Wet season nitrogen export from a residential stormwater pond

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Abstract

Stormwater runoff is recognized as a cause of water quality degradation because it may carry nitrogen (N) and other pollutants to aquatic ecosystems. Stormwater ponds are a stormwater control measure often used to manage stormwater runoff by holding a permanent pool of water, which reduces the peak flow, magnitude of runoff volume, and concentrations of nutrients and pollutants. We instrumented the outlet of a stormwater pond in an urban residential neighbourhood in Florida, United States to (1) investigate the concentration and composition of N forms during the summer rainy season (May to September 2016), and (2) determine the bioavailability of organic N in the stormwater pond with a bioassay experiment. A total of 144 outflow water samples over 13 storm events were collected at the outlet of the stormwater pond that collects runoff from the residential catchment. Samples were analysed for various inorganic N [ammonium (NH₄–N), nitrate (NO₃–N)], and organic N forms [dissolved organic nitrogen (DON), and particulate organic nitrogen (PON)]. Flow-weighted mean concentration of total N (TN) in pond outflow for all collected storm events was 1.3±1.42 mg L⁻¹, with DON as the dominant form (78%), followed by PON and NO₃–N (each at 8%), and NH₄–N (6%). In the bioassay experiment, organic N (DON+PON) was significantly decreased by 25–28% after 5 days of incubation, suggesting that a portion of the DON carried from the pond outflow to receiving water bodies may be bioavailable. These results suggest that efforts to mitigate stormwater N outflows from urban ponds should incorporate both inorganic and organic N in management plans.

Introduction

Stormwater runoff is recognized as an important source of nitrogen (N) in receiving water bodies, especially in urban landscapes with higher impervious surface area [1, 2]. The volume and flow velocity of stormwater runoff is generally higher on impervious surfaces than in natural areas. This increased water volume and velocity can change both the flow and quality of receiving streams, necessitating stormwater management practices that collect and mitigate stormwater flows [3–5]. Under the US Clean Water Act, states are required to monitor water
quality, report water bodies that do not meet designated water quality criteria, and develop action plans to bring impaired water bodies back into compliance with water quality standards. One part of meeting this goal is to reduce contaminant transport to water bodies via stormwater runoff. As a result, best management practices (BMPs) or stormwater control measures (SCM) are designed to reduce, treat, or store polluted stormwater runoff [5].

Stormwater pond systems are the most widely used type of SCM throughout the United States [3, 5], with stormwater ponds use increasing globally as stormwater legislation addresses changes associated with urbanization [6]. In particular stormwater ponds have been found to number from 76,000 to nearly 100,000 in Florida alone [7]. Stormwater ponds, also known as retention basins, wet ponds or wet detention basins are constructed to manage stormwater runoff by holding a permanent pool of water, thus reducing the peak runoff flow, tolerating the high magnitude of runoff volume, and potentially reducing the concentrations of pollutants and nutrients while often also contributing to groundwater recharge and river baseflow [5, 8, 9].

As compared to other SCMs, studies have shown that detention ponds are less effective in mitigating N loads [3, 10]. For example, a review of stormwater treatment options by Yang and Lusk [9] reports that N removal in ponds averages only 30–40%, whereas other SCMs such as bioretention and wetlands can achieve N removal up to 60–80%. A broad synthesis on stormwater BMPs by Koch et al. [4] reported that removal of N by stormwater ponds is variable, especially for inorganic N (NO\textsubscript{3}\text{-N} and NH\textsubscript{4}\text{-N}), with treatment efficacy ranging from up to 100% removal to no removal or even the net export of inorganic N from ponds. These ponds were reported to often be the source of NO\textsubscript{3}\text{-N} through biochemical transformations of sediment N that had settled in the ponds, in which in-pond mineralization of organic N was postulated as a cause of net export of inorganic N from the ponds [11]. Stormwater ponds may also increase the export of particulate organic matter and the N associated with particulates via internal production of algal biomass [12–14] Rosenzweig et al. [11] observed that the dissolved organic N (DON) load in pond outflow was two-times higher than the influent load, indicating the generation of DON in the ponds. Likewise, Lusk and Toor [15] and Williams et al. [16] provide evidence that urban stormwater ponds can have high levels of autochthonous dissolved organic matter production, suggesting that internal biogeochemical processes in the ponds could make the ponds net exporters of reactive N—potentially offsetting any pond water quality gains. Other recent studies have shown that DON can be a bioavailable N source in freshwater and marine ecosystems [17, 18]. This study investigates the bioavailability of DON in an urban stormwater pond as well as the concentration and composition of N in outflow from the pond during a summer rainy season. Further, our goal was to place DON outflow concentrations in context with other N forms in pond outflow and to assess the degree to which that DON may be bioavailable in downstream waters.

