1 Title

2 Hydrologic conditions drive denitrification and greenhouse gas emissions in stormwater
3 detention basins

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5 Authors

6 Lauren McPhillips* and M. Todd Walter

7

8 Affiliation

9 Biological and Environmental Engineering, 111 Wing Dr, Cornell University, Ithaca NY
10 USA

11 *Corresponding author: LEM36@cornell.edu

12

13 Keywords

14 Greenhouse gases; denitrification; methane; nitrous oxide; stormwater; urban systems

15

Abstract

Stormwater detention basins are primarily designed to detain large volumes of storm runoff and trap suspended sediments and associated pollutants. Detaining and retaining nutrients are often not a design focus. The combination of variable moisture patterns in stormwater basins along with potential nutrient influxes may make these basins hotspots for nitrogen transformations such as denitrification, as well as potential sources of greenhouse gases nitrous oxide (N₂O) and methane (CH₄). Nitrous oxide and CH₄ emissions were measured using static chambers in four stormwater detention basins—two fast-draining or ‘dry’ basins and two slow-draining or ‘wet’ basins. Denitrification potential of soils collected from these basins was also measured using the denitrification enzyme assay (DEA). While N₂O emissions were low, CH₄ emissions were higher in both wet basins, averaging 5667 µg C m⁻² hr⁻¹ in the wettest basin. Denitrification potential was higher in the wet basins (2.27 mg N kg⁻¹ hr⁻¹) compared to the dry basins (0.23 mg N kg⁻¹ hr⁻¹). Overall, wet detention basins had higher greenhouse gas emissions but also had higher potential for nitrate removal via denitrification. Designing future stormwater control measures to maintain a subsurface saturated zone rather than fully saturated soils should be considered to promote denitrification while also reducing CH₄ emissions at the surface.

1. Introduction

As land is urbanized, stormwater control measures (SCMs) are implemented to deal with runoff generated on impervious surfaces. These SCMs include structures such as detention ponds and basins and are intended to temporarily detain stormwater in order to reduce peak streamflows and nuisance flooding. As management of pollutants in urban runoff became a concern, SCMs have taken on an additional role as water quality best management practices. In the United States, SCMs are a key strategy supported by the U.S. Environmental Protection Agency (EPA) for managing stormwater in urbanized areas and satisfying Clean Water Act water quality goals (US EPA, 2014). The primary water quality target for SCMs has generally been sediment and associated pollutants such as heavy metals (Davis and McCuen, 2005). Metals and hydrocarbons are prevalent in urban runoff due to vehicle exhaust and weathering of vehicle and building components (Brown and Peake, 2006; Davis et al., 2001).

Nitrogen can also be a concern in urban areas due to sources such as atmospheric deposition on impervious surfaces (Bettez and Groffman, 2013), leakage of septic and sanitary sewer systems, lawn fertilizers and pet waste (Kaushal et al., 2006). However, nutrients, which are often in dissolved form and not readily treated through filtration or sorption, are generally not the primary focus of SCM design (Collins et al., 2010). More recently, there has been some consideration of how to optimize nitrogen removal in these systems using a subsurface saturated zone and/or carbon amendments (Hunt et al., 2012; Kim et al., 2003). Both of these promote denitrification, the microbially-mediated transformation of nitrate (NO_3^-) to nitrogen gases (Seitzinger et al., 2006). Older SCMs,

which were not designed explicitly for nitrogen removal, may still facilitate conditions that promote denitrification. Studies of SCMs in Baltimore, Maryland and Phoenix, Arizona found that these structures had higher denitrification potential than stream riparian areas, which are typically viewed as ‘biogeochemical hotspots’ for the transformation of inorganic nitrogen to gaseous nitrogen (Bettez and Groffman, 2012; Zhu et al., 2004).

Just as these SCMs can be hotspots for denitrification, they may also be hotspots for production of greenhouse gases (GHGs), namely nitrous oxide (N_2O) and methane (CH_4). N_2O has 298 times the warming potential of carbon dioxide (CO_2) (Solomon et al., 2007) and can be produced by denitrification as well as by nitrification, as an intermediary in the conversion of ammonia to nitrate (Firestone and Davidson, 1989). CH_4 has 25 times the warming potential of CO_2 (Solomon et al., 2007) and is produced by methanogenesis in the anaerobic respiration of organic molecules or reduction of CO_2 (Schlesinger, 1997). Production of either gas requires carbon substrate, which could be provided by the basin soil media or by particulate organic matter (OM) or degradation products of hydrocarbons in incoming runoff. These processes are also strongly controlled by oxygen status in the soil. Denitrification and methanogenesis are both promoted under anaerobic conditions, while variation between anaerobic and aerobic conditions can promote cycling between nitrification and denitrification and subsequent N_2O production (Burgin and Groffman, 2012; Christiansen et al., 2012). Thus, variation in soil moisture or existence of saturated zones in the SCM could influence these processes and associated GHGs. The only published data on GHG dynamics in SCMs thus far has been for bioretention cells in Melbourne, Australia (Grover et al., 2013). Bioretention systems expand on the typical wet

89 or dry detention basin to include an infiltration zone and plants to stimulate soil microbial
90 activity to provide overall better pollutant removal. The researchers found the cells to be
91 slight sources of N_2O and sinks of CH_4 under most conditions, but observed pulses of both
92 gases after simulated rain events (Grover et al., 2013).

