Reducing Stormwater Nitrogen with Denitrifying Bioreactors: Florida Case Study

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Abstract: Growth of suburban areas has led to significant nonpoint source nitrate (NO_3^-) pollution. Wet detention ponds reduce peak flows but are not designed to reduce NO_3^- loading downstream. Denitrifying bioreactors have shown high rates of NO_3^- removal in runoff and effluent from agricultural fields. Bioreactors modified for wet detention ponds may improve NO_3^- treatment in suburban settings. This study retrofitted two wet detention ponds with submerged denitrifying bioreactors and monitored water quality for 1 year. Samples taken after installation showed significant and persistent NO_3^- reductions compared with preinstallation measurements. This was coupled with decreased chlorophyll-a levels, suggesting a concurrent reduction of algae growth. High levels of dissolved organic carbon and reduced sulfate corroborate denitrification as the likely removal pathway. Estimates of the NO_3^- removal rate were much higher than observed in agricultural bioreactors. This may be due to increased pondwide denitrification supported by the release of dissolved carbon from the bioreactors into the surrounding pond. Further installations, broader sampling regimes, and longer monitoring are necessary to confirm the viability of bioreactor retrofits in wet detention ponds. **DOI: 10.1061/JSWBAY.0000867.** © *2018 American Society of Civil Engineers.*

Introduction

Suburban areas have been increasing in population and area in the United States and globally in the past half century and are a significant source of nitrogen (N) in surface water (Carpenter et al. 1998; Bettez and Groffman 2012). Nitrogen pollution in suburban watersheds originates largely from nonpoint sources, primarily N deposition and domestic fertilizers (Lovett et al. 2000; Osmond and Hardy 2004). This contributes to high nitrate (NO_3^-) loads that lead to eutrophication in estuarine and coastal waters (Kemp et al. 2005). Many stormwater control measures (SCMs) treat suburban runoff, including bioretention and wet detention ponds, with denitrification as a major mechanism of NO_3^- removal in SCMs (Bettez and Groffman 2012).

Wet detention ponds focus primarily on reduction of peak flows and treatment of particulate pollutants. They have little impact on dissolved NO_3^- load (Mallin et al. 1998) and can, instead, require algaecide use to control algae blooms (Collins et al. 2010). Conditions for denitrification are rarely achieved in constructed ponds due to the lack of organic matter and anaerobic zones in pond sediments (Mallin et al. 1998). Despite their limited ability to manage nutrient pollution, wet detention ponds are one of the most popular SCMs throughout the United States. Improving their function could have a great impact on water quality. Recent studies investigated retrofits for ponds to increase nutrient treatment using floating treatment wetlands (Borne et al. 2013), filtration (Winston et al. 2017), and dredging (Schwartz et al. 2017).

Strategies for NO_3^- removal in other settings may provide insight into improving suburban water quality. Denitrifying bioreactors efficiently reduce NO_3^- in agricultural tile drainage (Schipper et al. 2010). In these systems, high NO_3^- drainage water flows through a saturated bed of woodchips that provide conditions necessary to support denitrifying microbes (e.g., Schipper et al. 2010). Removal rate (RR) in bioreactors range from 1 to 30 $g\,N\,m^{-3}\,day^{-1}$, with outflow concentrations reduced below 2 $mg\,N\,L^{-1}$ in many cases (Bell et al. 2015; Addy et al. 2016). Some studies have influent NO_3^- concentration lower than 2 $mg\,N\,L^{-1}$, which could be biologically limiting for denitrification (Addy et al. 2016). Submerged denitrifying bioreactors in wet detention ponds could provide similar conditions to field bioreactors and could produce similar rates of denitrification.

This study investigates how modified denitrifying bioreactors for wet detention ponds could reduce NO_3^- and algae in ponds to decrease downstream nutrient pollution and improve pond aesthetics. Two bioreactors were installed in ponds near the Florida Gulf Coast and were monitored for a year. NO_3^- concentrations were expected to decrease at RRs comparable to field bioreactors.