Materials and methods

Site description

The study was conducted at a stormwater wet pond located in the Lakewood Ranch residential neighborhood, Bradenton, Florida, United States. The stormwater pond has a permanent pool of 0.22 ha in size and was built in 2003, making the pond 13 years old at the time of this study. The soil within this catchment is predominantly Myakka fine sand series (Sandy, siliceous, hyperthermic Aeric Alaquods). The pond was designed to mimic and function as a natural water body that can retain water during storm events and filter constituents before they drain via piped conveyances into Braden River, a sub-watershed of the Tampa Bay estuary. The physical features of the catchment area for the pond are described in Table 1. The site is 2 ha...
with 37% impervious surface area (Fig 1). The study area is characterized by a sub-tropical climate with average annual rainfall of 143 cm, of which approximately 60% (86 cm) occurs during the summer rainy season months of June 1 through September 30.

**Bioassay experiments**

We collected water samples from the pond and carried them through a 5-day incubation experiment to determine DON bioavailability. These water samples were collected on nine dates, spaced approximately 10 days apart during spring 2016. At each of the 9 collection dates, five 1-L grab samples were collected from the pond center and mixed in a bucket before taking a single composite 1-L sample in an amber glass bottle, which was kept on ice and transported to the lab for further processing and analyses. At the same time, three 1-L inoculum samples were collected in amber glass bottles at the most downstream site of Braden River, which receives a part of the pond outflow. Inoculum samples were filtered through 150 μm mesh to remove heterotrophic organisms prior to the bioassay experiment [19].

The bioassay experiment was carried out following the methods described by Osborne et al. [15, 19–21], (Fig 2). In brief, 320 mL of pond water sample was mixed with 100 mL of filtered inoculum in 1-L amber glass bottle. The mixed samples were divided into two portions and designated as T₀ (initial samples) and T₅ (incubated samples). Subsamples of T₀ were immediately filtered using Whatman #47 mm GF/F (0.45 μm pore size) filters and analyzed for total dissolved N (TDN), NH₄–N and NOₓ–N, whereas the unfiltered samples were analyzed for TN (see Nitrogen Forms and Concentrations Analysis, below). The samples designated as T₅ were incubated at a 12:12 hour dark: light cycle in the laboratory with temperature maintained at 22±2˚C for 5 days, after which the samples were analyzed for TN, TDN, NH₄–N, and NOₓ–N. After verifying normality of the T₀ and T₅ data, a paired t-test was used to test for statistical significance between the two sample points.

**Instrumentation**

We have several years of collaboration with the Lakewood Ranch Homeowners’ Association (HOA) and we were granted permission for access to the community to conduct research. As this is a residential community managed by a HOA, no permits were required for our field work. At the pond outflow, an ultrasonic flow transmitter (Signature flowmeter, Teledyne Isco, NE) was installed to measure flow leaving the pond. A rain gauge (Teledyne ISCO, NE) was used to measure the rainfall and an autosampler (Avalanche, Teledyne ISCO, NE) was programmed to collect pond outflow samples according to pond flow characteristics (see Pond Outfall Sampling, below). The autosampler had 14 (950 ml) plastic sample collection bottles, with a built-in refrigerator to keep the sample at 4˚C. The rain gauge and autosampler were programmed to download the data into FlowLink 5.1 software (Teledyne ISCO, NE), which
was used to track rainfall depth, pond outflow volume and sample collection time. Sample
dates and associated rainfall depths and pond outflow volumes are presented in Table 2.