93 As peri-urban land use expands (Brown et al., 2005) and more SCMs are built to
94 mitigate ensuing hydrologic alterations, it is important to understand the impact of these
95 structures on landscape biogeochemical processes. The ability of these structures to act as
96 hotspots of nutrient retention or as sources of greenhouse gases could have a substantial
97 impact when scaled up, and should be considered along with other ecosystem services
98 provided by green stormwater infrastructure. However, data on these processes in various
99 parts of urban ecosystems is still lacking (Pataki et al., 2011).

100 1.1. *Objectives/ Hypotheses*

101 The objective of this study was to survey greenhouse gas emissions (N_2O and CH_4)
102 and denitrification potential across four traditional stormwater detention basins in a
103 northern temperate climate, and identify drivers of observed patterns. We hypothesized
104 that rates of these processes would be higher within the basins than in adjacent lawns, due
105 to the influx of nutrients and variability in soil wetness resulting from periodic storm
106 runoff. We also hypothesized that the hydrologic regimes of the basins would be a major
107 control on differences in these biogeochemical processes across basins, with wetter basins
108 exhibiting greater denitrification and CH_4 emissions and drier basins having higher N_2O
109 emissions due to contributions from both denitrification and nitrification.

2. Methods

2.1. *Study site*

The four stormwater basins (Figure 1a) were located on the Cornell University campus in Ithaca, New York USA. This region is characterized by a temperate climate, with an average annual temperature of 8.1°C, average range of -9.2 to 26.6°C and average annual precipitation of 947 mm (NRCC, 2014). All basins were constructed between 2002 and 2007 and vary between 400 and 1410 m² in size, though the ratio of their watershed drainage areas compared to basin area were similar (Table 1). Designed as dry detention basins, they were planted with turfgrass (primarily *Lolium perenne*) and have 10-15 cm topsoil which is underlain by native silt loam, and then a layer of sand. Below the sand is an underdrain (perforated pipe) that connects to the storm sewer system and is intended to route water away during periods of saturation. All basins were intended to drain within approximately 24 hours of filling. Since construction, drainage in two of the basins has slowed, leading to wetter soils in these basins (Figure 2) and the emergence of vegetation common in local wetlands (e.g. *Juncus* sp., *Typha* sp.). Reasons for the change are uncertain, but may include reduced infiltration due to settling of fine particles (Paus et al., 2014), aggregate formation and pore clogging due to reactions with road salt (Kakuturu and Clark, 2015) or clogging of the underdrain.

Soil and gas measurements were made at three locations within each basin and two reference locations directly outside of each basin (Figure 1b). The outside locations provided references where the soil media was the same as within the basin itself (verified through textural analysis described below), but which did not receive the same inputs of

stormwater and nutrients as the basin.

Figure 1: (a) Photographs of four stormwater detention basins and (b) layout of sampling locations used for soil and gas flux measurements

Table 1: Basin design characteristics

	Basin Area (m ²)	Watershed Area (m ²)	Watershed Area: Basin Area	Year Built	Primary Inflow Source
Dry Basin 1	400	3000	7.5	2004	Driveway & roof
Dry Basin 2	500	5600	11.2	2002	Parking lot
Wet Basin 1	1410	8100	5.7	2007	Parking lot
Wet Basin2	550	4000	7.3	2006	Parking lot

2.2. Gas flux measurements

Emissions of CH₄ and N₂O were measured at the basins on seven dates between March and November 2013 that provided a range of temperature and moisture conditions. Average air temperature for the seven dates ranged from 1.7 to 18.9 °C and precipitation in the three preceding days for each measurement date ranged from 0 to 1.8 cm (NRCC, 2014). Flux measurements at the four basins occurred within three hours of each other on the same day for each timepoint. Fluxes were measured using *in situ* static chambers which

were 30 cm in diameter and constructed using two plastic buckets. The chamber base was created by cutting a five gallon bucket in half such that the ribbed top of the bucket could be installed in the soil. These bases remained in place for the entire duration of the study. Two 1.5 cm holes were drilled in each chamber base to allow for flow of water during storm events. In preparation for making a gas flux measurement, a 5 cm wide rubber band was placed around the chamber base and the two holes in the chamber base were plugged with rubber stoppers. The chamber top was constructed from a 3.5 gallon bucket equipped with a rubber septum for sampling and a vent tube. Additional chamber construction details are described in Molodovskaya et al. (2011).

For a single gas flux measurement, the chamber top was mounted on the base and a 20 mL syringe was inserted into the main septum to take an initial gas sample. Samples were injected into pre-evacuated 10 mL glass vials with butyl rubber septa. Vials were over-pressurized with injection of 15 mL gas in order to maintain the integrity of samples until analysis. Additional gas samples were taken from the chamber at 10, 20, and 30 minutes.