Methods

Pond Selection

Eight candidate ponds in suburban areas near Sarasota, Florida were chosen based on characteristics common in Florida, including pond surface area, depth, contributing drainage area, and land use. All ponds were in housing developments surrounded by fertilized lawns. Runoff served as the major source of water and nutrient influx. Ponds did not receive chemical herbicide applications in the year prior to or during the study. This common practice inhibits algae growth and could confound chlorophyll-a (chl-a) results. Initial grab samples were collected from prospective bioreactor installation locations from the eight ponds in August 2013 and analyzed as described in the following section (data not shown).

Two wet detention ponds were selected (labeled A and B; Fig. S1) based on levels of NO_3^- and chl-a that were notably higher than natural ponds in the region (Florida DEP 2015). Bioreactor

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Table 1. Comparison of ponds with bioreactor installations

Parameter	Pond A	Pond B
Selection characteristics		
Watershed area (ha)[a]	16.4	22.9
Pond area (ha)[a]	3.2	2.5
Sampling area (ha)	0.56	0.59
Initial NO_3^--N ($mg\,L^{-1}$)	7.0 ± 0.7[b]	4.3 ± 0.2[b]
Initial chlorophyll-a ($\mu g\,L^{-1}$)	39 ± 8[c]	40 ± 11[c]
Dates		
Bioreactor install	November 1, 2013	October 26, 2013
Pump start	November 2, 2013	November 5, 2013
Final sampling	November 18, 2014	November 18, 2014
Treatment time		
Sampling area (day)	210	221
Entire pond area (year)	3.3	2.6

[a]Physical characteristics are representative of wet detention ponds in suburban areas in Florida.
[b]Nitrate (NO_3^--N) concentration exceeds West Central Florida recommendation of 1.65 $mg\,L^{-1}$ (Florida DEP 2015).
[c]Chlorophyll-a level exceeds Florida DEP recommendation of 20 $\mu g\,L^{-1}$ for West Central Florida DEP (2015).

location in each pond was determined by sampling access and proximity to electricity to power pumps. We also selected locations in narrower portions of the ponds to amplify the effects of the bioreactors during the sampling period. Full transect samples were conducted in October 2013 for selected ponds to establish preinstallation conditions (Table 1, top portion).

Bioreactor Construction and Installation

The bioreactors were designed based on those used in agricultural applications. Each bioreactor consisted of an iron framework, lined with geotextile fabric to contain the woodchips (Fig. 1). A 50-mm (2-in.) perforated pipe, running the entire length of the bioreactor, was set in place when half of the bioreactor was filled with woodchips to ensure the pipe was centered in reactor. This was connected with inflow plumbing to facilitate radial inflow along the length of the bioreactor. More information on construction is provided in Table 1.

Bioreactors were placed half-submerged in the pond and filled with a mix of hardwood chips (mostly *Schinus terebinthifolius*).

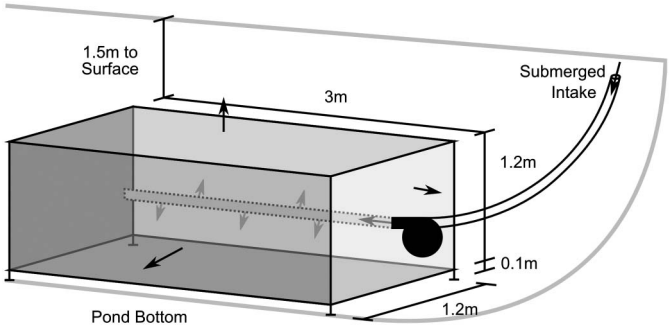

Fig. 1. Submerged denitrifying bioreactors for treatment of nitrate in wet detention ponds. Arrows indicate flow paths from intake, through the pump, and radially from the perforated pipe, through the woodchips, and out of the bioreactor. The metal frame was lined with geotextile fabric and secured with cable ties to contain the woodchips.

The woodchips were produced locally within a month before installation and were not rinsed. This occurred over the course of 2 days to allow the chips to saturate and sink before more woodchips were added on top. Bioreactors were then pulled into the pond and then fully submerged. The bioreactors floated for several minutes as the air escaped, and then sank to the pond bottom at least 1.5 m below the surface. The distributor pipes were connected to pumps pulling pond water from an intake approximately 10 m from the bioreactors (Fig. S1). The flow rate was 20 $L\,min^{-1}$, resulting in a theoretical average residence time of 2.3 h. We calculated the hypothetical time to treat all the water in the pond as well as the time to treat the portion represented by the sampling transects, referred to as the sampling area (Table 1). The sampling area accounts for 18% of Pond A and 35% of Pond B (Fig. S1).