Pond outflow sampling

Samples were collected in spring and summer 2016 from the pond outflow. At the beginning
of the collection period, as the water level in the outflow pipe was low (~0.4 cm) because of the

Fig 1. (A). Drainage area of the stormwater pond and (B) the various instruments installed including a) rain gauge, b) laser flow
meter, and c) autosampler. (Photo courtesy of author).

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Fig 2. Flow chart showing various steps used in the bioassay study (Jariani and Toor, 2018) modified from (Osborne et al, 2013). $T_0$ refers to initial (non-incubated) samples and $T_5$ refers to samples designated for 5-days incubation.

Table 2. Number of samples collected, rainfall amount (cm), and pond outflow volume (m$^3$) for 13 storm events from May to September 2016.

| Date     | Event | No. of Collected Samples | Total Rainfall (cm) | Outflow Volume (m$^3$) |
|----------|-------|--------------------------|---------------------|------------------------|
| 05/04/16 | 1     | 14                       | 1.68                | 6.9                    |
| 05/07/16 | 2     | 7                        | 0.05                | 14.37                  |
| 06/09/16 | 3     | 12                       | 12.75               | 879.12                 |
| 06/12/16 | 4     | 2                        | 0.05                | 25.20                  |
| 08/08/16 | 5     | 11                       | 3.30                | 18.27                  |
| 09/08/16 | 6     | 14                       | 2.49                | 955.08                 |
| 08/10/16 | 7     | 6                        | 5.38                | 479.64                 |
| 08/13/16 | 8     | 8                        | 0.36                | 124.80                 |
| 08/20/16 | 9     | 14                       | 1.40                | 466.98                 |
| 08/31/16 | 10    | 14                       | 5.82                | 210.24                 |
| 09/01/16 | 11    | 14                       | 0.23                | 415.44                 |
| 09/02/16 | 12    | 9                        | 2.97                | 69.36                  |
| 09/12/16 | 13    | 14                       | 0.03                | 64.32                  |

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preceding dry season, the flowmeter was programmed to enable sampling when the rain gauge captured 0.25 cm of rain and the level of water in the outflow pipe was 0.65 cm for the duration of 5 minutes. As the rainy season progressed, the level of water increased and there was outflow from the pond at all times, therefore, the sampling program was changed (e.g., level of water to start sampling and sampling intervals). The threshold level to initiate sampling ranged from 0.65 to 20.32 cm in the outflow pipe, and the sampling intervals between each sample varied between 10 min to 6 hr intervals. Samples were taken to the laboratory within 24 hr of collection. A total of 13 storm events (144 samples) were collected. Prior to the sampling, all sampling containers used were acid washed (10% hydrochloric acid, HCl) and rinsed with deionized water.

**Nitrogen forms and concentrations analysis**

Samples for the bioassay experiment and from the pond outflow collections were analyzed using a continuous flow ion analyzer (AA3, Seal Analytical Inc., Mequon, WI) for NH$_4^+$–N and NO$_x$–N (NO$_3^-$–N + NO$_2^-$–N) with USEPA Method 350.1 and 353.2, respectively. The filtered and unfiltered samples were analyzed for TDN and TN, respectively, using oxidative combustion-chemiluminescence (ASTM, 2015) by a Total Organic Carbon Analyzer (TOC-L CPH/CPN, Shimadzu Corp., Columbia, MD). Other N forms were calculated as follows: particulate organic nitrogen (PON) = TN–TDN and DON = TDN–(NO$_x$–N + NH$_4$–N).

**Flow-weighted mean concentrations analysis**

Flow-weighted mean concentrations (FWMC) (mg L$^{-1}$) were used to quantify the concentration proportional to a corresponding flow volume. The FWMC for each parameter were derived from the concentrations, sample time window, and flow volume for each sample. The equation is as follows:

$$FWMC = \frac{\sum_i (c_i \ast t_i \ast q_i)}{\sum_i (q_i)}$$

where $c_i$ = concentration in $i^{th}$ sample

$t_i$ = time (min) window of $i^{th}$ sample

$q_i$ = flow volume in $i^{th}$ sample

This equation allows the concentration in each sample to be considered in light of the time window and flow volume associated with it [22, 23].