Samples were analyzed for N_2O and CH_4 using an Agilent 6890N gas chromatograph equipped with a HP 7694 Headspace Autosampler (Hewlett-Packard Co.). N_2O separation was performed using a Supel-QTM PLOT capillary column (30m x 0.32mm; Supelco Inc.) with ultra-pure helium carrier gas (2.6 mL min^{-1}) and 95:5 Ar: CH_4 make-up gas (8.2 mL min^{-1}) and a μECD (electron capture detector) set to 250°C . CH_4 separation was performed using a Carboxen 1006 PLOT capillary column (30m x 0.32mm; Supelco, Inc.) and an FID (flame ionization detector) set to 200°C with H_2 gas (30 mL

min⁻¹), air (400 mL min⁻¹), and N₂ makeup gas (25 mL min⁻¹) . Oven temperature was initially set to -22°C for 4.7 min, then increased to 30°C for 2.3 min to allow for elution of both gases of interest. Calibration curves were made using serial dilutions of 1 ppm N₂O and 20 ppm CH₄ (Airgas Inc.) Gas fluxes were calculated by determining the linear slope of the concentrations of the four time-points (Hutchinson and Mosier, 1981; Rochette and Bertrand, 2008). Fluxes were converted from volumetric to mass-based units (µg gas m⁻² hr⁻¹) using the ideal gas law.

2.3. Denitrification potential

Denitrification was measured using the denitrification enzyme assay (DEA), which assesses potential denitrification when ample carbon and nitrate are available (Groffman et al., 1999). Soil samples were taken at each basin in October. For each of the three basin and two reference locations, five 5 cm long soil cores were collected and homogenized; from this, two replicate subsamples of 5-6 g were used for the assay. Assays were conducted in 125 mL glass serum bottles with butyl rubber stoppers. 10 mL media containing 200 mg/L NO₃⁻-N and 1000 mg/L glucose was added to the soils. Chloramphenicol was not used due to its adverse effects on existing denitrification enzymes (Pell et al., 1996). All assay bottles were evacuated and flushed with N₂ gas twice. 10 mL acetylene gas was added to each bottle to begin the assay, and inhibit production of N₂ from denitrification. 15 mL gas samples were taken from each bottle at 0, 20, 40 and 60 minute intervals and injected in to pre-evacuated vials. Following each sample extraction, 15 mL N₂ was immediately added to each assay bottle to keep bottles

roughly at atmospheric pressure. Between sampling times, bottles were shaken on a shake table at approximately 100 rpm. Gas vials were analyzed for N₂O concentration on the same gas chromatograph as described previously (section 2.2). N₂O fluxes were determined using the linear slope of the concentrations of the four time-points and converted to denitrification rates in mg N kg⁻¹ hr⁻¹ using the dry mass of the soil subsamples.

2.4. *Environmental conditions*

A Decagon EM50 datalogger (Decagon Devices, Inc.) was installed at each basin for monitoring of soil conditions. Each datalogger was connected to five Decagon 5TE sensors, which measured soil temperature, volumetric water content (VWC), and electrical conductivity. Sensors were located at each of the three basin and two reference locations at each site, and were buried at ~2.5 cm depth in the soil. On occasions when there were errors with the *in situ* Decagon sensors, VWC, temperature, and electrical conductivity were measured with handheld sensors which were calibrated to the Decagon sensors.

2.5. *Water quality sampling*

Inflowing stormwater was sampled at each of the four basins to characterize dissolved NO_x (NO₃⁻ + NO₂⁻) across multiple runoff events. Prior to anticipated storm events, 125 mL HDPE bottles were anchored below basin inlets (either direct pipes or grass/gravel where sheet flow runoff entered). Immediately after the storm event, bottles were retrieved and water was filtered using 0.45µm Pall mixed cellulose ester filters and

filtrate was stored at 4°C until analysis. Water samples were successfully obtained from each basin for at least ten runoff events. These runoff events were not sampled directly prior to measurements of gas fluxes, as the intent was to characterize the average NO_x concentration flowing into each basin over the year. Analysis of NO₃⁻ and NO₂⁻ was performed on a Dionex ICS-2000 Ion Chromatograph with an IonPac AS-18 analytical column.

2.6. Soil analysis

Soil samples were removed from each basin and reference location for textural and organic matter analysis. For each of the three basin and two reference locations, five 5 cm cores were homogenized. Soil particle size distribution was assessed on a ~40 g subsample using the hydrometer method (Kroetsch and Wang, 2008). The remaining soil was dried at 105°C, then ground and sieved to remove particles larger than 2 mm. Samples were analyzed for organic matter (OM) using the loss-on-ignition method, where ~6 g subsamples were heated to 360°C for two hours (Konen et al., 2002). Percent OM was calculated, based on empirical relationships developed for New York State soils (Ferguson and Swenson, n.d.) as

$$OM = 0.7 LOI - 0.23 \quad (1)$$

where LOI is % loss-on-ignition.