Sample Collection and Analysis

Sampling consisted of one preinstallation evaluation and seven postinstallation events. Two 100-m sampling transects extended from the bioreactor site to quantify spatial changes in NO_3^- concentrations as the bioreactors cycled the pond water. Samples were collected from a boat approximately 5 m from the bank at points 0, 5, 15, 30, 50, and 100 m from the bioreactor along two transects radiating in semiopposing directions. Capped polyethylene sample bottles were lowered 10 cm below the surface and then opened to avoid sampling of floating algae. Samples were immediately filtered using 0.45-μm filters and both filters and filtrate were stored on ice in the field. Filters were stored at −20°C and filtered water was refrigerated until analysis within 3 days of collection.

Four analytes were used to quantify water quality before and after bioreactor installation. The water was analyzed for NO_3^- plus nitrite nitrogen (NO_3^--N) and sulfate (SO_4^{2-}) using a Dionex ICS-2000 ion (Sunnyvale, California) chromatograph with detection limits of 0.05 $mg\,N\,L^{-1}$ and 0.05 $mg\,S\,L^{-1}$, respectively, according to Environmental Protection Agency (EPA) Method 300.0-2.1 (Pfaff 1993). Dissolved organic carbon (DOC) was analyzed with an OI Analytical Total Carbon Analyzer Model 1010 (OI Analytical, College Station, Texas) using EPA Method 415.3, and had a detection limit of 0.1 $mg\,DOC\,L^{-1}$ (Potter and Wimsatt 2009). Chl-a was analyzed by spectrophotometry based on the EPA Method 446.0-1 by Arar (1997). Most NO_3^- were analyzed within the recommended 48-h holding time. Results from samples analyzed within 72 h showed similar concentrations and were included in further analysis. Concentration values below instrument detection limit were assumed to be equal to half of the detection limit.

R version 3.2.1 (R Core Team 2017) was used for statistical analysis. Transects were compared with paired *t*-tests for each analyte. Paired samples from the transects were treated as replicates and averaged into a single data point for further statistical tests. Linear models were used to separately compare concentrations of each analyte with distance from the bioreactor and time since installation. Data were then binned based on natural breaks in pond physiology occurring roughly 20 m from the bioreactor at each pond. Concentrations for each of the analytes were nonnormal, based on Shapiro–Wilk tests. Kruskal–Wallis tests were used to determine significant difference with Dunn's tests post hoc (Dunn 1964).

Results

In both ponds, NO_3^--N dropped below 0.5 $mg\,N\,L^{-1}$ along the entire transect within 3 weeks and remained low for the remainder of the study [Fig. 2(a)]. Concentrations of chl-a [Fig. 2(b)] and SO_4^{2-} [Fig. 2(c)] were also significantly reduced in both ponds, with chl-a concentrations below the recommended limit of 20 $\mu g\,L^{-1}$