**Results and discussion**

**Bioavailability of organic nitrogen**

In the bioassay experiment, organic N (DON+PON) was significantly decreased ($p<0.05$) after 5-days of incubation. Mean DON concentrations were reduced by 25% (range: 18 to 30%), suggesting that a portion of DON was bioavailable (Fig 3). The mean PON concentration also showed a 28% (range: 2 to 52%) reduction during the incubation (Fig 3), suggesting that a portion of PON was also subject to biogeochemical transformation. In contrast to organic N, NO$_x$–N concentrations increased by 35–39% (mean: 30±38%) and NH$_4$–N concentrations increased by 9–39% (mean: 39±16%) (Fig 3). This finding is similar to Seitzinger and Sanders [24] and Jani and Toor [21], who reported an increase in DIN concentrations and decrease in DON concentrations in the bioassay experiments. This net increase in inorganic N was likely due to the mineralization of organic N to NH$_4$–N, which was further nitrified to NO$_x$–N [25–27]. However, it should be noted that our bioassay experiment likely took place
with elevated oxygen conditions relative to what would be expected in the ponds *in situ*. If the ponds were anoxic or stratified, we might not observe nitrification rates as high as reported by our laboratory bioassay study. Indeed if this was the case (low oxygen and stratified pond environment, then *in situ* pond nitrification may be limited [3, 28].

Decomposition of PON by microbial action might explain why DON was the most abundant N form in our stormwater pond (Fig 3) and why several authors have noted that these urban stormwater treatment ponds are net DON exporters (e.g., Lusk and Toor [15]). Lusk and Toor [15] study did not include analysis of PON but did show that DON concentration in pond outflow (mean 1.85 mg L⁻¹) was higher than that in pond inflow (mean 1.09 mg/L), suggesting that in-pond processes, including decomposition of PON, generated new DON. Further, Lusk and Toor [15] showed through high resolution mass spectrometry that the chemical composition of the DON was transformed inside the pond to produce DON compounds that were lower in molecular weight and more aromatic than those in the incoming runoff—again suggesting a degree of in-pond processing that changes the N signal of urban runoff. Numerous studies have reported that microbial populations are both consumers and producers of DON because they use and release reactive N exudates that can be consumed and reformed [29, 30]. Our study is the first of which we are aware that includes inspection of both DON and PON biodegradability within an urban stormwater pond, and that a third to a half of these ON forms were bioavailable in our study indicates that ON can be dynamic in urban aquatic systems. By including PON in our study, we show that a portion of PON can be utilized and transformed by microbes in the pond, implying that physical processes like sedimentation of particulates may have limited efficiency for reducing N export from the pond if PON degradation and utilization result in the generation of DON and/or dissolved inorganic N. In this way, the pond would function less as an N remover and more as merely an N transformer, though we did not specifically look at this process and it is certainly one that warrants further study [15, 16].
One important implication of this work comes from the fact that wet stormwater ponds are often connected to receiving water bodies and bioavailable N that leaves these ponds can thus add to the reactive N loads of downstream waters. We recognize that reactive N would likely be transported from urban landscapes to receiving streams even if stormwater ponds were not present, but our data highlights how outflows from these ponds should be recognized as potentially carrying a reactive N load. Gold et al. [3] observed little to no improvement in downstream water quality and nutrient concentrations after watershed-scale implementation of wet stormwater ponds in an urbanizing coastal area. A growing number of researchers are recognizing that in-pond nutrient cycling may make urban stormwater ponds function as sources of dissolved nutrients [31, 32], and there is a need for new research that investigates the mechanistic controls on nutrient cycling and downstream fate in these urban features of the built environment. We provide evidence here of the dynamic nature of in-pond DON and PON, and future studies should investigate this across temporal and spatial scales and in environments with varying ON sources such as with different types of vegetation.