2.7. Statistical analysis

Statistical analyses were conducted in R v. 3.1.2 (The R Project for Statistical

Computing). The Shapiro-Wilk test was used to verify whether data followed a normal distribution. For non-normal data, which only included gas fluxes, lognormal or Box-Cox transformations were attempted but were not successful in inducing a normal distribution for all datasets. Thus, the Kruskal-Wallis non-parametric test with pairwise comparison was used to assess differences between N₂O and CH₄ fluxes at the basin and reference sites. One-way analysis of variance (ANOVA) with Tukey honestly significant difference (HSD) pairwise comparison was used to assess differences between measured variables with normal distributions (e.g. denitrification potential) at the basin and reference sites. To assess any correlations between measured variables (including annual averages for gas fluxes and soil VWC and one-time measurements for all other variables), Pearson product-moment correlation analysis was used. Averaged inflow NO_x concentrations were included in this analysis for basin sampling sites only. A second correlation analysis was done comparing potential denitrification data to N₂O, CH₄, and VWC data from October only, since that was the month when soils were sampled for potential denitrification. Linear regression was also applied to the normalized gas flux timeseries to elucidate any temporal trends with soil temperature or moisture.

3. Results and Discussion

3.1. *Soil conditions*

Soil texture was the same across all basin and reference locations (loamy sand; Table 2). Soil VWC was significantly higher in both wet basins compared to their reference sites and to both dry basins ($p < 0.05$; Figure 2). OM content varied among basin

and reference sites, though was significantly higher in Wet Basin 1 (Table 2). Across all sites, soil OM was significantly positively correlated with VWC (Table 3), possibly due to decreased mineralization and subsequent accumulation of OM under wetter conditions (Bridgham et al., 1998). Soil concentrations of OM immediately after basin construction were unknown for the sites and, thus, assessment of OM accumulation over time was not possible.

Table 2: Basin soil conditions and inflowing NO_x. Reported values indicate mean $\pm$ standard error. Superscripted letters indicate which sites are significantly ($p < 0.05$) different than each other based on statistical tests.

Site	Analysis Location	Soil Texture	Soil VWC vol vol ⁻¹	Soil OM %	Inflow NO _x ⁻ mg N L ⁻¹
Dry Basin 1	Basin	loamy sand	0.20 $\pm$ 0.01 ^a	3.19 $\pm$ 0.40 ^a	0.54 $\pm$ 0.10 ^a
	Ref	loamy sand	0.17 $\pm$ 0.01 ^a	4.32 $\pm$ 0.12 ^a	
Dry Basin 2	Basin	loamy sand	0.24 $\pm$ 0.02 ^{ad}	4.63 $\pm$ 0.14 ^a	0.64 $\pm$ 0.13 ^a
	Ref	loamy sand	0.22 $\pm$ 0.02 ^{ad}	3.63 $\pm$ 0.05 ^a	
Wet Basin 1	Basin	loamy sand	0.49 $\pm$ 0.06 ^b	12.99 $\pm$ 1.54 ^b	0.63 $\pm$ 0.09 ^a
	Ref	loamy sand	0.32 $\pm$ 0.03 ^{cd}	3.88 $\pm$ 0.29 ^a	
Wet Basin 2	Basin	loamy sand	0.37 $\pm$ 0.02 ^c	4.55 $\pm$ 1.42 ^a	1.22 $\pm$ 0.23 ^a
	Ref	loamy sand	0.27 $\pm$ 0.01 ^d	5.27 $\pm$ 0.36 ^a	
Dry Basins	Basin	loamy sand	0.23 $\pm$ 0.01 ^a	3.91 $\pm$ 0.38 ^a	0.58 $\pm$ 0.08 ^a
	Ref	loamy sand	0.20 $\pm$ 0.01 ^a	3.98 $\pm$ 0.21 ^a	
Wet Basins	Basin	loamy sand	0.42 $\pm$ 0.03 ^c	8.77 $\pm$ 2.11 ^b	1.02 $\pm$ 0.16 ^b
	Ref	loamy sand	0.29 $\pm$ 0.02 ^b	4.57 $\pm$ 0.44 ^a	

Table 3. Pearson correlation coefficients for measured variables. For measurements made more than once throughout the year, average values were used in the analysis.

	N ₂ O $\mu\text{g N m}^{-2} \text{ hr}^{-1}$	CH ₄ $\mu\text{g C m}^{-2} \text{ hr}^{-1}$	Denit. Potential $\text{mg N kg}^{-1} \text{ hr}^{-1}$	Soil VWC $\text{vol}^{-1} \text{ vol}^{-1}$	OM %
N ₂ O					
CH ₄	-0.15				
Denit. Potential	-0.35	0.48*			
Soil VWC	-0.27	0.56**	0.66**		
OM %	-0.16	0.92***	0.56*	0.66**	
Inflow NO _x ⁻	-0.59*	-0.33	0.67*	0.23	-0.18

* $p < 0.05$

** $p < 0.01$

*** $p < 0.001$

Figure 2. Volumetric water content (VWC; $\text{m}^3 \text{ m}^{-3}$) during the 2013 sampling period for

(a) Dry Basin 1, (b) Dry Basin 2, (c) Wet Basin 1 and (d) Wet Basin 2. Vertical dotted lines indicate dates on which GHG fluxes were measured. A barplot of average VWC (e) is shown for all sites, for the dates when GHG fluxes were measured. Error bars represent standard error. Letters indicate which sites are significantly different than each other based on statistical tests.

