call for re-evaluating coastal N budgets. *Estuar. Coasts*. <http://dx.doi.org/10.1007/s12237-016-0116-y>.
- Newell, S.E., Pritchard, K., Foster, S., Fulweiler, R., 2016b. Molecular evidence for sediment nitrogen fixation in a temperate New England estuary. *PeerJ* 4, e1615. <http://dx.doi.org/10.7717/peerj.1615>.
- Piehl, M.F., Smyth, A.R., 2011. Habitat-specific distinctions in estuarine denitrification affect both ecosystem function and services. *Ecosphere* 2, art12. <http://dx.doi.org/10.1890/ES10-00082.1>.
- Poe, A.C., Piehler, M.F., Thompson, S.P., Paerl, H.W., 2003. Denitrification in a constructed wetland receiving agricultural runoff. *Wetlands* 23:817–826. [http://dx.doi.org/10.1672/0277-5212\(2003\)023\[0817:DIACWR\]2.0.CO;2](http://dx.doi.org/10.1672/0277-5212(2003)023[0817:DIACWR]2.0.CO;2).
- Redfield, A., 1934. On the proportion of organic derivatives in sea water and their relation to the composition of plankton. In: Daniel, R.J. (Ed.), *James Johnstone Meml. Vol.*, pp. 176–192.
- Redfield, A., 1958. *The biological control of chemical factors in the environment*. *Am. Sci.* 46, 205–221.
- Sanger, D., Blair, A., DiDonato, G., Washburn, T., Jones, S., Riekerk, G., Wirth, E., Stewart, J., White, D., Vandiver, L., Holland, A.F., 2013. Impacts of coastal development on the ecology of tidal creek ecosystems of the US southeast including consequences to humans. *Estuar. Coasts* 38:49–66. <http://dx.doi.org/10.1007/s12237-013-9635-y>.
- 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* 87:99–111. <http://dx.doi.org/10.1007/s10533-007-9171-6>.
- Seitzinger, S., Harrison, J.A., Böhlke, J.K., Bouwman, A.F., Lowrance, R., Peterson, B., Tobias, C., Drecht, G. Van, 2006. Denitrification across landscapes and waterscapes: a synthesis. *Ecol. Appl.* 16:2064–2090. [http://dx.doi.org/10.1890/1051-0761\(2006\)016\[2064:DALAWA\]2.0.CO;2](http://dx.doi.org/10.1890/1051-0761(2006)016[2064:DALAWA]2.0.CO;2).
- 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. *Estuar. Coasts* 36:44–55. <http://dx.doi.org/10.1007/s12237-012-9554-3>.
- Sønderup, M.J., Egemose, S., Hansen, A.S., Grudinina, A., Madsen, M.H., Flindt, M.R., 2016. Factors affecting retention of nutrients and organic matter in stormwater ponds. *Ecohydrology* 9:796–806. <http://dx.doi.org/10.1002/eco.1683>.
- 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. *J. Environ. Manag.* 127:317–323. <http://dx.doi.org/10.1016/j.jenvman.2013.05.052>.
- Song, K., Xenopoulos, M.A., Marsalek, J., Frost, P.C., 2015. The fingerprints of urban nutrients: dynamics of phosphorus speciation in water flowing through developed landscapes. *Biogeochemistry*. <http://dx.doi.org/10.1007/s10533-015-0114-3>.
- Terando, A.J., Costanza, J., Belyea, C., Dunn, R.R., McKerrow, A., Collazo, J.A., 2014. The southern megalopolis: using the past to predict the future of urban sprawl in the Southeast U.S. *PLoS One* 9, e102261. <http://dx.doi.org/10.1371/journal.pone.0102261>.
- Tillinghast, E.D., Hunt, W.F., Jennings, G.D., 2011. Stormwater control measure (SCM) design standards to limit stream erosion for Piedmont, North Carolina. *J. Hydrol.* 411: 185–196. <http://dx.doi.org/10.1016/j.jhydrol.2011.09.027>.
- Welschmeyer, N.A., 1994. Fluorometric analysis of chlorophyll a in the presence of chlorophyll b and pheopigments. *Limnol. Oceanogr.* 39, 1985–1992.
- Wetzel, R.G., 2001. *Limnology: Lake and River Ecosystems*. 3rd ed. Academic Press, San Diego, CA.
- Wilhelm, S., Adrian, R., 2008. Impact of summer warming on the thermal characteristics of a polymictic lake and consequences for oxygen, nutrients and phytoplankton. *Freshw. Biol.* 53:226–237. <http://dx.doi.org/10.1111/j.1365-2427.2007.01887.x>.
- Zhu, W.-X., Dillard, N.D., Grimm, N.B., 2004. Urban nitrogen biogeochemistry: status and processes in green retention basins. *Biogeochemistry* 71:177–196. <http://dx.doi.org/10.1007/s10533-004-9683-2>.