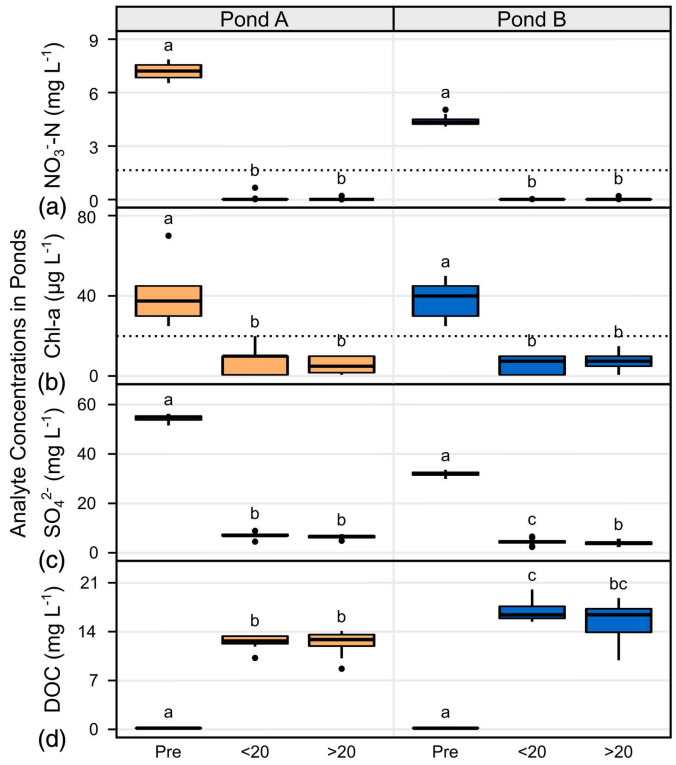

Fig. 2. Concentrations of analytes in Ponds A and B, measured before bioreactor installation (Pre) and postinstallation within 20 m of the bioreactor (<20) and beyond 20 m (>20). Dotted lines show levels recommended for West Central Florida by the Florida Department of Environmental Protection. Letters above each box indicate significant difference in mean concentration between groups compared at both ponds ($\alpha = 0.05$).

(Florida DEP 2015). DOC showed a significant increase after bioreactor installation [Fig. 2(d)]. There were no significant differences between samples within 20 m and greater than 20 m for any analyte.

For each pond and analyte, concentrations were not significantly different within or between transects, suggesting a well-mixed system. Linear models fitting concentrations of each analyte to distance from the bioreactor were not significant [Figs. S2(a–d) and Table S1]. Models comparing each analyte to sampling date were all highly significant (Table S1). When preinstallation samples were removed, only chl-a remained significant [Figs. S2(e–h) and Table S1].

Discussion

Evidence of Denitrification

Concentrations of NO_3^- and chl-a were significantly reduced ($P < 0.001$) after bioreactor installation in both wet detention ponds as hypothesized. The results of this study are highly dependent on initial sampling concentrations. While NO_3^- concentrations were similar to samples taken during site identification in August 2013, there was possibly a natural change in NO_3^- concentration during the dry season, which generally runs October to May. If NO_3^- concentrations fell between sampling in October and installation of the bioreactors in November, some natural NO_3^- decrease would have been attributed to the bioreactors. However, this is also the beginning of the period during which Floridians can apply fertilizer to residential areas, which would likely raise NO_3^- concentrations.

Denitrification is only one of several pathways for the reduction of NO_3^-. The significant decrease in chl-a suggests that assimilation is not a major contributor to N reduction in this study. Decreased concentrations of SO_4^{2-} suggest that it is also being biologically reduced and not facilitating NO_3^- reduction through sulfur oxidation. Low ammonium was observed at the end of the study (Pluer 2018). While this was not measured throughout the study, it provides anecdotal evidence that NO_3^- concentrations were not reduced via dissimilatory NO_3^- reduction to ammonium. Isotope labeling of NO_3^- and woodchip media would help confirm the internal processes.

Removal Rate Estimates

Removal rate ($g\,N\,m^{-3}\,d^{-1}$) is the commonly used metric to evaluate and compare efficiency of N treatment in agricultural denitrifying bioreactors (Schipper et al. 2010). This calculates the mass of N removed per time and normalizes it to the volume in which denitrification occurs. In traditional applications of bioreactors, mass of N removed per time is equal to the change in concentration between inflow and outflow NO_3^- multiplied by flow rate. Our design did not have a distinct outlet point and the intake was likely influenced by effluent from the bioreactor. Instead, we approximated the mass of N removed as the difference in concentration between sampling events multiplied by the volume of pond represented by the sample transects. This was divided by the time interval between sampling events and then normalized by bioreactor volume as before. Nitrate concentration dropped too quickly across the entire transect to use spatial statistics to calculate the decrease of NO_3^- concentration. This also limited calculation of RR to the first samples only. Estimated RRs using the sample interval from October to November 2013 were 1,026 and 470 $g\,N\,m^{-3}\,d^{-1}$ for Ponds A and B, respectively. These are notably larger than the highest annual average RR of 30 $g\,N\,m^{-3}\,d^{-1}$ reported in agricultural bioreactors (Bell et al. 2015). These are also higher than bioreactors used to treat aquaculture, where consistent flow rates are more comparable to our design (von Ahnen et al. 2016). We did not calculate RR between later sample intervals due to NO_3^- limitation (Addy et al. 2016).