3.2. Greenhouse gas emissions

3.2.1. Nitrous Oxide

N₂O fluxes were low across all basin and reference sites (Table 4) and fluxes were not significantly different ($p>0.05$) between any sites. There were no clear temporal trends, and fluxes varied between N₂O uptake and emission (Figure 3). The slight uptake may represent N₂O reduction to N₂ as part of denitrification (Firestone et al., 1980). Examining the data averaged across the year, Pearson correlation analysis revealed a slightly significant negative trend with basin N₂O fluxes and inflow NO_x concentrations (Table 3). This is counter-intuitive given that greater NO_x often promotes greater denitrification and thus greater N₂O emissions, as a product of incomplete denitrification (Firestone et al., 1980). However, higher NO_x concentrations were observed in the wet basins (Table 2), where wetter conditions likely promoted full denitrification to N₂.

The two highest emissions in this study were 93 and 231 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$ and occurred at reference sites during July and October, respectively. Typically, 'hot moments' of N₂O emission follow nutrient inputs or precipitation events (Molodovskaya et al., 2012). There was 1.9 cm of precipitation in the three days prior to the July flux measurement, which may have contributed to this hot moment. Given that the adjacent basin (Wet Basin 2) did not also experience a similar hot moment after this precipitation event, the basin, which had higher VWC during this time (Figure 2), was likely experiencing full denitrification to N₂. In October, several sites exhibited higher N₂O emissions relative to other dates. Precipitation seems unlikely to be the main driver (3-day antecedent precipitation = 0.5 cm). It is possible that there was an application of lawn fertilizer on campus lawns around this time, providing increased nutrient availability, but records are unavailable to confirm

this.

N₂O fluxes from these detention basins were low compared to the only other known N₂O data from SCMs (Grover et al., 2013). N₂O fluxes measured in two bioretention cells in Australia averaged 13.7 and 65.6 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$, which were higher than mean fluxes measured in this study. Grover et al. (2013) also observed pulses of N₂O as high as 1100 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$ after simulated precipitation events. Compared to forested riparian wetlands in upstate New York, mean N₂O emissions for all basins (4.6 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$) were higher than the mean wetland emissions of 0.9 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$ (Hopfensperger et al., 2009) though emissions from wet basins only (0.5 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$) were lower. Several studies of N₂O fluxes in grass lawns provide additional context. N₂O fluxes in these basin and reference sites fall largely within measurements made in Baltimore, Maryland which ranged from -0.07 to 63 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$ (Groffman et al., 2009; Raciti et al., 2011). Higher emissions have been observed in fertilized lawns, up to 720 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$ (Townsend-Small and Czimczik, 2010), indicating the importance of nitrogen inputs in driving emissions.

The detention basins in this study were not emission hotspots for N₂O, which is good given the high global warming potential of this gas. Though emissions from the reference lawn sites were statistically similar to the basins, the highest overall emissions came from the lawn sites. The relatively low soil VWC at these sites appears to have promoted periodic N₂O production via incomplete denitrification or nitrification. However, given that the lawns' VWC was not different than the dry basins' VWC, there are other factors influencing these hot moments, likely increased nutrient availability at the reference

lawn sites.

Table 4: Summary of denitrification and greenhouse gas fluxes. Reported values indicate mean $\pm$ standard error. Superscripted letters indicate which sites are significantly ($p < 0.05$) different than each other based on statistical tests.

Site	Analysis Location	Denit. Potential mg N kg ⁻¹ hr ⁻¹	N ₂ O Flux μ g N m ⁻² hr ⁻¹	CH ₄ Flux μ g C m ⁻² hr ⁻¹
Dry Basin 1	Basin	0.20 $\pm$ 0.04 ^a	12.4 $\pm$ 5.7 ^a	-16.0 $\pm$ 9.3 ^a
	Ref	0.45 $\pm$ 0.17 ^a	3.7 $\pm$ 3.0 ^a	-3.6 $\pm$ 15.7 ^a
Dry Basin 2	Basin	0.27 $\pm$ 0.04 ^a	6.9 $\pm$ 4.7 ^a	-6.8 $\pm$ 12.2 ^a
	Ref	0.38 $\pm$ 0.08 ^a	26.9 $\pm$ 16.9 ^a	9.8 $\pm$ 14.5 ^a
Wet Basin 1	Basin	2.00 $\pm$ 0.38 ^{bc}	3.7 $\pm$ 4.5 ^a	5666.9 $\pm$ 1523.6 ^b
	Ref	0.53 $\pm$ 0.06 ^a	3.9 $\pm$ 2.9 ^a	1.7 $\pm$ 9.5 ^a
Wet Basin 2	Basin	2.53 $\pm$ 0.64 ^b	-2.4 $\pm$ 4.0 ^a	121.1 $\pm$ 85.6 ^a
	Ref	0.86 $\pm$ 0.01 ^{ac}	4.4 $\pm$ 7.7 ^a	-16.8 $\pm$ 15.6 ^a
Dry Basins	Basin	0.23 $\pm$ 0.03 ^a	9.5 $\pm$ 3.6 ^a	-11.1 $\pm$ 7.7 ^a
	Ref	0.42 $\pm$ 0.08 ^a	16.2 $\pm$ 9.4 ^a	3.6 $\pm$ 10.5 ^a
Wet Basins	Basin	2.27 $\pm$ 0.35 ^b	0.5 $\pm$ 3.0 ^a	2755.4 $\pm$ 841.2 ^b
	Ref	0.70 $\pm$ 0.10 ^a	4.2 $\pm$ 4.3 ^a	-8.3 $\pm$ 9.5 ^a
All Basins	Basin	1.25 $\pm$ 0.35	4.6 $\pm$ 2.4	1484.3 $\pm$ 480.0
	Ref	0.56 $\pm$ 0.08	10.2 $\pm$ 5.2	-2.3 $\pm$ 7.1