**Distribution of nitrogen forms in pond outflow waters**

Given the above result that a portion of the ON in our pond was bioavailable, our second objective was to place ON concentrations and proportions in context with inorganic N forms in the pond outflow. The FWMC of pond outflow TN for all storm event was $1.31 \pm 1.42 \text{ mg L}^{-1}$ (range: 0.53 to 5.88 mg L$^{-1}$). For the entire wet season, DON concentration was higher than other N forms for most storm events and ranged from 0.28 to 5.56 mg L$^{-1}$ (mean: 1.03 mg L$^{-1}$), followed by PON (0.02 to 0.32 mg L$^{-1}$; mean: 0.11 mg L$^{-1}$), NO$_3$–N (0.02 to 0.33 mg L$^{-1}$; mean: 0.10 mg L$^{-1}$), and NH$_4$–N (0.001 to 0.19 mg L$^{-1}$; mean: 0.07 mg L$^{-1}$) (Fig 4). The highest mean concentration of TN for the season was observed in the last event with 5.88 mg L$^{-1}$ (Fig 4).

There are scarce reports in the literature that include both DON and PON in investigations of N forms in urban runoff and stormwater ponds. Our observation that DON was the dominant N form in the pond outflow was similar to findings by Lusk and Toor [15], who reported DON as the dominant form of N in outflow from a residential wet pond, and in line with Taylor et al. [33] who observed that DON was likewise the dominant N form in urban runoff. At the beginning of the season, (events 1 to 5), the ranking of strength in distribution among N forms in the pond outflow was DON $>$ NO$_3$–N $>$ NH$_4$–N $>$ PON (Fig 4). This pattern remained until the middle of the season (events 6 to 9) when PON increased as the second highest N form after DON, suggesting at this stage of the season, the stormwater pond may be highly influenced by sources of particulate N, such as grass clippings, leaf litter, and plant debris that was carried by stormwater runoff and that did not settle in the pond (Fig 4). A study by Rosenzweig et al. [11] reported that particulate N ranged from 26 to 38% of total N transport and the fraction was greater during storm events. At the end of the season in September (events 10 to 13), our data showed that NH$_4$–N concentrations increased, but DON remained as having the highest concentration, especially in event 13 that resulted an anomalous one-time spike in TN (Fig 4), the source of which we did not investigate.

Our data revealed that organic N was a significant portion of N in the pond outflow, suggesting that reduction of NO$_3$–N and NH$_4$–N alone might not be adequate to mitigate downstream loading of TN. For example, in our study area, summer rainy season bans on turf fertilizers that contain inorganic N are common. The premise behind these bans is that summer rains drive inorganic N to runoff and stormwater ponds. Our study demonstrates that reactive N may still be transported from these ponds even when such bans are in place. Furthermore, the FWMC and proportion of DON remained fairly steady throughout the wet season, suggesting a constant catchment and/or in-pond source of DON. Potential catchment
sources of ON to urban runoff are numerous and include atmospheric deposition, plant material, soils, fertilizers, reclaimed water used for irrigation, and pet waste [9, 34–36].

Overall, the composition of N forms in our pond outflow are similar with our previous study [17] conducted in a longitudinal gradient from freshwater (Braden River) to estuarine (Tampa Bay) systems that showed organic N as the dominant N form (86% TN). The Braden River is directly connected to our pond outflow, together with many other ponds in the Braden
river watershed, suggesting that pond outflow from residential areas is one contributor of organic N input to the river ecosystems.

Conclusions
This study was conducted to investigate the magnitude of organic and inorganic N forms and the bioavailability of N in a stormwater pond during a rainy season. The main conclusions from the study are (1) pond outflow was dominated by DON (78% of TN over the season), and (2) a portion of DON in stormwater ponds was bioavailable, ranging from 18–30% of the DON pool and 2–52% of the PON pool. These suggest that stormwater pond management for N removal should incorporate not only inorganic N but also organic N strategies. From an ecosystem standpoint, we also argue that greater emphasis should be placed on the role of urban wet stormwater ponds in downstream ecology. Our evidence of ON bioavailability suggests that these ponds may transport reactive ON and thus exacerbate water quality degradation in downstream waters.

Supporting information
S1 Data.
(XLSX)

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