These rates were normalized by bioreactor pore volume, which allowed for comparison between bioreactors of different sizes, including lab-scale and field-scale bioreactors. This was an appropriate measure for conventional bioreactors with defined inflow and outflow points and a contained volume, as described by Schipper et al. (2010). While the media was contained in the submerged bioreactors, the boundaries for denitrification to occur were not as clear. Dissolved organic carbon increased in the ponds after installation, with pond concentrations similar to agricultural bioreactor effluent (Hassanpour et al. 2017). Concentrations increased along the entire length of sampling transects, likely aided by particulate carbon and sawdust in the woodchips (Rambags et al. 2016) and disturbance in the pond from installation. The alleviation of a DOC limitation could have encouraged denitrification beyond the bioreactor. However, there were no visual or odor indications that reduced conditions existed in the water column. Evidence from wetland soils show rapid activation of denitrification when the right conditions occur (Zhi and Ji 2014) and a number of studies have documented high rates of denitrification in the top 10 cm of soil and pond sediment (Hill 1996; Li et al. 2010; Brauer et al. 2015). If we assume that high DOC activated denitrification in 10 cm of pond sediment in the entire sampling area in addition to the bioreactor volume, RR was 7.9 and 3.4 $g\,N\,m^{-3}\,d^{-1}$ in Pond A and B, respectively.

Extensions

The narrow locations within the ponds where the bioreactors were located potentially limited pumps mixing water from the entire pond. However, samples collected greater than 20 m from the bioreactors extended well into open portions of the pond and NO_3^- was not significantly higher than within 20 m ($P = 0.32$). This suggests that water quality impacts and mixing were not limited to the portion closest to the bioreactor. Instead, the extent of water quality benefits may not be fully recognized because of our assumption that treatment was confined to the sampling area. In addition, measurements of NO_3^- concentration at the pump intake would allow for calculation of RR that is more similar to agricultural bioreactor calculations.

Further work is necessary to verify these results in other wet detention ponds and climates. Our experimental design can be substantially improved by including control or *paired* ponds instead of relying solely on a before–after sampling approach. We also recommend additional sampling at a higher temporal resolution immediately after the bioreactor is installed and sampling transects that cover the entire pond area to improve RR estimates. High RRs and elevated DOC suggest that carbon is leaching from the bioreactors. This may shorten media life and decrease RR as DOC is consumed; long-term monitoring is necessary to quantify this. Analysis of nitrous oxide and methane emissions from the pond surface would quantify the ratio of complete denitrification and the potential greenhouse gas impacts of reducing conditions throughout the pond. If denitrification is occurring outside of the bioreactor, the large structure and pumping may be unnecessary. Instead, large-scale denitrification may be achievable with woodchips dispersed throughout the pond.

Conclusion

This was a case study with few replicates and limited transect length and study period. Based on the data collected, the two pond bioreactors successfully reduced NO_3^- concentrations below 2 mg N L^{-1}, probably via denitrification in the entire sampling area. Analysis of other indicators, including chl-a and SO_4^{2-}, corroborates this conclusion. The low NO_3^- and chl-a concentrations suggest that bioreactors may be a potential alternative to chemical herbicides in addition to providing efficient nutrient treatment. The rapid rate of removal and the mixing throughout the entire sampling transects did not allow us to model the progress of NO_3^- reduction throughout the ponds. Because of this, RRs were estimates based only on the first sampling interval and the sampling area. This study shows the potential for denitrifying bioreactors, which have been successfully implemented to treat NO_3^- in agricultural runoff, to be applied to suburban systems for water quality improvement and management. The ubiquity of wet detention ponds throughout suburban areas make them an ideal candidate for bioreactor installations to reduce N pollution to waterbodies. A simple retrofit, like the one described in this study, could significantly reduce the footprint of society on the N cycle close to the source and benefit estuarine and coastal waters.

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Supplemental Data

Figs. S1 and S2 and Table S1 are available online in the ASCE Library (www.ascelibrary.org).

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