Figure 3: N₂O fluxes for seven measurement points in 2013 at (a) Dry Basin 1, (b) Dry Basin 2, (c) Wet Basin 1, and (d) Wet Basin 2. 3-day averaged precipitation (a) and daily

352 air temperature (c) obtained from a campus weather station are also shown. 3-day
 353 precipitation prior to gas flux sampling is indicated as black bars (a).

354

355 Figure 4: CH_4 fluxes for seven measurement points in 2013 at (a) Dry Basin 1, (b) Dry
 356 Basin 2, (c) Wet Basin 1, and (d) Wet Basin 2. 3-day averaged precipitation (a) and daily

air temperature (c) obtained from a campus weather station are also shown. 3-day
precipitation prior to gas flux sampling is indicated as black bars (a).

3.2.2. Methane

CH₄ fluxes were low across the dry basins (Table 4) and fluxes were not significantly different between the basin and reference sites. At Dry Basin 1, there was a slight negative trend in flux over the year, moving from CH₄ emissions during the spring towards CH₄ uptake in the summer and autumn (Figure 4a). Dry Basin 2 wavered between slight CH₄ emission and uptake throughout the year. Different patterns were observed at the wet basins. Wet Basin 1 had significantly higher ($p < 0.001$) CH₄ emissions than the reference site at that location and all other sampled sites. Emissions were highest during the summer (Figure 4c), and reached a peak of 23,248 $\mu\text{g C m}^{-2} \text{ hr}^{-1}$. Wet Basin 2 also exhibited some substantial CH₄ emissions during summer (Figure 4d) but CH₄ fluxes were not significantly different between the basin and reference sites. Intra-basin variability may have contributed to this finding. The coefficient of variation of CH₄ fluxes was higher within Wet Basin 2 than Wet Basin 1 (3.2 vs. 1.2, respectively), although a Kruskal-Wallis test indicated that there were not significant differences within either wet basin.

The CH₄ fluxes in the dry detention basins and the reference sites were similar to observations from the bioretention cells in Australia. As in this study, CH₄ fluxes were, on average, negative (mean = -3.8 and -18.3 $\mu\text{g C m}^{-2} \text{ hr}^{-1}$ for two cells), indicating overall uptake or oxidation of CH₄ (Grover et al., 2013). Similarly, studies of lawns have observed slight negative CH₄ fluxes (Groffman and Pouyat, 2009; Livesley et al., 2010). In both the bioretention cells and lawns, fluxes varied from slight uptake to slight emissions depending on soil moisture conditions. The wet detention basins in this study, particularly Wet Basin 1, exhibited CH₄ trends far different than observations in these other urban sites. The measured emissions (wet basin mean = 2756 $\mu\text{g CH}_4\text{-C m}^{-2} \text{ hr}^{-1}$) were more similar to those

reported in various wetland studies. In natural fens in central New York and southeastern New Hampshire, mean fluxes of 734- 5933 $\mu\text{g CH}_4\text{-C m}^{-2} \text{ hr}^{-1}$ have been observed (Frolking and Crill, 1994; Smemo and Yavitt, 2006). Research in constructed wetlands provides an additional benchmark. These designed systems generally have higher nutrient inputs since they are often intended to treat wastewater. Constructed wetlands in northern Europe were found to emit an average of 5700 $\mu\text{g CH}_4\text{-C m}^{-2} \text{ hr}^{-1}$, which is roughly double what was observed in the wet basins in this study (Sovik et al., 2006).

Given the variability observed in CH_4 fluxes in our study, it is important to understand drivers of these patterns. For most basin and reference sites in this study, there were no clear trends between CH_4 fluxes and soil moisture or temperature at the time of measurement. The only site for which there was a significant relationship was Wet Basin 1. There was only a significant relationship between CH_4 (Box-Cox transformed) and temperature ($p < 0.01$; $R^2 = 0.93$).

This positive correlation with temperature concurs with findings in northern latitude wetlands (Frolking and Crill, 1994). Since CH_4 in these environments is generated by microbial processes, temperature can strongly influence availability of carbon substrate via decomposition and mineralization (Walter and Heimann, 2000). While soil moisture or water table height has also been found to control CH_4 fluxes (Moore and Roulet, 1993), it is not surprising that soil moisture was not a significant control on CH_4 variability for this particular site, given that Wet Basin 1 maintained high soil moisture for much of the year. When average annual fluxes for all basin and reference sites were examined against other environmental variables using Pearson correlation coefficients, soil VWC was significantly

positively related to CH₄ fluxes (Table 3). Additionally, soil OM was significantly positively related to CH₄ fluxes, which makes sense given that OM is the substrate that is transformed by microbes to generate CH₄.

3.3. Denitrification

Potential denitrification was significantly higher ($p < 0.05$) within each of the wet basins compared to either dry basin (Figure 5; Table 4). Additionally, potential denitrification in the wet basins was significantly higher ($p < 0.05$) than their reference sites. Soil VWC was strongly positively correlated with potential denitrification (Table 3). This is consistent with other studies examining SCMs (Bettez and Groffman, 2012). Inflow NO_x and soil organic matter were also significantly positively correlated with denitrification potential (Table 3). Correlations between denitrification and other environmental variables only differed marginally when using annually averaged data versus October data only (when potential denitrification was assessed) and there was no difference in what relationships were statistically significant; thus only results using annually averaged data are presented in Table 3.

Figure 5: Denitrification potential (mg N kg soil⁻¹ hr⁻¹) for soils within each basin and at reference locations directly outside of basins. Error bars denote standard error.

Superscripted letters indicate which sites are significantly ($p < 0.05$) different than each other based on statistical tests.

Average potential denitrification across all basins was very similar to that measured in a suite of wet and dry ponds and detention basins in Maryland ($1.2 \mu\text{g N m}^{-2} \text{ hr}^{-1}$), where overall climate is similar to that of our study (Bettez and Groffman, 2012). Slightly lower average rates of $0.74 \mu\text{g N m}^{-2} \text{ hr}^{-1}$ were measured in grassed dry detention basins in Arizona; grassed city parks in the same system also had an average rate of $0.74 \mu\text{g N m}^{-2} \text{ hr}^{-1}$ (Zhu et al., 2004). Though the Zhu et al. (2004) study is in a more arid and warm climate than ours, the similar SCM design including retention time of stormwater, vegetation, and nutrient inputs may ‘homogenize’ these types of systems, i.e. make them behave similarly despite considerable climatic differences. This theory of urban homogenization, where urbanization is leading to similar ecosystem structure or function across cities that differ in their geographical and biogeophysical surroundings, has been observed in other aspects of urban ecosystems including lawn care and surface water distribution (Polsky et al., 2014; Steele et al., 2014). There is limited information

synthesizing design and implementation of SCMs across different biogeophysical settings. For satisfying U.S. EPA stormwater management requirements, some states have developed manuals with guidelines tailored to goals more relevant in that particular area (e.g. groundwater recharge in arid states), while some states defer to broad federal SCM design manuals (NRC, 1997). Thus it is hard to know the extent that homogenization of nutrient cycling responses may be occurring due to broad implementation of similar SCM designs.

These measurements of potential denitrification in SCMs are powerful for assessing the overall capacity of a soil microbial community to denitrify NO_3^- , where this capacity has developed based on exposure to moisture conditions and soil C and N at the site (Zhu et al., 2004). It is a useful metric for comparing the maximum denitrification rate among different sites and SCM designs, though it is important to acknowledge that the actual denitrification rates can vary based on temporal variability of moisture, temperature, and nutrients. While denitrification is regarded as an important ecosystem service for removal of excess nitrogen in SCMs, there are other processes that can provide a sink for incoming nitrogen. Recent work in lab-scale bioretention mesocosms found that denitrification contributed to substantial NO_3^- removal at higher concentrations ($>10 \text{ mg N L}^{-1}$) but that assimilation was the dominant nitrogen sink at lower NO_3^- concentrations (Payne et al., 2014a). The experiment did not differentiate between assimilation by microbes versus plants, but treatments with differing plant communities and subsequently differing NO_3^- removal responses indicated that plants played a strong role. It is important to note that assimilation does not permanently remove inorganic nitrogen from the system,

as denitrification does, though plants can provide additional benefits of providing labile carbon which can help promote processes like denitrification (Kastovska et al., 2015). Thus in addition to promoting conditions (e.g. higher soil moisture) that favor denitrification in SCM design, it is important to consider plant communities.

3.4 Considerations for optimizing SCM design

Simply considering the biogeochemical processes measured in this study, it is challenging to find a single SCM configuration that optimizes all functions. An ideal design would maximize the water quality service of denitrification while minimizing emissions of the greenhouse gases CH_4 and N_2O . In this study, though, the high soil moisture and soil organic matter that promoted greater potential denitrification also spurred CH_4 emissions. With regards to OM, it may be possible to reduce the amount of OM added to SCM soil media during installation in order to reduce CH_4 emissions; however some OM is necessary to promote beneficial microbial processes like denitrification, as well as to aid in metal and hydrocarbon sorption (Hunt et al., 2012). One solution that addresses the hydrologic controls is to maintain a subsurface saturated zone, rather than having fully saturated soil profiles as was the case with traditional wet detention basins, to which the wet basins studied here have effectively evolved. More recently, some bioretention SCM designs have included subsurface saturated zones using an upturned elbow in the underdrain pipe (Hunt et al., 2012; Payne et al., 2014b). This configuration could allow for removal of NO_3^- via denitrification in the saturated zone, while CH_4 generated in this zone could have an opportunity to be oxidized in the vadose zone and thus reduce total

emissions at the soil surface. A bioretention cell with a subsurface saturated zone was included in Grover et al.'s (2013) study, in which they observed minimal CH₄ emissions, but also elevated N₂O emissions compared to a cell without a saturated zone. Research is needed to resolve the tradeoffs associated with strategies for optimizing these processes.

In addition to the functions considered here, there are numerous other ecosystem services that could be provided by SCMs. For example, an ecosystem service related to the processes studied here is carbon sequestration. Carbon sequestration could potentially offset GHG emissions but there are few data on overall carbon balances in SCMs. In constructed wetlands in northern Europe, the system was determined to be a net carbon sink, based on comparison of GHG emissions and carbon sequestration (de Klein and van der Werf, 2014). However, the carbon footprint of construction and maintenance was not considered in this analysis. A recent study calculated carbon footprints for various SCM types (e.g. green roofs, detention ponds) incorporating construction and maintenance, as well as literature-based carbon sequestration estimates (Moore and Hunt, 2013). Even without factoring in direct GHG emissions from the SCMs (such as measured in this study), Moore and Hunt (2013) found that stormwater wetlands and grassed swales were the only SCMs that acted as carbon sinks.

Beyond water quality services and carbon budgets, there are myriad other ecosystem services or co-benefits that can be provided by these SCMs. These include aesthetic benefits and habitat provision for aquatic macroinvertebrates, insects, and birds (Moore and Hunt, 2012). Many of these could be influenced by the hydrologic regime of the basins, and thus choosing an SCM design for particular water quality and/or

biogeochemical function can also influence the provision of these co-benefits. Additionally, as is the case with GHGs, there can be dis-services such as provision of mosquito habitat that can be linked to SCM design (Gingrich et al., 2006).

For any of the functions of these designed SCMs discussed above, there could be substantial implications when scaled up to the whole landscape. Unfortunately there is a lack of synthesized data on the spatial extent of SCMs at higher-order landscape levels. Additionally, this research demonstrates the variability in the nutrient cycling response of different basin designs and how basin characteristics and associated ecosystem functions can evolve over time, as in the case of the wet basins in this study which were originally designed as dry detention basins. Thus, there are still knowledge gaps to be addressed before we can make reasonable upscaling estimates for GHGs and other ecosystem services. With peri-urban land use expanding in the United States (Brown et al., 2005), and the U.S. EPA continuing to support implementation of SCMs to mitigate ensuing impacts (US EPA, 2014), the relative impact of SCMs in the landscape and the potential benefits from improved design will only continue to increase.

4. Conclusions

This study surveyed nutrient cycling processes in four stormwater detention basins in central New York and sought to elucidate what design-related or environmental factors drove observed patterns. Two of the basins were dry while the other two were consistently saturated. There were no notable trends in N_2O , though several emission spikes were measured at adjacent lawn sites. CH_4 fluxes were driven by soil moisture and soil organic

matter and were higher in the wet basins. CH₄ emissions in the wet basins were comparable to those in natural wetlands, averaging 2755 µg CH₄-C m⁻² hr⁻¹. Potential denitrification was also controlled by soil moisture and organic matter, in addition to incoming NO_x, and was significantly higher in the two wet basins. To better balance the water quality service of denitrification with greenhouse gas emissions, design of future SCMs should consider a subsurface saturated zone rather than fully saturated soils, though monitoring of nutrient fluxes will be necessary to confirm that this system indeed functions better. Additionally, future work should attempt a full carbon balance of SCMs in order to better understand their overall contribution to landscape carbon cycling and global climate change.

5. Acknowledgements

Assistance with field sampling was provided by Rachel Whiteheart, Andrea Fortman, Christine Georgakakos and Breann Liebermann and help with GC method development was provided by Cedric Mason. Valuable comments on the manuscript were provided by Natalie Morse and Allison Truhlar. Information on detention basin construction and management was provided by Robert Chiang and Linda Aarismaa of Cornell's Engineering and Environmental Compliance divisions. Funding for this work was provided by the New York State Water Resources Institute and Cornell Engineering Learning Initiatives as well as by the National Science Foundation Graduate Research Fellowship Program under Grant No. 1144153 and the Cornell Cross-Scale Biogeochemistry & Climate IGERT under NSF Grant No. 1069193.

561 6. Abbreviations

Abbreviation	Full Term
GHG	Greenhouse gas
NO _x	NO ₃ ⁻ + NO ₂ ⁻
LOI	Loss-on-ignition
OM	Organic matter
SCM	Stormwater control measure
VWC	Volumetric water content

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